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REFERENCE BOOK FOR THE NITROGEN INDUSTRY WORKER. VOLUME 2, (U)
MAR 82 M A MINOVICH, Y Y MEL'NIKOV
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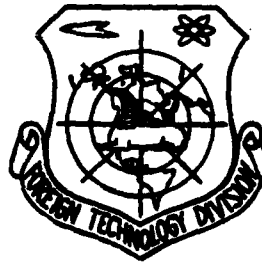
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FOREIGN TECHNOLOGY DIVISION



REFERENCE BOOK FOR THE NITROGEN INDUSTRY WORKER
VOLUME TWO



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WP.AFB, OHIO.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ъ, ы; e elsewhere.
When written as ë in Russian, transliterate as yë or ë.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh ⁻¹
cos	cos	ch	cosh	arc ch	cosh ⁻¹
tg	tan	th	tanh	arc th	tanh ⁻¹
ctg	cot	cth	coth	arc cth	coth ⁻¹
sec	sec	sch	sech	arc sch	sech ⁻¹
cosec	csc	csch	csch	arc csch	csch ⁻¹

Russian English

rot curl
lg log

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this translation were extracted from the best quality copy available.

The second volume of the reference book under the general editorship of Ye. Ya. Mel'nikov examines the physical and chemical fundamentals of the processes and industrial plans for the production of nitric acid and nitrogen fertilizers.

This volume presents the properties and areas of application of metals and alloys which are used as construction materials in the nitrogen industry, as well as the properties of refractory and heat-insulating materials. It makes recommendations on the use of a number of anticorrosion materials, and gives the characteristics and calculations for the main equipment and the most important information on the thermal and electrical engineering equipment. Questions of accident prevention are briefly touched upon.

The reference book is intended for engineering and technical workers of enterprises of the nitrogen and other sectors of the chemical industry, for specialists working in scientific research and planning institutes, design offices and other organizations, as well as for teachers of VUZ's [higher educational institutions] and students who are specializing in the field of the technology of inorganic products.

The reference book contains 444 pages, 239 tables, 242 figures and 294 bibliographic references.

Foreword

As a result of the significant development of the domestic nitrogen industry, it has become necessary to provide the numerous workers of chemical enterprises, educational institutions, scientific research, planning-design and other organizations with a reference manual which would generalize the results of theoretical research and the rich practical experience accumulated by now in this sector of the chemical industry. This Reference Book whose compilation was worked on by a large group of leading specialists of the State Scientific Research and Planning Institute of the Nitrogen Industry and Products of Organic Synthesis (GIAP), has systematized the results of both the many years of production experience, and the new scientific research and planning-design work.

The Reference Book for the Nitrogen Industry Worker is published in two volumes. Volume I which was previously published, describes the physical and chemical properties of gases and liquids, methods of production and purification of production gases, and the processes of synthesis of ammonia and methanol. Since the USSR has introduced the International System of Units (SI) starting with 1 January 1963, the compilers considered it useful to place in the beginning of Volume I a list of the most important units of this system and the coefficients for converting certain units of engineering and other measurement systems into SI units.

The second volume consists of five sections. The section "Production of Nitric Acid" concisely describes the raw material and certain auxiliary materials, examines the properties of nitric acid and nitric oxides, states the fundamentals for the processes of contact oxidation of ammonia and refining of nitric oxides into acid, gives the necessary information on catalysts, presents industrial plans for producing diluted (weak) nitric acid and new methods of producing it, and shows the main production equipment of nitric acid systems and the principles of their automation. This section describes the direct synthesis of concentrated nitric acid from liquid nitric oxides and processes of concentrating nitric acid with the help of sulfuric acid and magnesium nitrate.

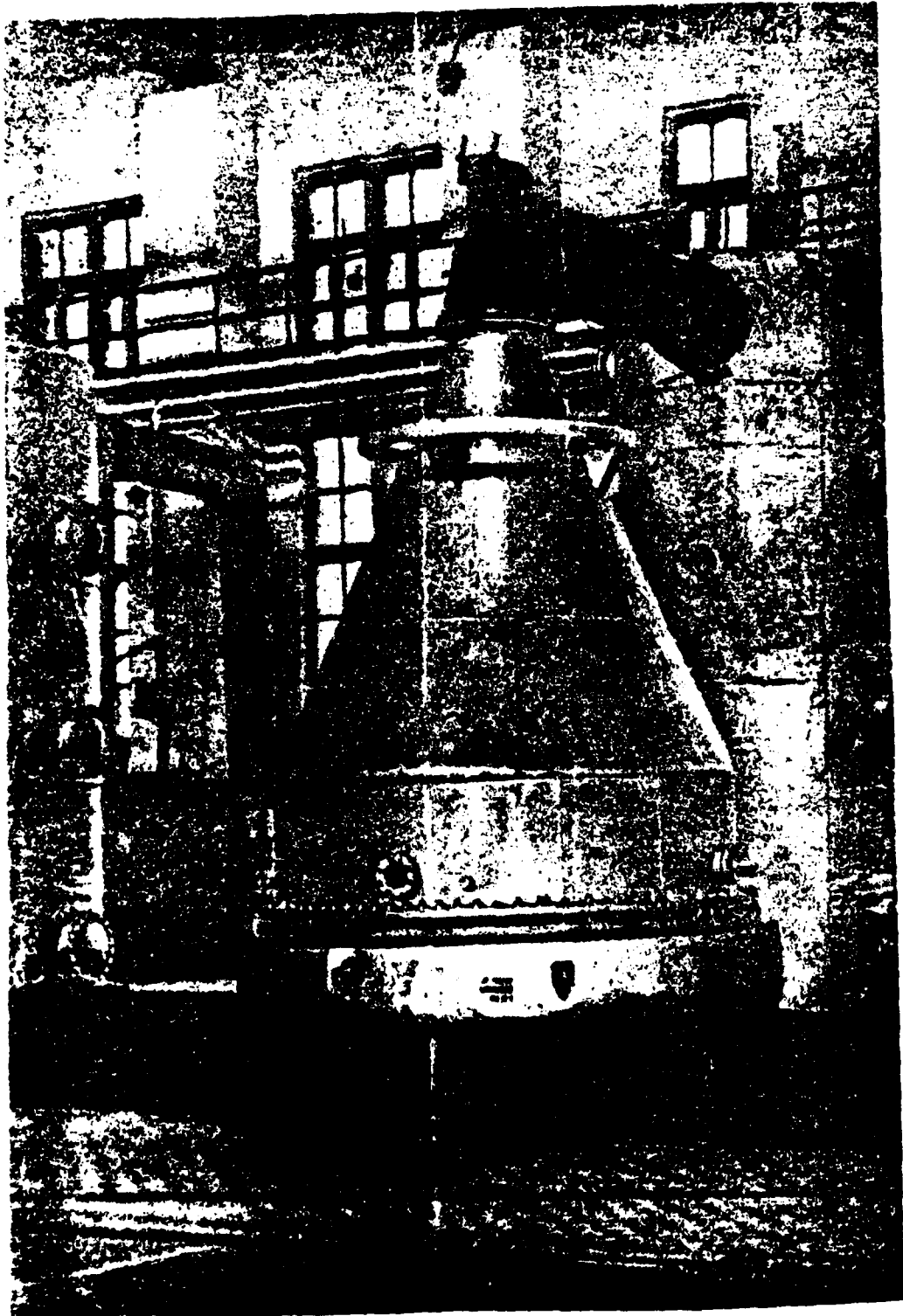
The second section, "Production of Nitrogen Fertilizers" examines the physical and chemical properties and processes of producing ammonia, calcium, potassium and sodium nitrates, ammonium sulfate, carbamide, liquid nitrogen fertilizers, and also covers questions of the quality and application of the listed products.

The third section briefly describes the design, corrosion-resistant, refractory and thermal-insulating materials used in the nitrogen industry, and presents necessary data on compressors, pumps, high pressure vessels and gas holders.

The fourth section covers questions of the energy supply for nitrogen plants. It contains the basic data on thermal and electrical equipment, describes the most important thermal engineering equipment and electrical equipment, and makes recommendations for its selection as applied to the operating conditions in different spheres of chemical production.

The fifth section presents the basic information on accident prevention in the nitrogen industry in the form of tables.

The editorial staff hopes that the Reference Book for the Nitrogen Industry Worker will be a useful manual for the workers of the chemical industry and will give them specific help in their daily work. Comments and remarks of the readers which are aimed at improving the contents of the Reference Book will be gratefully received by the group of authors.



I. Production of Nitric Acid
Editor-in-chief of the section B. P. Samarin

Nitric acid belongs to the most important products of the chemical industry. It is used to produce nitrogen fertilizers, technical-grade nitrates, explosives, dyes and many other products. The industry manufactures diluted (weak) and concentrated (strong) nitric acid, as well as comparatively small quantities of reactive and especially pure acid.

Below is the volume of production* of nitric acid in the technically developed capitalist countries (in million m of 100% HNO₃):

Countries	1962-1963	1965-1966	Countries	1962-1963	1965-1966
United States	3.4	4.7	Norway	1.0	1.25
FRG	2.2	2.55	Netherlands	0.7	0.95
France	1.73	2.2	England	0.6	0.90
Italy	1.05	1.3			

In 1965-1966, nitric acid accounted for about 22.5% of the world production of bound nitrogen.

Modern methods for producing diluted nitric acid are based on the use of synthetic ammonia and atmospheric air as the raw material. The process of its production consists of two basic stages: 1) conversion (oxidation) of ammonia and nitric oxide by air oxygen in the presence of a catalyst; 2) oxidation of nitric oxide into higher nitric oxides and their absorption by water with the formation of diluted nitric acid.

Concentrated nitric acid is produced by two methods: distillation with sulfuric acid (vitriol oil) or with a melt of magnesium nitrate used as the water-removing substances, and by direct synthesis from liquid nitric oxides, water (or diluted nitric acid) and pure oxygen under 50 atm. pressure.

The greater part of the diluted nitric acid is processed into nitrogen fertilizers and technical-grade nitrates at the same enterprises where it is produced. Concentrated nitric acid and blend (mixture of it with sulfuric acid) are manufactured as commercial

* Platinum Metals Review, 11, No. 1, 2, 1967.

Indicators	Grade		
	first	second	third
HNO ₃ concentration, % no less	55	47	45
Content of nitric oxides, % no more	0.15	0.2	0.2
Calcined residue, %, no more	0.05	0.1	0.1

products.

Concentrated nitric acid is manufactured in three grades according to GOST 701-68 [state standard]:

Indicators	Grade		
	highest	first	second
HNO ₃ concentration, % no less	98.5	98	97
Content, %, no more			
H ₂ SO ₄ nitric oxides (in conversion for N ₂ O ₄)	0.05	0.08	0.12
calcined residue	0.3	0.3	0.4
	0.015	0.02	0.04

The following requirements are made of the diluted nitric acid (MRTU 6-03-159-63): (see the table at the top of the page).

Industrial systems for producing diluted nitric acid are mainly distinguished in pressure at the main stages of production. The nitric acid systems are customarily divided into the following groups:

systems which operate under pressure close to atmospheric;
 systems which operate under increased pressure;
 systems which operate by combined method (oxidation of ammonia is done with pressure close to atmospheric or moderate pressure, absorption of the formed nitric oxides is at high pressure).

Raw Material and Certain Auxiliary Materials

The chief raw material for nitric acid production is gaseous ammonia, air and water. In individual cases, technical-grade oxygen is used to intensify the production of diluted nitric acid. The former is also used to produce concentrated nitric acid obtained by the method of direct synthesis.

Ammonia

Gaseous ammonia is usually obtained from liquid ammonia which must meet the requirements of GOST 6221-62 (see volume I, p. 370). In addition to admixtures of oil, particles of catalyst for the synthesis of ammonia and products of corrosion of equipment and pipelines, liquid ammonia contains up to 2 g/l of ammonium carbonate and up to 0.5% dissolved gases (hydrogen, methane, as well as argon and other inert gases). During evaporation of liquid ammonia, part of these admixtures become gaseous ammonia.

Table I-1 presents the main thermodynamic properties of ammonia (see also volume I, section I).

Air

The most important condition for reaching a high degree of conversion of ammonia into nitric oxide is the sufficient purity of the ammonia-air mixture. The main source of its contamination with admixtures is air. In the production of diluted nitric acid, air is generally taken in directly at the contact sections. It must not contain more than 0.007 mg/m³ of mechanical admixtures (scale, silicates, etc.), as well as chemical admixtures, the majority of which irreversibly poison the catalysts of ammonia oxidation into nitric oxide.

The properties of air are presented in volume I, section I. Some data are given in tables I-2 and I-2a.

Oxygen

Oxygen is used in the production of diluted nitric acid to enrich the air used in contact oxidation of ammonia. In direct synthesis of concentrated nitric acid, oxygen is one of the main reagents. Oxygen is generally used which was obtained by the method of deep air cooling. The content of organic compounds in it must not be higher than 16 mg/m³.

TABLE I-1. MAIN THERMODYNAMIC PROPERTIES OF AMMONIA

Temperature °C	Absolute pressure kg-f/cm ²	Density		Enthalpy		Heat of steam forma- tion, kcal/kg
		of li- quid kg/l	of steam kg/m ³	of li- quid	of steam	
40	15,850	0,5795	12,005	145,52	408,37	262,85
38	14,990	0,5827	11,353	143,16	408,23	265,07
36	14,165	0,5859	10,731	140,82	408,06	267,24
34	13,374	0,5890	10,138	138,48	407,88	269,40
32	12,617	0,5921	9,573	136,16	407,67	271,51
30	11,895	0,5952	9,034	133,84	407,43	273,59
28	11,204	0,5983	8,521	131,54	407,17	275,63
26	10,544	0,6013	8,031	129,24	406,89	277,65
24	9,915	0,6043	7,564	126,94	406,59	279,65
22	9,314	0,6073	7,119	124,66	406,27	281,61
20	8,741	0,6103	6,694	122,38	405,93	283,55
18	8,196	0,6132	6,289	120,11	405,57	285,46
16	7,677	0,6161	5,904	117,85	405,19	287,34
14	7,183	0,6190	5,537	115,59	404,79	289,20
12	6,715	0,6218	5,189	113,35	404,38	291,03
10	6,271	0,6247	4,859	111,11	403,95	292,84
8	5,849	0,6275	4,546	108,87	403,50	294,63
6	5,450	0,6303	4,250	106,65	403,04	296,39
4	5,073	0,6331	3,969	104,43	402,55	298,12
2	4,716	0,6358	3,703	102,21	402,04	299,83
0	4,379	0,6386	3,452	100,00	401,52	301,52
-2	4,060	0,6413	3,216	97,79	400,98	303,19
-4	3,761	0,6440	2,991	95,59	400,42	304,83
-6	3,481	0,6467	2,779	93,40	399,85	306,45
-8	3,216	0,6497	2,579	91,21	399,27	308,06
-10	2,966	0,6520	2,390	89,03	398,67	309,64
-12	2,732	0,6546	2,213	86,85	398,06	311,21
-14	2,514	0,6572	2,046	84,68	397,44	312,76
-16	2,309	0,6598	1,889	82,50	396,79	314,29
-18	2,117	0,6624	1,742	80,33	396,13	315,80
-20	1,940	0,6650	1,604	78,17	395,46	317,29
-22	1,774	0,6676	1,474	76,01	394,77	318,76
-24	1,619	0,6701	1,354	73,86	394,07	320,21
-26	1,475	0,6726	1,242	71,71	393,36	321,65
-28	1,342	0,6752	1,136	69,59	392,64	323,08
-30	1,219	0,6777	1,038	67,42	391,91	324,49
-32	1,105	0,6801	0,948	65,28	391,17	325,89
-34	1,000	0,6826	0,863	63,15	390,41	327,26
-36	0,903	0,6851	0,785	61,01	389,65	328,64
-38	0,814	0,6875	0,712	58,88	388,88	330,00
-40	0,732	0,6900	0,645	56,80	388,10	331,30
-42	0,657	0,6924	0,583	54,60	387,30	332,7
-44	0,588	0,6948	0,526	52,50	386,5	334,0
-46	0,526	0,6972	0,473	50,40	385,7	335,3
-48	0,469	0,6996	0,425	48,40	384,9	336,6
-50	0,417	0,7020	0,381	46,20	384,1	337,9

The oxygen obtained by water electrolysis is usually contaminated³ with hydrogen (1-3%) and finely dispersed particles of alkali ("alkali fog") whose content is 25-150 mg/m³. The use of electrolytic oxygen for production of concentrated nitric acid is categorically forbidden because of the possible formation of explosive mixtures with hydrogen.

The use of electrolytic oxygen is permitted in the production of diluted nitric acid only after it has been purified of alkali fog. The properties of oxygen are presented in volume I of the Reference.

TABLE I-2. PHYSICAL PROPERTIES OF DRY AIR¹ AT
760 mm Hg

t, °C	ρ , kg/m ³	c_p kcal kg·deg	$\lambda \cdot 10^8$ kcal m·h·deg	$\alpha \cdot 10^6$ m ² /h	$\mu \cdot 10^6$ kg-f·s m ²	$\nu \cdot 10^6$ m ² /s	Pr
-50	1,584	0,242	1,75	4,57	1,49	9,23	0,728
-40	1,515	0,242	1,82	4,96	1,55	10,04	0,728
-30	1,453	0,242	1,89	5,37	1,60	10,80	0,723
-20	1,395	0,241	1,96	5,83	1,65	12,79	0,716
-10	1,342	0,241	2,03	6,28	1,70	12,43	0,712
0	1,293	0,240	2,10	6,77	1,75	13,28	0,707
+10	1,247	0,240	2,16	7,22	1,80	14,16	0,705
20	1,205	0,240	2,23	7,71	1,85	15,06	0,703
30	1,165	0,240	2,30	8,23	1,90	16,00	0,701
40	1,128	0,240	2,37	8,75	1,95	16,96	0,699
50	1,093	0,240	2,43	9,26	2,00	17,95	0,698
60	1,060	0,240	2,49	9,79	2,05	18,97	0,696
70	1,029	0,241	2,55	10,28	2,10	20,02	0,694
80	1,000	0,241	2,62	10,87	2,15	21,09	0,692
90	0,972	0,241	2,69	11,48	2,19	22,10	0,690
100	0,946	0,241	2,76	12,11	2,23	23,13	0,688
120	0,898	0,241	2,87	13,26	2,33	25,45	0,686
140	0,854	0,242	3,00	14,52	2,42	27,80	0,684
160	0,815	0,243	3,13	15,80	2,50	30,09	0,682
180	0,779	0,244	3,25	17,10	2,58	32,49	0,681
200	0,746	0,245	3,38	18,49	2,65	34,85	0,680
250	0,674	0,248	3,67	21,96	2,79	40,61	0,677
300	0,615	0,250	3,96	25,76	3,03	48,33	0,674
350	0,566	0,253	4,22	29,47	3,20	55,46	0,676
400	0,524	0,255	4,48	33,52	3,37	63,09	0,678
500	0,456	0,261	4,94	41,51	3,69	79,38	0,687
600	0,404	0,266	5,35	49,78	3,99	96,89	0,699
700	0,362	0,271	5,77	58,82	4,26	115,4	0,706
800	0,329	0,276	6,17	67,95	4,52	134,8	0,713
900	0,301	0,280	6,56	77,84	4,76	155,1	0,717
1000	0,277	0,283	6,94	88,53	5,00	177,1	0,719

Designations: t--temperature; c_p --heat capacity; λ --heat conductivity; α --temperature conductivity; μ --dynamic viscosity; ν --kinematic viscosity; Pr--Prandtl criterion.

Water

For absorption of nitric oxides, pure condensate of water vapor is used, and often the condensate of liquor-tanned vapor from the production of ammonium nitrate. In individual cases, chemically purified water in a mixture with water vapor condensate is used. It must contain no more than 5 mg/l of chlorides. The water must not contain a greater quantity of admixture of sodium chlorides since the latter interact with nitric acid:

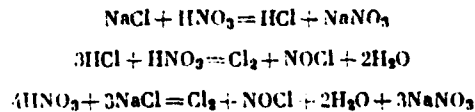


TABLE I-2a. AIR DENSITY ρ , CONTENT IN IT OF MOISTURE W AND PRESSURE OF WATER VAPOR $P_{\text{H}_2\text{O}}$ AT 760 mm Hg AND COMPLETE SATURATION WITH MOISTURE²

t, °C	ρ kg/m ³	W g/m ³	$P_{\text{H}_2\text{O}}$ mm Hg	t, °C	ρ kg/m ³	W g/m ³	$P_{\text{H}_2\text{O}}$ mm Hg
-30	1,449	0,44	0,4	18	1,213	15,31	15,4
-27	1,435	0,57	0,5	21	1,201	18,25	18,5
-24	1,418	0,71	0,6	24	1,189	21,68	22,2
-21	1,401	0,95	0,8	27	1,177	25,84	26,5
-18	1,384	1,25	1,1	30	1,165	30,21	31,5
-15	1,368	1,58	1,4	33	1,154	35,48	37,4
-12	1,353	1,98	1,8	36	1,142	41,51	44,2
-9	1,337	2,49	2,3	39	1,131	48,40	52,0
-6	1,322	3,13	2,9	42	1,121	56,25	61,1
-3	1,308	3,92	3,6	45	1,109	65,14	71,4
0	1,293	4,89	4,6	48	1,107	75,22	83,2
3	1,279	5,98	5,7	49	1,103	78,86	87,5
6	1,265	7,28	7,0	50	1,093	82,63	92,0
9	1,252	8,82	8,6	—	—	—	—
12	1,239	10,64	10,5	—	—	—	—
15	1,226	12,82	12,7	—	—	—	—

As a result, the nitric acid is contaminated the sodium nitrate and the equipment in the absorption part is very corroded under the influence of the released chlorine and nitrosyl chloride.

Chemically purified water which does not contain over 250 mg/l of salts, including less than 100 mg/l of iron and no more than 50 mg/l of copper is used to feed the boiler-recovery units.

The condensate of liquor-tanned vapor from the production of ammonium nitrate contains an admixture of ammonia and saltpeter. Therefore, before using it in the production of nitric acid, it is sometimes cleaned with the help of ionites.

Alkalis

Solutions of alkalis are used in the units to produce diluted nitric acid at atmospheric pressure to absorb nitric oxides of low concentration with subsequent reprocessing of the nitrite-nitrate

solutions obtained in this case into solid salts (pp. 184, 189).

TABLE I-3. DENSITY AND CONCENTRATION OF AQUEOUS SOLUTIONS OF CAUSTIC SODA⁴

1 Плотность при 20° C г/см ³	2 Содержание NaOH		1 Плотность при 20° C г/см ³	2 Содержание NaOH		1 Плотность при 20° C г/см ³	2 Содержание NaOH	
	3 вес. %	4 г/л		3 вес. %	4 г/л		3 вес. %	4 г/л
1.054	5	52.69	1.197	18	215.5	1.469	44	646.1
1.109	10	110.9	1.219	20	243.8	1.487	46	684.2
1.131	12	135.7	1.328	30	398.4	1.507	48	723.1
1.153	14	161.1	1.430	40	572.0	1.525	50	782.7
1.175	16	188.0	1.449	42	608.7			

Key:

1. Density at 20°C g/cm³
2. NaOH content
3. Weight %
4. g/l

TABLE I-4. RELATIVE DENSITY d_{20}^{20} AND CONCENTRATION OF MILK OF LIME³

d ₂₀ ²⁰	1 Содержание CaO		d ₂₀ ²⁰	1 Содержание CaO		d ₂₀ ²⁰	1 Содержание CaO	
	2 вес. %	3 г/л		2 вес. %	3 г/л		2 вес. %	3 г/л
1.009	0.99	10	1.097	11.86	130	1.118	17.43	200
1.017	1.96	20	1.104	12.68	140	1.191	21.84	260
1.025	2.93	30	1.111	13.50	150	1.198	22.55	270
1.032	3.88	40	1.119	14.30	160	1.205	23.24	280
1.039	4.81	50	1.126	15.10	170	1.213	23.92	290
1.083	10.18	110	1.133	15.89	180	1.220	24.60	300
1.090	11.01	120	1.140	16.67	190			

Key:

1. CaO content
2. Weight %
3. g/l

TABLE I-5. DENSITY AND CONCENTRATION OF AQUEOUS SOLUTIONS OF CALCINED SODA⁴

1 Содержание Na ₂ CO ₃		4 Плотность при 20° C г/см ³	5 Содержание Na ₂ CO ₃ ·10H ₂ O		1 Содержание Na ₂ CO ₃		4 Плотность при 20° C г/см ³	5 Содержание Na ₂ CO ₃ ·10H ₂ O	
2 вес. %	3 г/л		2 вес. %	3 г/л	2 вес. %	3 г/л		2 вес. %	3 г/л
5	52.51	1.050	13.5	141.8	12	134.9	1.124	32.4	364.3
8	86.53	1.082	21.6	233.6	13	147.6	1.135	35.1	398.6
10	110.30	1.103	27.0	297.8	14	160.5	1.146	37.8	433.3
11	122.5	1.114	29.7	330.8					

- Key:
1. Na₂CO₃ Content
 2. Weight %

3. $\frac{g}{l}$
4. Density at 20°C $\frac{g}{cm^3}$
5. $Na_2CO_3 \times 10 H_2O$ Content

TABLE I-6 . SPECIFIC HEAT CAPACITY c OF AQUEOUS SOLUTIONS OF CAUSTIC SODA AND CAUSTIC POTASH⁴ AT 16-20°C

NaOH Solutions			KOH Solutions		
concentration mole H_2O mole NaOH	density $\frac{g}{cm^3}$	c cal/(g x deg)	concentration mole H_2O mole KOH	density $\frac{g}{cm^3}$	c cal/(g x deg)
7.5	1.2576	0.847	30	1.0887	0.876
15	1.1450	0.878	50	1.0550	0.916
30	1.0782	0.919	100	1.0284	0.954
50	1.0486	0.942	200	1.0144	0.975
100	1.0246	0.968			
200	1.0124	0.983			

TABLE I-7. VISCOSITY OF AQUEOUS SOLUTIONS OF ALKALIS (in centipoise)⁵

Dissolved substance	Concentration weight. %	Temperature, °C		
		20	30	40
NaOH	5	1.3	1.0	0.85
	15	2.78	2.1	1.65
	25	7.42	5.25	3.86
Na_2CO_3	10	1.7	1.4	1.1
	20	4.0	2.9	2.25
	30	—	8.35	5.6
KOH	10	1.23	1.0	0.83
	20	1.63	1.33	1.11
	30	2.36	1.93	1.57

TABLE I-8. HEAT CONDUCTIVITY OF AQUEOUS SOLUTIONS OF ALKALIS AND CERTAIN SALTS⁵ AT 20°C [in kcal/(m x h x deg)]

Dissolved substance	Concentration of dissolved substance, weight. %					
	0	10	20	30	40	50
KOH	0.515	0.519	0.515	0.502	0.485	0.461
KOH *	0.531	0.533	0.522	0.512	0.494	0.472
NaOH	0.515	0.539	0.550	0.555	0.565	—
$NaNO_3$	0.515	0.509	0.502	0.494	0.482	—
$NaNO_2$	0.515	0.508	0.499	0.489	0.478	—
Na_2CO_3	0.515	0.522	—	—	—	—
KNO_3	0.515	0.502	0.487	0.470	0.453	0.437
KNO_2	0.515	0.502	0.487	—	—	—
K_2CO_3	0.515	0.509	0.501	0.485	0.464	0.438
$Ca(NO_3)_2$	0.515	0.507	0.497	0.486	0.473	0.478

* At 30°C.

TABLE I-9. DENSITY AND CONCENTRATION OF SULFURIC ACID²

1 Плотность при 20 °C г/см ³	2 Содержание H ₂ SO ₄		1 Плотность при 20 °C г/см ³	2 Содержание H ₂ SO ₄		1 Плотность при 20 °C г/см ³	2 Содержание H ₂ SO ₄	
	3 вс. %	4 г/л		3 вс. %	4 г/л		3 вс. %	4 г/л
1.4983	60	808,8	1,0574	74	1226,0	1,8022	88	1586
1.5200	62	924,4	1,6810	76	1278,0	1,8144	90	1633
1.5421	64	986,9	1,7043	78	1329	1,8245	92	1678
1.5646	66	1033,0	1,7272	80	1382	1,8312	94	1721
1.5874	68	1079,0	1,7491	82	1434	1,8355	96	1762
1.6105	70	1127,0	1,7893	84	1486	1,8365	98	1799
1.6338	72	1176,0	1,7872	86	1537			

- Key:
1. Density at 20°C, g/cm³
 2. H₂SO₄ content
 3. Weight %
 4. g/l

TABLE I-10. HEAT CAPACITY AND ENTHALPY OF SOLUTIONS OF SULFURIC ACID²

1 Концентрация H ₂ SO ₄ вс. %	2 Теплоем- ность при 20 °C кал/ г·град	3 Энтальпия, ккал/г								
		20 °C	40 °C	60 °C	80 °C	100 °C	120 °C	150 °C	200 °C	250 °C
5	0,951	19,0	38,0	57,1	76,1	95,3	—	—	—	—
15	0,861	17,2	34,1	51,9	69,5	87,3	—	—	—	—
35	0,704	14,0	28,2	42,7	57,6	72,5	—	—	—	—
65	0,517	10,1	20,7	31,6	43,0	54,7	66,8	85,7	—	—
70	0,4894	9,5	19,6	29,9	40,8	51,9	63,5	81,7	—	—
75	0,4629	9,1	18,5	28,3	38,3	48,7	59,4	76,0	105	—
85	0,4118	8,1	16,5	25,1	33,9	43,0	52,3	66,8	92,0	118
90	0,3869	7,7	15,5	23,6	31,9	40,5	49,3	62,7	86,9	112
95	0,3624	7,15	14,5	22,2	30,0	38,1	46,5	59,6	82,3	107

- Key:
1. Concentration of H₂SO₄, weight %
 2. Heat capacity at 20°C cal/g x deg.
 3. Enthalpy, cal/g.

TABLE I-11. VISCOSITY OF AQUEOUS SOLUTIONS OF SULFURIC ACID² (in centipoise)

1 Концен- трация H ₂ SO ₄ вс. %	2 Температура, °C					1 Концен- трация H ₂ SO ₄ вс. %	2 Температура, °C				
	15	20	30	40	50		15	20	30	40	50
50	4.65	3.58	2.72	2.30	1.90	92	31.85	23.05	15.55	12.0	8.40
60	7.15	5.50	4.28	3.42	2.77	93	31.7	23.1	15.6	12.05	8.40
65	9.32	7.10	5.78	4.55	3.35	94	31.85	23.2	15.65	12.2	8.5
70	12.8	9.65	7.90	6.10	4.20	95	32.0	23.4	15.75	12.35	8.7
90	31.7	23.1	15.55	11.9	8.45						

Key:

1. H₂SO₄ concentration, weight. %
2. Temperature, °C

TABLE I-12. HEAT CONDUCTIVITY OF AQUEOUS SOLUTIONS OF SULFURIC ACID³ [in kcal/(m x h x deg)]

Концентрация H ₂ SO ₄ вес. % (1)	Температура, °C (2)					
	0	20	40	60	80	100
25	0,422	0,457	0,484	0,505	0,524	0,537
50	0,375	0,403	0,424	0,441	0,455	0,463
75	0,328	0,344	0,361	0,377	0,390	0,397
96	0,273	0,280	0,286	0,292	0,298	0,303

Key:

1. H₂SO₄ concentration, weight. %
2. Temperature, °C.

TABLE I-13. SURFACE TENSION OF SULFURIC ACID SOLUTIONS³ (in dyne/cm)

Концентрация H ₂ SO ₄ вес. % (1)	Температура, °C (2)					Концентрация H ₂ SO ₄ вес. % (1)	Температура, °C (2)				
	10	20	30	40	50		10	20	30	40	50
20	75.32	74.13	73.09	72.13	70.95	70	74.72	74.42	74.16	73.87	73.56
40	77.22	76.37	75.52	74.83	73.83	75	73.34	73.09	72.81	72.56	72.31
50	77.27	76.50	76.33	75.44	74.73	90	63.37	62.67	63.39	63.12	62.86
60	76.39	76.05	75.71	75.38	74.93	95	58.39	58.08	57.78	57.49	57.22
65	75.72	75.38	75.08	74.77	74.38						

Key:

1. H₂SO₄ concentration
2. Temperature, °C.

Sulfuric Acid

According to one of the methods for producing concentrated nitric acid, 92.5-94% sulfuric acid (commercial sulfuric acid) is used as the water-removing substance. In this case, treated sulfuric acid is obtained which contains a small quantity of dissolved nitric oxides. (p. 103).

Below are the freezing temperatures t_3 of sulfuric acid solutions of varying density³ ρ , measured at 15°C:

$\rho, \text{ g/cm}^3$ 1.671 1.732 1.778 1.807 1.822 1.840
 $t, \text{ }^\circ\text{C}$ -20 -8.5 -8.5 -9.0 -20.0 -20.0

TABLE I-14. NO SOLUBILITY IN SULFURIC ACID³ AT ROOM TEMPERATURE

1	2	1	2	1	2
Концентрация H ₂ SO ₄ вес. %	Растворимость 10 ³ вес. %	Концентрация H ₂ SO ₄ вес. %	Растворимость 10 ³ вес. %	Концентрация H ₂ SO ₄ вес. %	Растворимость 10 ³ вес. %
8.8	8.72	66.5	2.54	90.4	3.22
18.2	6.97	70.8	2.54	91.9	3.22
28.0	6.03	76.7	2.42	92.4	3.34
38.0	5.10	78.0	2.54	95.0	5.10
48.0	3.89	88.3	2.68	95.9	5.62
52.6	3.22	89.1	2.81	-	-

Key:

1. H₂SO₄ concentration, weight. %
2. Solubility 10³, weight. %

TABLE I-15. NITRATE COOLING AGENTS (BRINES)³

Brines	Composition, %			Freezing temperature, °C
	Ca(NO ₃) ₂	Mg(NO ₃) ₂	NaNO ₃	
Of calcium nitrate	44.0	-	-	-28.0
Of magnesium nitrate	-	32.3	-	-31.8
The same, with NaNO ₃ added	-	30.8	5.2	-36.2

Cooling Agents

Brines, solutions of calcium or magnesium nitrates, as well as mixtures of solutions of magnesium and sodium nitrates are used as the cooling agents in the production of concentrated nitric acid by the method of direct synthesis.

Under normal conditions, a fairly low temperature (minus 20 - minus 22°C) is obtained with the use of 42-44% brine of calcium nitrate (the properties of the calcium nitrate solutions are presented on on (p. 163). If it is necessary to reach lower temperatures, brine of magnesium nitrate can be used with an addition of 5.2% sodium nitrate.

Porolite Pipes³

Porolite pipes are made of highly porous material based on

kieselguhr, quartz, fireclay, etc. They are used to clean the air or the ammonia-air mixture of mechanical admixtures.

Depending on the purpose, pipes of brands f, m and g are manufactured, as well as pipes of the NIistroykeramika [State Scientific Research Institute of Building Ceramics]. Pipes of brand f, m and of the NIistroykeramika are used on units which produce nitric acid at atmospheric and increased pressures; those of brand g are only used on units that operate at atmospheric pressure.

The porolite pipes must meet the requirements of TU GIAP 232-50. The chief of these requirements: gluing of the individual pipe pieces is not permitted; the surface of the pipes must be even, without cracks and twists over the length; individual grains of porolite must not be painted during testing by the accepted technique; the tensile strength during compression for pipes of brand f must be 180 kg-f/cm^2 , for pipes of brand q--about 150 kg-f/cm^2 .

Pipes of the following dimensions are supplied (in mm):

Diameter	50/30	58/38	58/38
Length	762	350	210
Bead	60/12	70/10	70/10

Deviations are permitted in the dimensions of the pipes for length and diameter $\pm 1 \text{ mm}$, dimensions of the beads $\pm 0.2 \text{ mm}$. The pipes must have porosity (free volume in % of total volume) in limits of 40-52%. The pore size must be 110-120 μ for brand m pipes, and 80-100 μ for brand f.

The gas permeability of the pipes in conversion for air with resistance of 30 mm wat. col. and 20°C for brand m must be 280-320 m^3/h per 1 m^2 of outer surface, and for brand f, in limits of 250-270 $\text{m}^3/(\text{m}^2 \times \text{h})$.

The porolite pipes are packed in groups of 60 in wooden boxes. Each pipe must be wrapped in paper.

Physical-Chemical Properties of Nitric Oxides⁶⁻¹²

The following nitric oxides are known: nitrous N_2O , nitric NO , nitrous anhydride N_2O_3 , dioxide NO_2 , its dimer (tetroxide) N_2O_4 and nitric anhydride N_2O_5 .

Nitric anhydride is a solid substance, the other nitric oxides are gases under normal conditions.

The heat of formation of nitric oxides made of simple substances⁶ (in cal/mole):

$N_2 + 1/2 O_2 = N_2O$ gas	19 490	$1/2 N_2 + O_2 = NO_2$ gas	8 091
$1/2 N_2 + 1/2 O_2 = NO$ gas	21 600	$N_2 + 2O_2 = N_2O_4$ gas	2 309
$N_2 + 3/2 O_2 = N_2O_3$ gas	20 000	$N_2 + 2 1/2 O_2 = N_2O_5$ solid . . .	-10 000

Below we will examine in detail the properties of nitric oxides. Additional data on their properties can be found in volume I of the Reference Book (pp. 28, 47, 53).

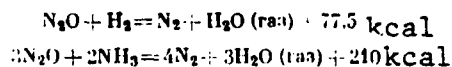
Nitrous oxide N_2O is a colorless gas with weak pleasant smell and sweetish taste. It has the following main properties:

Molecular weight	44.013	Critical temperature, °C	36.5
Density at 20°C, g/cm ³	1.978	Critical pressure, atm.	71.7
Molar volume at 0°C and 760 mm Hg, l	22.250	Heat, cal/mole of evaporation	5.99
Temperature at 760 mm Hg, °C		of melting	1.555
of boiling	-88.5	Heat capacity ^{6,7} at 1 atm, cal/(g x deg)	
of melting ⁶	-90.8	at 20°C	0.201
the same ⁸	-100	at 26-103°C	0.892

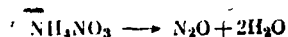
Density of N_2O at 25°C on the gas-liquid equilibrium line⁹ is 0.18 g/cm³ for gas and 0.75 g/cm³ for liquid.

Nitrous oxide does not interact with water, solutions of acids, alkalis or oxygen, however, hyponitrous acid $H_2N_2O_4$ which easily breaks down into water and nitrous oxide formally corresponds to it. At 520°C, nitrous oxide noticeably dissociates. At 900°C, or under the influence of an electrical current, it completely breaks down according to the reaction: $2N_2O = 2N_2 + O_2 + 39$ kcal.

At a high temperature, N₂O displays strong oxidizing properties. Such strong oxidizers as KMnO₄, Cl₂O and others almost do not oxidize nitrous oxide.¹⁰ Mixtures of N₂O with hydrogen, ammonia or carbon monoxide explode with certain ratios of the components. In this case, the following reactions occur:



Nitrous oxide is obtained during the interaction of nitric or nitrous acid with different reducing agents (hydrogen sulfide, sulfuric acid, etc.). A small quantity of N₂O is formed during conversion of ammonia into nitric oxide. N₂O is produced in industry by thermal breakdown of ammonium nitrate:



This process is accompanied by release of heat and occurs with increasing velocity, therefore special caution is required during its execution.

When a mixture of air and N₂O is inhaled, a condition occurs which is close to intoxication (the name for N₂O "laughing gas" comes from here).

The solubility of N₂O in water¹¹:

Temperature, °C	0	5	10	15	20	25
Solubility, cm ³ /cm ³ of water	1.2469	1.048	0.8878	0.7377	0.6294	0.5443

The solubility of N₂O in sulfuric acid⁸ at room temperature:

H ₂ SO ₄ concentration, weight. %	36.9	77.2	17.7
Solubility, cm ³ /100 cm ³ H ₂ SO ₄	66.0	39.1	33.0

Pressure of vapors¹⁰ above liquid N₂O:

Temperature, °C	-80.5	-39.5	-24.0	0	+18	35.4
Pressure of vapors, atm.	1.6	9.7	16.5	30.3	49.5	75.0

Pressure of vapors¹⁰ above solid N₂O:
 Temperature, °C -170 -165 -160 -157.5 -154.5 -152.5 -150.0 -131.3
 Pressure of vapors, mm Hg 0.0013 0.0096 0.030 0.059 0.114 0.182 0.306 6.99

TABLE I-16. HEAT CAPACITY, ENTHALPY AND ENTROPY OF NITROUS OXIDE¹ AT 1 atm

t, °C	c _p	c _v	c _p	c _v	c' _p	c' _v	i	i'	s	s'
	$\frac{\text{ккал}}{\text{кмоль} \cdot \text{град}}$ 1		$\frac{\text{ккал}}{\text{кг} \cdot \text{град}}$ 2		$\frac{\text{ккал}}{\text{м}^3 \cdot \text{град}}$ 3		$\frac{\text{ккал}}{\text{кг}}$ 4	$\frac{\text{ккал}}{\text{м}^3}$ 5	$\frac{\text{ккал}}{\text{кг} \cdot \text{град}}$ 6	$\frac{\text{ккал}}{\text{м}^3 \cdot \text{град}}$ 7
0	8.945	6.959	0.2032	0.1581	0.3991	0.3105	0	0	0	0
100	9.988	8.000	0.2269	0.1817	0.4455	0.3569	21.55	42.32	0.0681	0.1338
200	10.811	8.825	0.2456	0.2005	0.4823	0.3937	45.22	88.82	0.1243	0.2441
300	11.493	9.507	0.2641	0.2160	0.5127	0.4241	70.61	138.7	0.1730	0.3397
400	12.062	10.076	0.2740	0.2289	0.5381	0.4495	97.37	191.2	0.2161	0.4243
500	12.542	10.556	0.2849	0.2398	0.5595	0.4709	125.3	246.1	0.2548	0.5003
600	12.946	10.960	0.2941	0.2490	0.5776	0.4890	154.3	303.0	0.2918	0.5731
700	13.282	11.296	0.3017	0.2566	0.5926	0.5040	184.1	361.6	0.3224	0.6331
800	13.573	11.587	0.3084	0.2632	0.6055	0.5169	214.7	421.6	0.3523	0.6918
900	13.824	11.838	0.3141	0.2689	0.6167	0.5281	245.8	482.7	0.3801	0.7464
1000	14.038	12.052	0.3189	0.2738	0.6263	0.5377	277.5	544.9	0.4060	0.7973
1100	14.226	12.240	0.3232	0.2789	0.6347	0.5461	309.6	607.9	0.4303	0.8449

Key:

1. $\frac{\text{kcal}}{\text{kmole} \times \text{deg}}$
2. $\frac{\text{kcal}}{\text{kg} \times \text{deg}}$
3. $\frac{\text{kcal}}{\text{m}^3 \times \text{deg}}$
4. $\frac{\text{kcal}}{\text{kg}}$
5. $\frac{\text{kcal}}{\text{m}^3}$
6. $\frac{\text{kcal}}{\text{kg} \times \text{deg}}$
7. $\frac{\text{kcal}}{\text{m}^3 \times \text{deg}}$

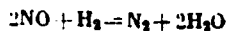
Nitric oxide NO is a colorless gas which at atmospheric pressure and at -151.8°C (for other data at -151.4°C) is converted into a colorless liquid. Nitric oxide is polymerized in the liquid state.

Below are the main properties of nitric oxide:

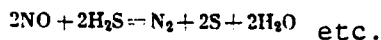
Molecular weight	30.006	Temperature at 760 mm Hg, °C	
Density at 20°C, g/cm ³	1.340	of boiling	-151.8
Molar volume at 0°C		of melting	-163.7
and 760 mm Hg, l	22.388	Heat capacity at 1 atm and	

Critical pressure, atm	51.6 64.6	15°C, cal/(g x deg)	0.242
Critical temperature, °C	-92.9		

Nitric oxide is prone to reactions of oxidation, reduction and addition. It belongs to the very reaction-capable substances. The oxidizing properties of NO appear, for example, during interaction with hydrogen



or with hydrogen sulfide



A mixture of equal volumes of hydrogen and nitric oxide explodes when heated. At temperatures above 330°C, nitric oxide partially reduces nitrates to nitrites with the release of nitrogen peroxide. Interacting with hydrogen sulfide and sulfides, NO is partially converted into nitrous oxide under certain conditions.

Hydrogen peroxide, potassium permanganate, lead or manganese peroxide, hypochlorous acid rapidly oxidize NO into NO₂. Concentrated nitric acid even with relatively low temperatures (for example, 0-3°C) oxidizes NO, being restored to nitric acid. Easily oxidized substances (coal, magnesium, etc.) intensively burn in a medium of nitric oxide. If nitric oxide at normal temperature is mixed with oxygen, red-brown vapors of higher nitric oxides are instantly formed. The nitric oxide oxidation reaction



in contrast to the majority of other reactions is drastically slowed down with a rise in temperature.

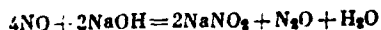
Aqueous solutions of certain salts join NO, forming complex compounds (for example, FeSO₄ x NO, CuCl₂ x NO). When such solutions are heated, nitric oxide is completely volatilized from them. Chlorine interacts with NO, forming chlorous nitrosyl NOCl. NO is not very soluble in water.

The coefficients of absorption* α of nitric oxide by water^{11,12}:

Temperature, °C	0	10	15	60	80	90	100
$\alpha \times 10^3$	73.81	57.09	51.47	29.5	27.0	26.48	26.28

Nitric oxide is practically completely insoluble in a saturated NaCl solution and is not very soluble in sulfuric acid. With a change in the concentration of sulfuric acid, the solubility of nitric oxide changes comparatively little.

NO does not interact with diluted solutions of alkalis. It begins to react with concentrated solutions after lengthy contact:



Nitric oxide which is stable under normal conditions at temperatures above 1200°C breaks down into nitrogen and oxygen:



The opposite reaction, the formation of NO from nitrogen and oxygen can only occur with very high temperatures, since it requires outlays of a great quantity of heat.

Nitric oxide is produced in industry by catalytic oxidation of ammonia. Under laboratory conditions it is produced by the reaction:



TABLE I-17. VAPOR PRESSURE¹⁰ ABOVE LIQUID NO

Temperature °C	Pressure atm.	Temperature, °C	Pressure atm.	Temperature, °C	Pressure atm.
-188.2	8.95	-120.6	13.3	-100.7	45.7
-125.9	9.80	-120.3	14.1	-97.3	53.1
-124.0	10.7	-112.6	21.6	-96.3	55.6
-122.9	11.9	-109.2	27.7	-95.1	58.0
-122.2	12.4	-102.9	41.0	—	—

* The volume of gas (relative to normal conditions) absorbed by a unit of volume of solvent.

The vapor pressure above the liquid nitric oxide is computed from the equation¹²:

$$\lg p = 9.562128 - \frac{776}{T} - 0.002364T$$

where p--pressure of vapor in mm Hg;
T--absolute temperature.

TABLE I-18. RATIO BETWEEN NO AND NO₂ WITH DIFFERENT TEMPERATURES³

Temperature °C	Degree of dissociation %	Constant of rate of oxidation, k x 10 ⁻⁴	Time for oxidation of 10% NO, s
0	0,0	4,7	0,44
30	0,0	2,8	0,98
90	0,0	1,8	2,05
150	1,5	1,17	4,35
300	31,0	0,6	16,00
400	65,0	0,45	30,20

The time (in s) that is necessary for oxidation of NO into NO₂ with absolute pressure of 1-6 atm (the original gas contains 9% NO and 7% O₂)^{13,14}:

Pressure atm.	Degree of oxidation of NO, %			
	70	80	90	98
1	35	67	178	1200
2	9.5	18.2	48	326
3	4.7	9	24	161
4	2.9	5.6	15	100
5	2.5	4	11	72
6	1.7	3.3	9	59

Nitrogen Peroxide NO₂ and Nitrogen Tetroxide N₂O₄

Nitrogen peroxide (tetroxide) is a reddish-brown gas with noxious smell. It is easily compressed at atmospheric pressure at 21.15°C into a reddish-brown liquid. At -10.2°C the liquid hardens, forming colorless crystals.

Below are the main properties of NO₂ and N₂O₄:

Molecular weight		Temperature at 760 mm Hg, °C	
NO ₂	46.01	of boiling	20.7
N ₂ O ₄	92.02	of melting	-9.3
NO ₂ density at 20°C, g/cm ³	1.491	Heat, cal/g of evaporation	100

Molar volume of N₂O₄ at 760 mm Hg. 22.370 of melting 32.2
 Critical pressure, atm. 99 Molar heat capacity at 1 atm., cal/(mole x deg) NO₂ 8.43
 Critical temperature, °C 158.2 N₂O₄ 14.85

TABLE I-19. HEAT CAPACITY, ENTHALPY AND ENTROPY OF NITRIC OXIDE¹ AT 1 ATM.

t, °C	c _p	c _v	c _p	c _v	c _p	c _v	i	i'	s	s'
	(1)		(2)		(3)		(4)	(5)	(6)	(7)
	$\frac{\text{KCAL}}{\text{KMOL} \cdot \text{град}}$		$\frac{\text{KCAL}}{\text{KG} \cdot \text{град}}$		$\frac{\text{KCAL}}{\text{M}^3 \cdot \text{град}}$		$\frac{\text{KCAL}}{\text{KG}}$	$\frac{\text{KCAL}}{\text{M}^3}$	$\frac{\text{KCAL}}{\text{KG} \cdot \text{град}}$	$\frac{\text{KCAL}}{\text{M}^3 \cdot \text{град}}$
0	7.160	5.174	0.2386	0.1724	0.3194	0.2308	0	0	0	0
100	7.148	5.160	0.2381	0.1719	0.3188	0.2303	23.80	31.87	0.0742	0.0994
200	7.245	5.259	0.2414	0.1752	0.3232	0.2346	47.76	63.94	0.1311	0.1756
300	7.418	5.432	0.2472	0.1810	0.3309	0.2423	72.18	96.63	0.1780	0.2384
400	7.603	5.617	0.2534	0.1872	0.3392	0.2500	97.20	130.1	0.2182	0.2922
500	7.784	5.798	0.2594	0.1932	0.3473	0.2587	122.8	164.4	0.2537	0.2397
600	7.946	5.960	0.2648	0.1986	0.3545	0.2659	149.0	199.6	0.2856	0.3824
700	8.087	6.101	0.2695	0.2033	0.3608	0.2722	175.8	235.3	0.3146	0.4213
800	8.209	6.223	0.2736	0.2074	0.3662	0.2776	203.0	271.7	0.3413	0.4569
900	8.311	6.325	0.2770	0.2108	0.3708	0.2822	230.5	308.5	0.3658	0.4898
1000	8.399	6.413	0.2799	0.2137	0.3747	0.2861	258.3	345.8	0.3885	0.5203
1200	8.537	6.551	0.2845	0.2183	0.3809	0.2923	314.8	421.8	0.4298	0.5753
1400	8.644	6.658	0.2881	0.2219	0.3856	0.2970	372.1	498.1	0.4663	0.6242
1600	8.724	6.738	0.2907	0.2245	0.3892	0.3006	430.1	575.1	0.4990	0.6680
1800	0.788	6.802	0.2928	0.2267	0.3921	0.3035	488.3	653.8	0.5285	0.7076
2000	8.843	6.857	0.2947	0.2285	0.3945	0.3059	547.2	732.4	0.5555	0.7437
2200	8.884	6.898	0.2960	0.2299	0.3963	0.3077	606.3	811.8	0.5805	0.7771
2400	8.921	6.935	0.2973	0.2311	0.3980	0.3094	665.5	890.9	0.6038	0.8081

Key:

- $\frac{\text{kcal}}{\text{kmole} \times \text{deg.}}$
- $\frac{\text{kcal}}{\text{kg} \times \text{deg}}$
- $\frac{\text{kcal}}{\text{m}^3 \times \text{deg.}}$
- $\frac{\text{kcal}}{\text{kg}}$
- $\frac{\text{kcal}}{\text{m}^3}$
- $\frac{\text{kcal}}{\text{kg} \times \text{deg}}$
- $\frac{\text{kcal}}{\text{m}^3 \times \text{deg.}}$

Nitrogen peroxide has the capacity to be polymerized:

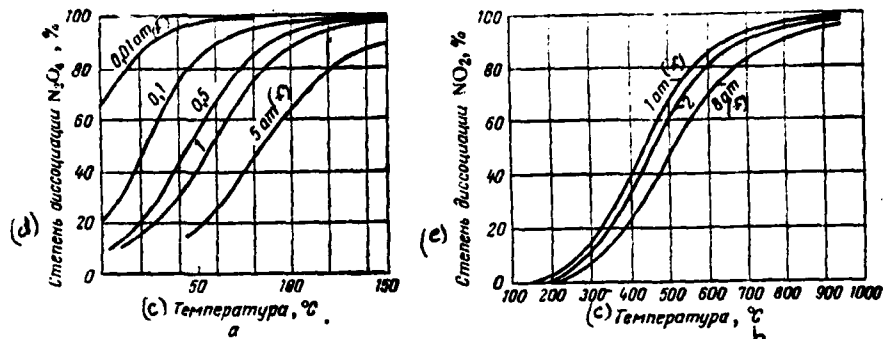
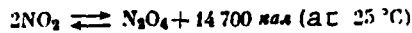


Figure I-1. Dependence of Degree of Dissociation of Nitric Oxides on Pressure and Temperature

Key:

- a. Nitrogen tetroxide
- b. Nitrogen peroxide¹³
- c. Temperature, °C
- d. Degree of dissociation of N_2O_4 , %
- e. Degree of dissociation of NO_2 , %
- f. atmospheres

In the temperature interval from -10 to 135°C , a definite equilibrium is established between the NO_2 and the N_2O_4 molecules. The lower the temperature and the higher the NO_2 concentration in the gas, the greater the quantity of it is polymerized. The breakdown of N_2O_4 molecules increases with a decrease in concentration, and especially with an increase in temperature.

The degree of N_2O_4 and NO_2 dissociation is presented in figures I-1 and I-2.

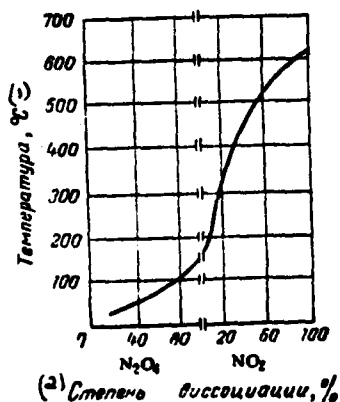


Figure I-2. Dependence of the Composition of Nitric Oxides on Temperature.¹¹

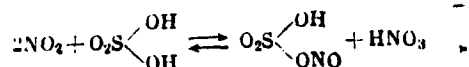
Key:

1. Temperature, °C
2. Degree of dissociation, %

The effect of temperature on the breakdown of N_2O_4 and NO_2 into nitric oxide and oxygen is apparent from the following data:

Temperature, °C	26.7	49.6	70	80.8	111.3	135	80	494	620
Breakdown, %									
N_2O_4	20	40	65.8	76.6	92.7	98.7	—	—	—
NO_2	—	—	—	—	—	—	5.0	56.5	100

Nitrogen peroxide and nitrogen tetroxide interact with water, forming nitric and nitrous acids, and nitrates and nitrites with caustic alkalis and calcined soda. Nitrogen peroxide is easily absorbed by concentrated sulfuric acid, forming nitrosylsulfuric acid:



The rate of the inverse reaction is somewhat diminished with an increase in temperature.

Nitrogen peroxide is a very strong oxidizer. Potassium, carbon, sulfur and other substances easily burn in its atmosphere. NO_2 forms explosive mixtures with the vapors of many organic compounds. A strong explosion occurs when carbon disulfide mixes with nitrogen peroxide.

Like nitric acid, NO_2 can form complex compounds, for example: $FeCl_3 \times NO_2$, $4FeCl_2 \times NO_2$, $BiCl_3 \times NO_2$, etc.

N_2O_4 reacts violently with liquid, and in certain ratios with gaseous ammonia, forming water, nitric acid, elementary nitrogen and small quantities of N_2O .

NO_2 reacts with hydrogen in the presence of catalysts (platinum, palladium etc.) with the formation of water and ammonia.

At definite temperatures, ammonium nitrate partially or completely is destroyed by liquid N_2O_4 .

TABLE I-20. NO₂ DENSITY ON SATURATION LINE*

(1) Темпе- ратура °C	(2) Давле- ние, атм	(3) Плотность, г/см ³		(1) Темпе- ратура °C	(2) Давле- ние, атм	(3) Плотность, г/см ³	
		(4) жидко- сти	(5) пара			(4) жидко- сти	(5) пара
21,2	1,04	1,440	0,0034 ⁴	126,7	44,8	1,087	0,1146
43,3	2,71	1,390	0,00782	137,8	60,7	1,005	0,163
60,0	5,21	1,344	0,0142	148,9	81,4	0,887	0,248
71,4	7,82	1,316	0,0207	158,2**	103,0	—	0,552
104,4	23,39	1,201	0,0584	—	—	—	—

* Reamer, H. and Sage, B. Ind. Eng. Chem., 44, No. 1
1963, 185.

** Critical temperature

Key:

1. Temperature °C
2. Pressure, atm₃
3. Density, g/cm³
4. of liquid
5. of steam

The density of gaseous NO₂:

Temperature, °C	30	50	70	90	100
Density, g/cm ³	0.00490	0.00890	0.01200	0.0190	0.0266

The density^{3,10} of liquid N₂O₄:

Temperature, °C	-20	-20	-10	-5	0	10	15	20	38,75	78,45	100
Density, g/cm ³		1.533	1.5124	1.5035	1.4935	1.4680	1.4740	1.4470	1.398	1.284	1.204

The viscosity μ of gaseous^{15,16} NO₂:

Temperature, °C	-75	-50	-25	0	20	25	50	75	100
$\mu \times 10^7$, poise	990	1115	1240	1360	1455	1480	1590	1710	1820

The freezing temperatures³ of mixtures of N₂O₄ and N₂O₃:

N ₂ O ₃ content in mixture, %	3.8	5.7	9.1	12.8
Temperature, °C	-13.7	-17	-19	-23.2

TABLE I-21. VISCOSITY (IN CENTIPOISE) OF LIQUID¹⁷ NO₂

(1) Темпера- тура °C	(2) Давление, атм					(1) Темпера- тура °C	(2) Давление, атм				
	20	60	100	200	300		20	60	100	200	300
10	0.471	0.479	0.498	0.509	—	70	0.229	0.236	0.243	0.253	0.262
30	0.379	0.385	0.391	0.406	0.421	90	0.170	0.183	0.194	0.208	0.215
50	0.296	0.302	0.308	0.318	0.327	100	—	0.161	0.173	0.187	0.195

Key:

1. Temperature, °C
2. Pressure, atm.

TABLE I-22. VAPOR PRESSURE¹⁰ ABOVE LIQUID N₂O₄

(1) Температура °C	(2) Давление мм рт. ст.	(1) Температура °C	(2) Давление мм рт. ст.	(1) Температура °C	(2) Давление мм рт. ст.
-25.2	69,6	11.4	467,5	40,0	1751,5
-21,0	84,6	17,0	613,5	44,83	2125,0
-10,0	147,5	21,5	752,0	48,95	2522,0
-3,1	225,3	25,05	913,9	55,4	3261,0
0	257,5	34,8	1403,0	60,0	3980,0

Key: (1) Temperature, °C; (2) Pressure, mm.

Vapor pressure above pure liquid¹⁷ N₂O₄:

Temperature, °C	-100	-80	-25	-11.2+0.84	10	15	21.2	
Vapor pressure, mm Hg	1.1	5.3	70	139.8	266	454	569.4	760

TABLE I-22a. VAPOR PRESSURE¹⁰ ABOVE LIQUID MIXTURE OF N₂O₄ and N₂O₃ (IN mm Hg)

(1) Температура °C	(2) Содержание N ₂ O ₃ в смеси, вес. %					
	0	20	40	60	80	100
-16	108	168	260	409	685	1250
-8	172	262	398	623	1018	1785
0	258	400	600	925	1475	2480
+8	396	590	882	1331	—	—
16	598	880	1270	1857	—	—
20	684	1040	1520	2130	3280	5000

Key: (1) Temperature, °C; (2) N₂O₃ content in mixture, weight %.

The vapor pressure³ above the liquid nitric oxides that contain 2-4 weight.% of water and up to 0.2% N₂O₃:

Temperature, °C	-20	-10	0	10	20
Vapor pressure, mm Hg	70	192	244	396	598

The breakdown of ammonium nitrate¹⁸ in liquid N₂O₄:

Temperature, °C	25	25	25	0	0	0
Content of ammonium nitrate in liquid N ₂ O ₄	6.0	12.5	16.0	0.5	9.8	16
Reaction time, h	2	2	2	16	16	16
Degree of NH ₄ NO ₃ breakdown, %	46.5	44.0	47.0	36.0	37.0	39.0

The specific heat capacity³ c_p of gaseous N₂O₄ at 1 atm:

Temperature, °C	33.7	42.5	58.0	67.0	80.9	97.5
c _p x kcal/(kg x deg)	0.124	0.130	0.162	0.171	0.175	0.190

Heat conductivity λ of gaseous NO_2 (at 580 mm Hg)⁶:

Temperature, °C	18	33	55	65	84	120	134
$\lambda \times 10^3$, kcal/(m x h x deg)	24.2	32.7	32.0	37.2	26.4	7.53	6.52

Nitrous Anhydride

Nitrous anhydride (nitrogen trioxide) N_2O_3 is a reddish-brown or chestnut gas which is condensed during cooling into a dark blue liquid that burns with breakdown at 3.5°C. In the solid state it is crystals of a blue or dark blue color.

Below are the main properties of nitrous anhydride:

Molecular weight	76.01	Temperature, °C	
Density (liquid), g/cm ³	1.449	of boiling	3.5
Heat of evaporation, kcal/mole	9.3	of melting	-102

Nitrous anhydride is an unstable compound. At -2°C it is almost completely dissociated into NO and NO_2 . Its dissociation is apparently associated with the catalytic effect of water traces. N_2O_3 is only located in a comparatively stable state at -27°C.

N_2O_3 has limited mixing with water. With alkalis it forms nitrites with admixtures of nitrates. With sulfuric acid it forms nitrosylsulfuric acid. Nitrous anhydride is found, in addition to N_2O_4 , in a mixture containing oxide and nitrogen peroxide.

The vapor pressure³ above liquid N_2O_3 :

Temperature, °C	-70	-60	-50	-40	-30	-20	-10	0	3.5
Pressure, mm Hg	171	176	182	200	227	264	310	455	760

The density³ of liquid N_2O_3 :

Temperature, °C	-8	-4	-1	0	1	2
Density, g/cm ³	1.464	1.455	1.451	1.449	1.448	1.447

TABLE I-23. EFFECT OF PRESSURE AND TEMPERATURE¹⁹
ON ASSOCIATION OF NO AND NO₂ WITH FORMATION OF N₂O₃

(1) Давление газа атм	(2) Содержание N ₂ O ₃ в смеси (NO+NO ₂), вес. %				(1) Давление газа атм	(2) Содержание N ₂ O ₃ в смеси (NO+NO ₂), вес. %			
	(3) при 0 °C	(3) при 25 °C	(3) при 50 °C	(3) при 100 °C		(3) при 0 °C	(3) при 25 °C	(3) при 50 °C	(3) при 100 °C
0.01	1.2	0.35	0.1	0.03	2.0	—	15.0	9.1	2.4
0.05	3.6	1.40	0.5	0.10	2.5	—	16.5	10.4	2.9
0.1	5.5	2.4	0.9	0.15	4.0	—	—	13.5	4.3
0.2	8.0	4.0	1.7	0.25	6.0	—	—	16.5	5.9
0.4	11.3	6.3	3.0	0.50	8.0	—	—	19.0	7.3
0.8	15.6	9.3	5.0	1.0	10	—	—	—	8.6
1.0	—	10.5	5.8	1.2	20	—	—	—	13.5
1.5	—	13.0	7.6	1.8					

Key:

1. Gas pressure, atm.
2. N₂O₃ content in mixture (NO + NO₂) weight, %
3. at

TABLE I-24. PRESSURE OF VAPORS ABOVE SYSTEM NO-NO₂
WITH DIFFERENT CONTENTS OF N₂O₃ AND GAS TEMPERATURE
(in mm Hg)

(1) Содержание N ₂ O ₃ вес. %	(2) Температура газа, °C					(1) Содержание N ₂ O ₃ вес. %	(2) Температура газа, °C				
	20	30	40	50	60		20	30	40	50	60
18.8	1010	1430	2130	—	—	34.0	1380	1910	2760	3860	5200
23.2	1120	1560	2320	3330	4390	35.6	1420	1960	2820	3930	5280
26.8	1200	1650	2420	3440	4700	43.6	1620	2210	3170	4420	5930
29.4	1270	1760	2570	3630	4930	52.0	1860	2570	3680	5120	6880
32.2	1340	1870	2710	3800	5130						

Key:

1. N₂O₃ content, weight, %
2. Temperature of gas, °C

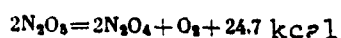
Nitric Anhydride

Nitric anhydride (nitrogen pentoxide) N₂O₅ at normal temperature is a very unstable solid substance which diffuses in the air. It is in the form of colorless needle-shaped crystals or rhombic plates.

Below are the main properties of nitric anhydride:

Molecular weight	108.01	Heat, kcal/mole	
Density (solid) at 20°C,	1.642	of formation from simple	
g/cm ³		substances	-10
Temperature, °C		of evaporation	13.6
of melting	~30	of dissolving in water	16.8
of sublimation	32.4		

When solid N₂O₅ is melted, liquid of intensive yellow color is formed. Under the influence of light and gradual heating, liquid N₂O₅ actively breaks down according to the reaction:



In the case of rapid heating, the breakdown occurs with an explosion of great force (there are also known cases of explosions of N₂O₅ when it is stored under normal conditions). The breakdown of N₂O₅ during heating occurs according to an equation of the first order. At 0°C, roughly half of the N₂O₅ from its original quantity is broken down in 10 days, and at 20°C, in 10 h. Nitric anhydride reacts violently with water forming nitric acid. It is restored by nitric acid according to the reaction:



Nitric anhydride is the strongest oxidizer. Carbon, phosphorus, sulfur and other easily oxidized substances rapidly burn under the influence of N₂O₅. Many organic substances nitrate N₂O₅. The degree of nitration is the same as under the influence of a mixture of concentrated nitric and sulfuric acids.

Under normal conditions, N₂O₅ is not formed during oxidation of NO by oxygen.²¹ It can be obtained from concentrated nitric acid by removing water with the help of P₂O₅ or by oxidation by ozone of gaseous NO₂ or liquid N₂O₄ according to the equation:



A method has also been developed for obtaining N₂O₅ from N₂O₄ and oxygen at 2000 atm. N₂O₅ is not formed when diluted nitric

acid is produced.

The attempts to formulate a method for producing N_2O_5 for industrial purposes have not yielded positive results.

Vapor pressure^{9,10} above solid N_2O_5 :

Temperature, °C	-20	-10.7	0	10.5	32.5
Vapor pressure, mm Hg	10	18.6	51.5	132	760

Heat capacity³ c of solid N_2O_5 :

Temperature, °C	-173.1	-121.1	-73.1
c, kcal/(kg x deg)	0.140	0.200	0.241

Physical-Chemical Properties of Nitric and Nitrous Acids^{3,9,10,12,22-24}

Anhydrous nitric acid is a not very stable compound. At normal temperature, it is a colorless liquid with caustic noxious smell. Commercial-grade nitric acid has a yellowish color that is governed by the presence in it of a small quantity of dissolved nitric acids.

The main properties of nitric acid are presented below:

		Heats of formation	kcal/mole
Molecular weight	63.01		
Density at 15°C, g/cm ³	1.53	$\frac{1}{2}N_2 + \frac{3}{4}O_2 + \frac{1}{2}H_2 = HNO_3$ (gas)	34.4
Temperature, °C of boiling	86	$\frac{1}{2}N_2 + \frac{3}{4}O_2 + \frac{1}{2}H_2 = HNO_3$ (liq.)	41.66
of melting	-42.0	$\frac{1}{2}N_2 + \frac{3}{4}O_2 + \frac{1}{2}H_2 = HNO_3$ (solid)	49.1
Heat, cal/g of melting	9.5	$NO + O_2 + \frac{1}{2}H_2 = HNO_3$ (liquid)	63.49
of evaporation ⁹⁷	115	$NO_2 + \frac{1}{2}O_2 + \frac{1}{2}H_2 = HNO_3$ (liquid)	42.52
the same ⁹⁸	148.5	$\frac{1}{2}N_2O_4 + \frac{1}{4}O_2 + \frac{1}{2}H_2O =$	
of dilution	118.5	$= HNO_3$ (liquid)	18.67

There are two known crystal hydrates of nitric acid (fig. 3):

trihydrate $HNO_3 \times 3 H_2O$ (53.8% HNO_3), melting point -18 °C;
 monohydrate $HNO_3 \times H_2O$ (77.8% HNO_3), melting point -38 °C.

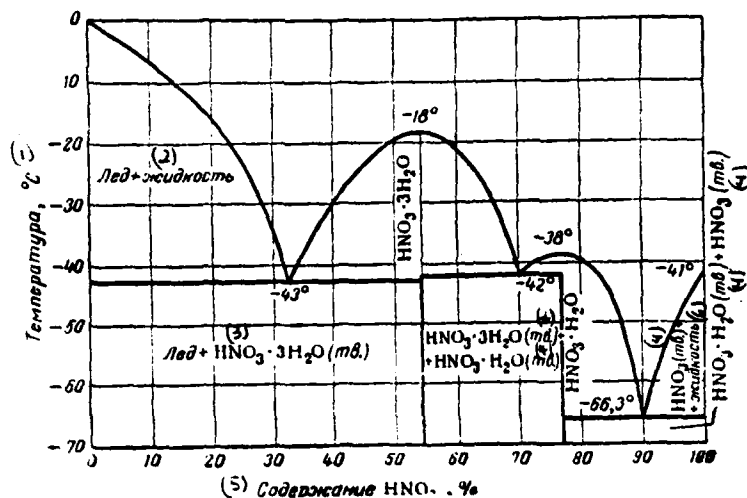


Figure I-3. Diagram of Crystallization of HNO₃-H₂O System

Key:

1. Temperature, °C
2. Ice + liquid
3. Ice + HNO₃ x 3 H₂O (solid)
4. (solid)
5. Content of HNO₃, %
6. + liquid

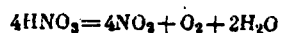
There are eutectic points on the curve of crystallization of the HNO₃-H₂O system: at -63.1°C (89.95% HNO₃), at -42°C (70.5% HNO₃) and -43°C (32.7% HNO₃).

Nitric acid mixes with water in any ratios. The boiling temperature of aqueous solutions increases with a rise in the concentration, reaching the maximum of 121.9°C with a content of 68.4 weight.% HNO₃ (pressure 1 atm.), and diminishes with a further rise in concentration.

During distillation of aqueous solutions of nitric acid, water vapors are initially primarily present in the vapor phase. They are gradually enriched with HNO₃ vapors, and when the boiling temperature of 121.9°C is reached, an azeotropic mixture is formed. The content of HNO₃ both in liquid and in vapors is 68.4%.

Concentrated nitric acid during heating in light and under

the influence of reducers is broken down according to the reaction:



Nitric acid is a strong oxidizer. All the metals, except platinum, rhodium, iridium, titanium, tantalum and gold, are dissolved in nitric acid. In this case oxides of metals or nitrates are formed. With an increase in temperature, the effect of HNO_3 on metals and their alloys is considerably intensified.

Special steels (for example, certain chrome-nickel steels) are resistant in a medium of nitric acid with concentration to 70% HNO_3 . An alloy of iron and silicon (ferrosilide) is practically resistant with any concentration and any temperature of nitric acid.

Of the widespread metals, aluminum is the most resistant to the effect of concentrated nitric acid. A thin layer of aluminum oxide which protects the metal from further destruction is formed on the surface of aluminum in a medium of nitric acid.

Concentrated nitric acid destroys many organic substances: paper, straw, wood, sawdust, cotton fibers, fabric etc. Under the influence of HNO_3 they are carbonized, and under certain conditions, may ignite. In this case the acid breaks down, releasing nitric oxides. It actively interacts with nonmetals: sulfur is oxidized into sulfuric acid, coal ignites under certain conditions, etc. During the interaction of concentrated HNO_3 and cyclic organic compounds, one or several atoms of hydrogen are replaced by a nitro-group. The acid forms nitric acid ethers, etc. with organic substances that contain the OH group. The interaction of HNO_3 with carbon, turpentine, alcohol and certain other substances can be accompanied by an explosion.

A mixture of 1 part of concentrated nitric acid and 3.6 parts of concentrated hydrochloric acid that has been called aqua regia, is the strongest oxidizer. Even platinum and gold dissolve in it.

TABLE I-25. DENSITY OF AQUEOUS SOLUTIONS OF NITRIC ACID^{3,12} AT 20°C

(1) Плотность г/см ³	(2) Концентрация		(1) Плотность г/см ³	(2) Концентрация		(1) Плотность г/см ³	(2) Концентрация	
	(3) вес. %	(4) г/л		(3) вес. %	(4) г/л		(3) вес. %	(4) г/л
1,026	5	51,3	1,246	40	498,5	1,339	55	736,3
1,054	10	105,4	1,253	41	513,6	1,345	56	753,1
1,084	15	162,6	1,259	42	529,8	1,351	57	769,8
1,115	20	223,0	1,266	43	544,2	1,356	58	786,5
1,147	25	286,7	1,272	44	559,6	1,361	59	803,2
1,180	30	364,0	1,278	45	575,2	1,367	60	820,0
1,187	31	367,9	1,285	46	591,0	1,372	61	836,9
1,193	32	381,9	1,291	47	606,8	1,377	62	853,7
1,200	33	396,1	1,298	48	622,8	1,382	63	870,5
1,207	34	410,4	1,304	49	639,0	1,387	64	887,4
1,214	35	424,9	1,310	50	655,0	1,391	65	904,3
1,2205	36	439,4	1,316	51	671,2	1,396	66	921,3
1,277	37	454,0	1,322	52	687,4	1,400	67	938,3
1,234	38	468,7	1,328	53	703,7	1,405	68	955,3
1,240	39	483,6	1,334	54	720,1	—	—	—

Key:

1. Density, g/cm³
2. Concentration
3. weight. %
4. g/l

Note: With temperature above or below 20°C, the following corrections should be made for the density values of each degree:

Density, g/cm ³	Correction	Density, g/cm ³	Correction
1,026—1,239	—	1,321—1,342	0,0013
1,240—1,250	0,0010	1,343—1,370	0,0013
1,251—1,320	0,0011	1,371—1,406	0,0014

TABLE I-26. DENSITY OF AQUEOUS SOLUTIONS OF NITRIC ACID (IN g/cm³) WITH DIFFERENT TEMPERATURE^{3,12}

(1) Концентрация вес. %	(2) Температура, °C							
	5	10	20	30	40	60	80	100
5	1,0290	1,0282	1,0256	1,0222	1,0084	1,0084	0,9965	0,9829
10	1,0594	1,0578	1,0543	1,0503	1,0455	1,0347	1,0221	1,0083
15	1,0909	1,0887	1,0842	1,0794	1,0739	1,0619	1,0485	1,0341
40	1,2613	1,2560	1,2463	1,2370	1,2270	1,2069	1,1858	1,1638
50	1,3277	1,3215	1,3100	1,2987	1,2867	1,2628	1,2377	1,2118
55	1,3583	1,3518	1,3393	1,3270	1,3141	1,2883	1,2615	1,2339
60	1,3868	1,3801	1,3667	1,3533	1,3398	1,3124	1,2839	1,2547
70	1,4362	1,4285	1,4134	1,3983	1,3837	—	—	—
95	1,5198	1,5109	1,4932	1,4761	—	—	—	—
98	1,5260	1,5176	1,5009	1,4837	—	—	—	—
99	1,5310	1,5227	1,5055	1,4887	—	—	—	—

Key:

1. Concentration, weight. %
2. Temperature, °C

When nitric acid is neutralized by alkalis, salts are formed which crystallize well (NaNO_3 , KNO_3 and others).

Surface tension σ of anhydrous nitric acid²²:

Temperature, °C	0	10	20	30	40	50	60	70	80
σ , erg/cm	20.5	19.5	18.4	17.4	16.3	15.3	14.3	13.2	12.2

TABLE I-27. HEAT CAPACITY OF AQUEOUS SOLUTIONS OF NITRIC ACID⁹ [in cal/(g x deg)]

Концентрация HNO_3 , вес. %	(2) Температура, °C				Концентрация HNO_3 , вес. %	(2) Температура, °C			
	2.5	21.1	39.5	60.1		2.5	21.1	39.5	60.1
1	0.993	0.990	0.985	0.990	50	0.667	0.680	0.693	0.710
2	0.978	0.980	0.973	0.980	55	0.649	0.660	0.675	0.690
4	0.953	0.950	0.951	0.960	60	0.630	0.640	0.654	0.670
6	0.927	0.930	0.929	0.940	65	0.607	0.620	0.629	0.640
10	0.884	0.890	0.891	0.900	70	0.583	0.590	0.603	0.610
15	0.838	0.840	0.851	0.860	75	0.558	0.570	0.574	0.580
20	0.799	0.800	0.815	0.830	80	0.535	0.540	0.548	0.560
25	0.767	0.780	0.786	0.800	85	0.515	0.520	0.521	0.530
30	0.739	0.760	0.764	0.780	90	0.490	0.490	0.493	0.500
35	0.716	0.740	0.744	0.770	95	0.456	0.460	0.461	0.460
40	0.698	0.720	0.726	0.750	100	0.418	0.420	0.425	0.430
45	0.682	0.700	0.709	0.730	—	—	—	—	—

Key:

1. HNO_3 concentration, weight. %
2. Temperature, °C

TABLE I-28. HEAT CONDUCTIVITY OF AQUEOUS SOLUTIONS OF NITRIC ACID²² [in kcal/(m x h x deg)]

Концентрация HNO_3 , вес. %	(2) Температура, °C						Концентрация HNO_3 , вес. %	(2) Температура, °C					
	0	20	40	60	80	100		0	20	40	60	80	100
5	0.467	0.505	0.533	0.554	0.567	0.573	65	0.341	0.347	0.350	0.355	0.353	0.359
15	0.451	0.484	0.508	0.528	0.538	0.544	75	0.310	0.310	0.310	0.310	0.310	0.310
25	0.433	0.459	0.478	0.495	0.505	0.509	85	0.275	0.273	0.271	0.269	0.267	0.265
35	0.413	0.434	0.448	0.461	0.469	0.473	95	0.239	0.236	0.232	0.228	0.225	0.221
45	0.392	0.408	0.418	0.428	0.434	0.436	100	0.221	0.216	0.212	0.208	0.205	0.201
55	0.369	0.379	0.387	0.394	0.399	0.400	—	—	—	—	—	—	—

Key:

1. Concentration of HNO_3 , weight. %
2. Temperature, °C

The vapor pressure p_{HNO_3} above anhydrous nitric acid:

t, °C	5	15	25	35	45	55	65	75	85
p_{HNO_3} , mm Hg	16.7	31.2	57	102	170	262	385	540	720

TABLE I-29. VISCOSITY OF AQUEOUS SOLUTIONS OF NITRIC ACID²³ (in centipoise)

(1) Концентрация HNO ₃ вес. %	(2) Температура, °C					(3) Концентрация HNO ₃ вес. %	(4) Температура, °C				
	0	10	20	30	40		0	10	20	30	40
10.5	—	1.38	1.25	0.87	0.749	64.0	3.18	2.48	2.00	1.65	1.290
15.3	1.68	1.38	1.21	0.88	0.760	79.1	2.81	2.52	1.63	1.37	1.140
23.0	1.94	1.52	1.24	1.02	0.885	90.2	2.17	1.73	1.38	1.06	0.947
35.5	2.34	1.80	1.48	1.25	—	99.5	1.18	0.947	0.836	0.753	0.684
53.9	3.22	2.38	1.94	1.66	1.290						

Key:

1. HNO₃ concentration, weight. %
2. Temperature, °C

TABLE I-30. FREEZING TEMPERATURE OF AQUEOUS SOLUTIONS OF NITRIC ACID²⁴

(1) Концентрация HNO ₃ , вес. %	(2) Температура °C	(3) Концентрация HNO ₃ , вес. %	(4) Температура °C	(5) Концентрация HNO ₃ , вес. %	(6) Температура °C
2.6	-1.7	46.0	-22.6	80.0	-37.8
5.3	-3.9	49.9	-18.9	81.4	-39.1
11.0	-7.5	50.7	-19.0	83.8	-42.9
14.0	-10.3	54.0	-18.5	84.7	-44.4
19.6	-15.7	58.7	-19.0	89.9	-66.5
25.0	-26.5	64.7	-28.6	90.5	-64.5
30.7	-37.7	69.46	-39.6	94.9	-40.7
32.8	-43.01	75.5	-38.2	98.8	-42.3
40.6	-27.5				

Key:

1. HNO₃ concentration, weight. %
2. Temperature, °C

TABLE I-31. VALUES OF PRANDTL'S CRITERION FOR AQUEOUS SOLUTIONS OF NITRIC ACID^{3,96}

(1) Концентрация HNO ₃ вес. %	(2) Температура, °C					(3) Концентрация HNO ₃ вес. %	(4) Температура, °C				
	10	30	40	60	100		10	30	40	60	100
20	9.11	5.78	4.90	3.27	1.85	70	15.78	10.28	8.49	6.40	3.45
40	11.84	7.67	6.42	4.45	2.67	90	11.94	7.51	6.59	5.24	3.17
50	14.00	9.39	7.52	5.28	3.12	95	9.12	6.40	5.81	4.72	3.01
60	15.64	10.35	8.58	6.05	3.38						

Key:

1. HNO₃ concentration, weight. %
2. Temperature, °C

TABLE I-32. PARTIAL PRESSURES OF VAPORS OF NITRIC ACID p_{HNO_3} , WATER $p_{\text{H}_2\text{O}}$ and TOTAL PRESSURE P ABOVE AQUEOUS SOLUTIONS OF NITRIC ACID^{9,12,25} (IN mm Hg)

Temperature, °C	p_{HNO_3}	$p_{\text{H}_2\text{O}}$	P	p_{HNO_3}	$p_{\text{H}_2\text{O}}$	P	p_{HNO_3}	$p_{\text{H}_2\text{O}}$	P
	30% HNO ₃			40% HNO ₃			45% HNO ₃		
5	—	5.0	5.0	—	4.2	4.2	0.05	3.6	3.6
15	—	9.7	9.7	0.07	8.0	8.0	0.10	6.9	7.0
25	—	17.8	17.8	0.12	14.6	14.7	0.23	12.7	13
35	0.07	31.1	31.2	0.25	25.5	25.7	0.48	22.3	22.8
45	0.17	53.0	53.2	0.52	43.2	43.7	0.95	38.0	39
55	0.35	87.0	87.3	1.04	71	72	1.83	62.5	64
65	0.71	140	141	2.05	114	116	3.47	100	103.5
75	1.38	217	218.4	3.80	178	182	6.20	158	164
85	2.53	325	328	6.83	268	275	10.7	240	251
95	4.53	478	483	11.7	394	406	17.8	355	373
105	7.9	690	698	20.0	573	593	29.2	520	549
115	—	—	—	32.5	810	843	46	740	786
	50% HNO ₃			55% HNO ₃			60% HNO ₃		
5	0.14	2.8	3.0	0.18	2.5	2.7	0.29	1.8	2.1
15	0.33	5.5	5.8	0.39	4.9	5.2	0.62	3.6	4.2
25	0.52	10.7	11.2	0.66	9.1	9.8	1.21	7.7	8.9
35	0.80	19.0	19.8	1.30	16.1	17.4	2.28	13.6	15.9
45	1.57	32.5	34	2.50	28	30.5	4.20	23.7	28
55	2.95	54	57	4.54	46.0	51	7.45	39	46
65	5.46	88	93	8.13	76	84	13.0	64	77
75	9.6	138	148	13.9	120	134	21.8	102	124
85	16.3	211	227	23.0	182	205	34.8	156	191
95	26.8	315	342	37.3	272	309	55.0	233	288
105	43.0	463	506	58.5	400	459	84.5	345	430
115	67	665	732	90	575	665	126	495	620
120	84	785	869	110	685	795	156	590	746
	65% HNO ₃			70% HNO ₃			90% HNO ₃		
5	0.60	1.3	1.9	1.10	0.92	2.02	10.7	0.13	10.8
15	1.21	2.8	4.0	2.20	1.97	4.2	19.5	0.31	19.8
25	2.32	6.4	8.7	4.10	5.1	9.2	29	0.8	29.8
35	4.26	11.6	15.9	7.30	9.8	17.1	47	1.8	49
45	7.55	20.0	27.6	12.6	16.7	29.3	80	3	83
55	12.8	33.0	46	21.0	27.3	48	127	5	132
65	21.7	54.5	76	34.5	44.5	79	192	8	201
75	35.0	86	121	54.5	70	124	282	13	295
85	54.5	131	186	83	107	190	405	20	425
95	83.5	195	279	125	158	283	570	29	599
105	124	288	412	183	231	414	790	42	832
115	181	410	591	262	330	592	—	—	—
125	260	580	840	372	469	841	—	—	—

Figures I-4-I-13 present the properties of anhydrous and diluted nitric acid under different conditions.

Nitrous acid HNO_2 is an unstable compound which exists only in diluted aqueous solutions. It is formed in solution together with nitric acid during absorption of nitric acids by water. In addition, nitrous acid is formed in the majority of processes where HNO_3 is used as an oxidizer, during transmission of nitrous anhydride in cold water, or an equimolecular mixture of NO and NO_2 , etc.

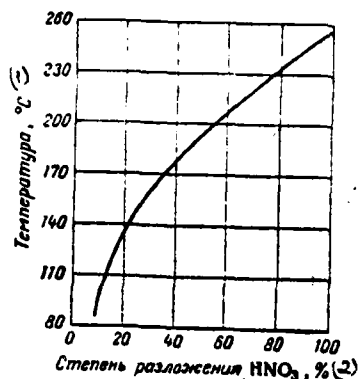


Figure I-4. Dependence of Degree of Nitric Acid Breakdown on Temperature

Key:

1. Temperature, °C
2. Degree of breakdown of HNO₃, %

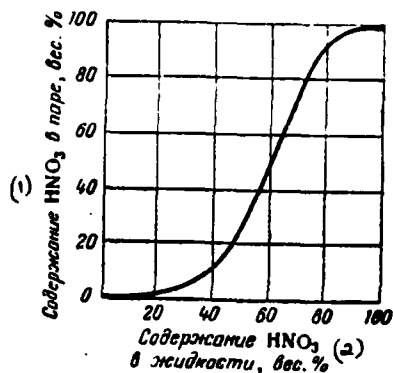


Figure I-5. HNO₃ Content in Liquid and Gaseous Phases at Boiling Point

Key:

1. HNO₃ content in vapor, weight. %
2. HNO₃ content in liquid, weight. %

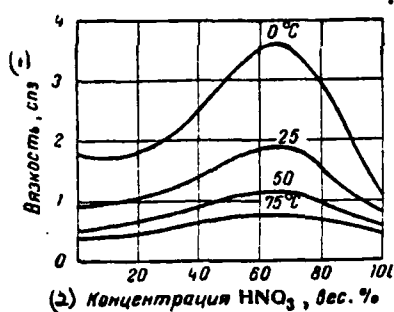


Figure I-6. Viscosity of Aqueous Solutions of Nitric Acid

Key:

1. Viscosity, centipoise
2. HNO₃ concentration weight. %

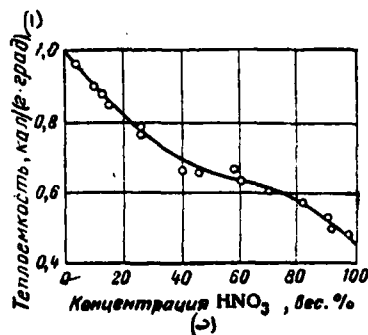


Figure I-7. Heat Capacity of Aqueous Solutions of Nitric Acid at Room Temperature

Key:

1. Heat capacity, cal/(g x deg)
2. HNO₃ concentration, weight. %

Below are certain properties of nitrous acid:

Molecular weight	47
Heat of formation from simple substances (at 18°C and 760 mm Hg), kcal/mole	28.5

Heat of breakdown according to reaction
 $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$, kcal -18.4(-18.13)
 Heat of neutralization of aqueous
 solutions according to reaction NaOH
 (or KOH) + HNO_2 , kcal 11.1

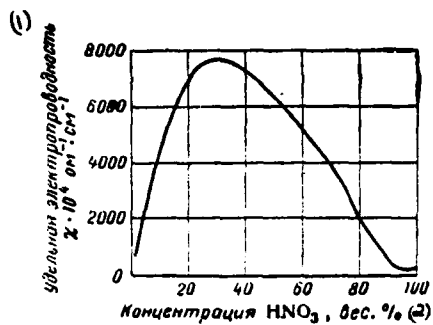


Figure I-8. Electrical Conductivity of Aqueous Solutions of Nitric Acid at 15°C

- Key:
1. Specific electrical conductivity, $\chi \times 10^4 \text{ Ohm}^{-1} \times \text{cm}^{-1}$
 2. HNO_3 concentration, weight, %

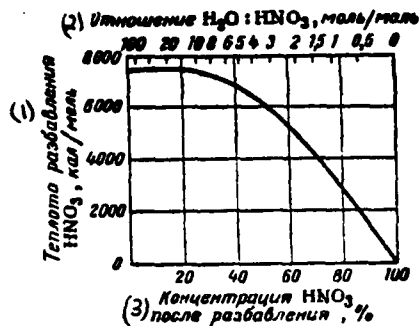


Figure I-9. Heats of Dilution of Nitric Acid by Water

- Key:
1. Heat of dilution of HNO_3 , cal/mole
 2. Ratio of $\text{H}_2\text{O}:\text{HNO}_3$, mole/mole
 3. HNO_3 concentration after dilution, %

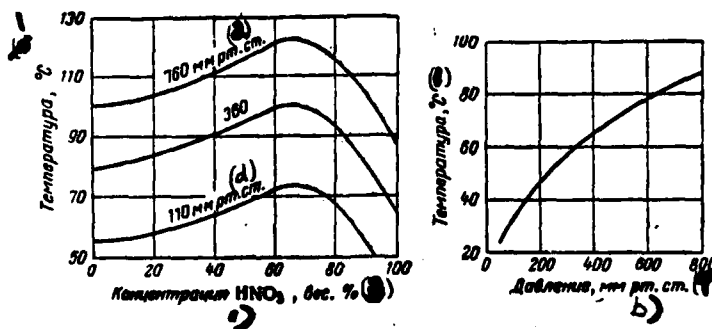


Figure I-10. Boiling Points of Nitric Acid

- Key:
- a. Aqueous solutions
 - b. Anhydrous
- Key:
1. Temperature, °C
 2. mm Hg
 3. HNO_3 concentration, weight. %
 4. Pressure, mm Hg

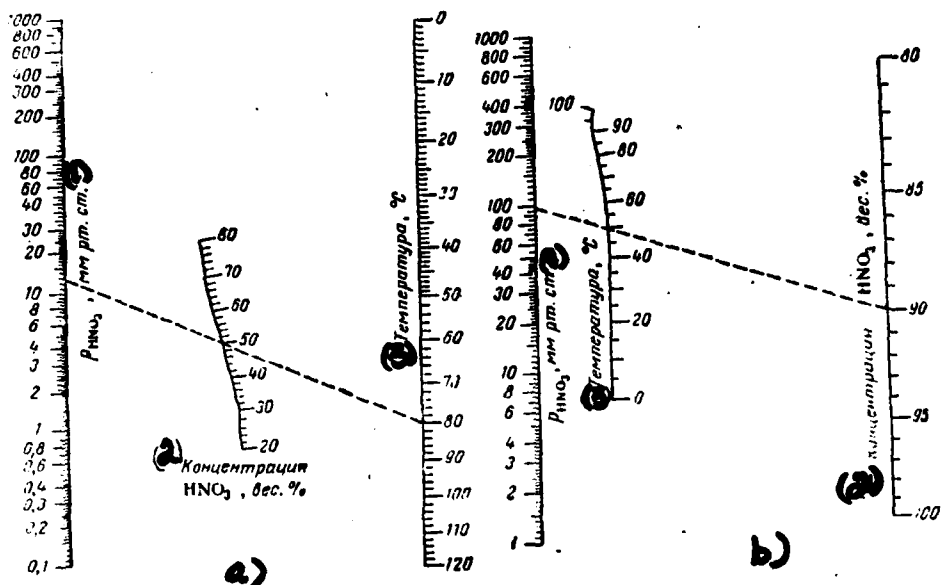


Figure I-11. Nomograms to Determine Partial Pressure of HNO₃ Vapors above Solutions of Nitric Acid

~~Key~~

- a. concentration of 20-80% HNO₃
 b. concentration of 80-100% HNO₃
 Key: 1. mm Hg
 2. concentration of HNO₃, weight. %
 3. Temperature, °C

Depending on the nature of the substances reacting with HNO₂, it may be an oxidizer or a reducer. Thus, hydrogen peroxide, ozone, permanganates and other strong oxidizers oxidize nitric acid into HNO₃. Hydrogen iodide and hydrogen sulfide reduce it to NO.

Carbamide during interaction with HNO₂ is broken down according to the reaction:



Under the influence of strong acids, nitrous acid is also broken down:



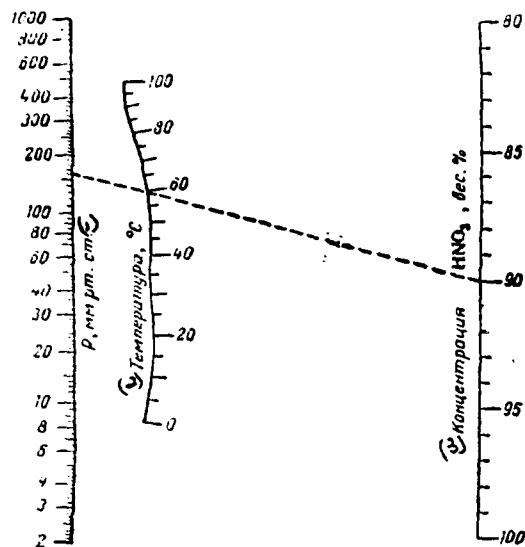


Figure I-12. Nomogram to Determine Total Pressure of HNO_3 Vapors and H_2O Vapors above 80-100% Nitric Acid

Key:

1. p , mm Hg
2. HNO_3 Concentration, weight %

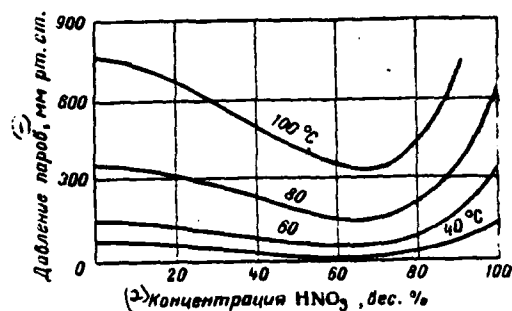


Figure I-13. Vapor Pressure above Solutions of Nitric Acid of Varying Concentration

Key:

1. Vapor pressure, mm Hg
2. HNO_3 concentration, weight %

HNO_2 with sulfuric acid forms nitrosylsulfuric acid, and with alkalis--nitrites.

Diluted nitric acid that is obtained under industrial conditions always contains HNO_2 whose quantity sometimes reaches several grams per 1 l of solution. Increased partial pressure of NO during absorption of nitrous gases in the production of HNO_3 promotes an increase in the HNO_2 content in nitric acid.

Solutions of Concentrated Nitric Acid Containing Nitric Oxides

The heat conductivity λ of a solution of concentrated nitric acid²⁶ that contains 2.5-5 weight.% of N_2O_4 and up to 2% H_2O :

t, °C

λ, kcal/(m x h x deg)

-20 0 +20 40 80 100 120
0.223 0.231 0.240 0.249 0.266 0.275 0.284

TABLE I-33. DENSITY OF ANHYDROUS NITRIC ACID (in g/cm³) CONTAINING DISSOLVED NITRIC OXIDES¹²

(1) Содержание NO ₂ , вес. %	(2) Температура, °C			(1) Содержание NO ₂ , вес. %	(2) Температура, °C		
	0	12,5	25		0	12,5	25
0	1,5472	1,5245	1,5018	28	1,6550	1,6340	1,6106
2	1,5549	1,5323	1,5105	30	1,6601	1,6393	1,6160
4	1,5626	1,5402	1,5193	32	1,6643	1,6433	1,6200
10	1,5867	1,5646	1,5443	38	1,6718	1,6500	1,6268
14	1,6027	1,5806	1,5606	42	1,6727	1,6503	1,6265
20	1,6274	1,6054	1,5838	48	1,6887	1,6454	1,6196
22	1,6353	1,6132	1,5910	50	1,6662	1,6430	1,6160
24	1,6425	1,6207	1,5982	52	1,6662	1,6430	1,6160
26	1,6494	1,6278	1,6047	54	1,6597	1,6354	1,6080

Key:

1. NO₂ content, weight. %
2. Temperature, °C

TABLE I-34. DENSITY OF SOLUTIONS OF NITRIC ACID (in g/cm³) CONTAINING NITRIC TETROXIDE²⁷

(1) Содержание N ₂ O ₄ , вес. %	(2) Температура, °C			(1) Содержание N ₂ O ₄ , вес. %	(2) Температура, °C		
	20	10	0		20	10	0
98,2% HNO ₃				96,0% HNO ₃			
20,00	1,5856	1,6037	1,6197	44,34	1,6088	1,6295	1,6488
25,09	1,5984	1,6167	1,6332	46,93	1,6066	1,6278	1,6475
30,35	1,6136	1,6314	1,6490	94,2% HNO ₃			
34,81	1,6227	1,6406	1,6579	25,50	1,5812	1,5990	1,6175
35,62	1,6239	1,6412	1,6590	29,70	1,5867	1,6055	1,6230
38,95	1,6280	1,6470	1,6645	35,45	1,5954	1,6165	1,6340
42,14	1,6286	1,6480	1,6662	38,80	1,5975	1,6174	1,6357
43,93	1,6284	1,6482	1,6667	40,20	1,5980	1,6190	1,6380
45,83	1,6289	1,6453	1,6654	43,90	1,5927	1,6134	1,6334
49,07	1,6228	1,6430	1,6625	46,10	1,5913	1,6124	1,6322
50,01	1,6159	1,6365	1,6574	92,2% HNO ₃			
51,35	1,6140	1,6355	1,6556	20,80	1,5552	1,5730	1,5904
96,0% HNO ₃				24,86	1,5652	1,5830	1,6020
19,93	1,5757	1,5936	1,6103	29,03	1,5742	1,5921	1,6104
24,94	1,5897	1,6076	1,6242	34,19	1,5815	1,6011	1,6195
30,59	1,6007	1,6185	1,6361	39,80	1,5851	1,6050	1,6240
34,73	1,6090	1,6252	1,6430	42,50	1,5824	1,6026	1,6224
38,13	1,6094	1,6283	1,6464	44,45	1,5802	1,6008	1,6208
40,78	1,6105	1,6305	1,6467	47,81	1,5772	1,5973	1,6168
41,81	1,6100	1,6298	1,6480				

[Key on next page]

Key:

1. N_2O_4 content, weight. %
2. Temperature, °C

TABLE I-35. DIFFERENTIAL HEAT OF DISSOLUTION³
OF LIQUID N_2O_4 IN SOLUTIONS OF $HNO_3 + NO_2$
(in kcal/kg N_2O_4)

(1) Содержание N_2O_4 , вес. %	(2) Температура °C		(1) Содержание N_2O_4 , вес. %	(2) Температура °C		(1) Содержание N_2O_4 , вес. %	(2) Температура °C	
	0	20		0	20		0	20
0	59,1	64,6	18	42,3	34,7	34	20,5	11,3
2	58,1	62,7	22	36,9	27,8	36	18,0	8,7
4	58,8	60,3	24	34,1	24,8	40	13,3	—
6	55,1	57,3	26	21,8	31,1	44	9,3	—
8	53,2	54,2	28	19,5	28,3	48	5,2	—
10	51,4	50,7	30	16,3	25,8	50	3,1	—
14	47,0	43,0	32	13,9	23,1	—	—	—

Key:

1. N_2O_4 content, weight. %
2. Temperature, °C

TABLE I-36. HEAT CAPACITY OF ANHYDROUS NITRIC ACID
CONTAINING DISSOLVED NITRIC OXIDES³
[(in cal/(g x deg)]

(1) Содержа- ние NO_2 вес. %	(2) Температура, °C					(1) Содержа- ние NO_2 вес. %	(2) Температура, °C			
	0	18	35	42	50		0	18	35	42
2	0,417	0,447	0,448	0,449	0,453	26	0,429	0,450	0,467	0,498
4	0,421	0,447	0,449	0,452	0,457	30	0,431	0,451	0,472	0,508
6	0,423	0,448	0,450	0,455	0,464	34	0,432	0,452	0,477	—
8	0,424	0,448	0,451	0,458	0,468	38	0,433	0,452	0,482	—
12	0,425	0,449	0,454	0,465	0,484	40	0,434	0,453	0,485	—
18	0,426	0,449	0,459	0,478	0,510	45	0,436	—	—	—
22	0,428	0,450	0,463	0,488	0,531	—	—	—	—	—

Key:

1. NO_2 content, weight. %
2. Temperature, °C

The thermal conductivity λ of a solution of concentrated nitric acid²⁶ which contains 2.5 - 5 wt.% N_2O_4 and up to 2% H_2O :

t, °C	-20	0	+20	40	80	100	120
λ , kcal/(m·hr· degree	0.223	0.231	0.240	0.249	0.266	0.275	0.284

The freezing temperature²⁸ of 20.8% solution of N_2O_4 in anhydrous nitric acid is $-55.6^\circ C$.

The viscosity of solutions of nitric acid that contain over 20 weight % NO_2 at $0^\circ C$:

NO ₂ content, weight. %	22	24	26	28	30	40	50
Viscosity, centipoise	2.48	2.66	2.86	3.05	3.24	4.18	4.39

TABLE I-37. VISCOSITY OF SOLUTIONS OF ANHYDROUS NITRIC ACID (IN CENTIPOISE) CONTAINING NITRIC OXIDES²⁹

(1) Содержание NO ₂ , вес. %	(2) Температура, °C			(1) Содержание NO ₂ , вес. %	(2) Температура, °C		
	0	25	40		0	25	40
2	1,18	0,79	0,65	12	1,74	1,13	0,91
4	1,27	0,85	0,70	14	1,87	1,20	0,96
6	1,38	0,91	0,74	16	2,00	1,28	1,01
8	1,49	0,97	0,80	18	2,14	1,35	1,05
10	1,61	1,05	0,85	20	2,30	1,41	1,10

Key:
 1. NO₂ content, weight. %
 2. Temperature, °C

TABLE I-38. BOILING POINT ($t_{кип}$) OF SOLUTIONS OF NITRIC ACID CONTAINING NITRIC OXIDES, AND THEIR CONCENTRATION IN VAPORS³

(1) Содержание NO ₂ в растворе HNO ₃ вес. %	(2) Давление, мм рт. ст.					
	760		600		350	
	$t_{кип}$, °C	NO ₂ + N ₂ O ₄ ⁽³⁾ в паре вес. %	$t_{кип}$, °C	NO ₂ + N ₂ O ₄ ⁽³⁾ в паре вес. %	$t_{кип}$, °C	NO ₂ + N ₂ O ₄ ⁽³⁾ в паре вес. %
4	77	59	67	54	56	50
8	68	60	60	74	50	65
12	62	88	54	84	45	74
16	54	92	49	88	40	81
20	51	93	44	92	35	86
24	46	95	49	93	31	90
28	42	96	35	94	28	93
32	37	97	31	96	19	95
36	33	98	27	97	19	96
40	29	98	23	98	18	97
44	25	99	—	—	—	—
49	24.5	99	—	—	—	—

Key:
 1. NO₂ content in HNO₃ solution, weight. %
 2. Pressure, mm Hg
 3. NO₂ + N₂O₄ in vapor, weight. %

Figure I-14 presents data on the vapor pressure above liquid N₂O₄, and figure I-15 presents the diagram of boiling of the HNO₃-N₂O₄ system with different pressures.

TABLE I-39. PARTIAL PRESSURES p OF VAPORS $^{30} \text{N}_2\text{O}_4$, NO_2 AND HNO_3 ABOVE SYSTEM $\text{HNO}_3\text{-N}_2\text{O}_4$ (IN mm Hg)

(1) Содержание N_2O_4		(2) p при -10°C			(2) p при 0°C			(2) p при $+10^\circ\text{C}$		
(3) вес. %	(4) мол. %	N_2O_4	NO_2	HNO_3	N_2O_4	NO_2	HNO_3	N_2O_4	NO_2	HNO_3
0	0	0	0	6.94	0	0	14.15	0	0	26.73
5	3.48	0.20	1.18	6.52	0.34	2.12	13.74	0.50	3.93	26.47
15	10.80	1.82	3.13	5.80	3.54	6.85	11.74	6.25	13.9	22.55
25	18.58	8.58	6.80	4.62	16.20	14.88	9.12	27.20	29.00	7.30
30	22.73	15.20	9.08	4.00	26.80	18.87	7.99	46.65	37.97	15.38
40	31.33	37.45	14.28	2.17	67.52	29.96	5.72	116.20	59.67	10.63
50	40.50	89.00	21.90	1.40	149.70	44.65	2.65	232.4	84.53	6.30
52	42.60	105.20	—	—	172.64	46.90	(2.50)	—	—	—
54	44.55	123.30	—	—	199.40	49.50	(1.9)	308.50	97.66	1.50

(5) Область расслоения *

97	95.60	122.50	—	—	203.60	50.90	0	326.70	100.50	(0)
98.5	97.92	123.30	—	—	206.32	51.88	(0)	330.90	101.20	(0)
100	100	121.10	—	—	209.70	52.70	(0)	339.60	102.90	(0)

Key:

1. N_2O_4 content
2. p at
3. weight. %
4. mol. %
5. area of stratification

*With concentration over 54 weight. % NO_2 in solution, it is stratified all the way to an increase in the N_2O_4 content in a mixture with HNO_3 to 97 weight. %.

TABLE I-40. VAPOR PRESSURE ABOVE 90% and 80% SOLUTIONS OF NITRIC ACID CONTAINING NITRIC OXIDES ^{7,31}

(1) Содержание N_2O_4 в растворе вес. %	(2) Давление, мм рт. ст.					
	$p_{\text{N}_2\text{O}_4}$	p_{NO_2}	$p_{\text{N}_2\text{O}_4+\text{NO}_2}$	p_{HNO_3}	$p_{\text{H}_2\text{O}}$	$p_{\text{сум}}$
90% HNO_3 at 10°C						
3.2	4.5	11.9	16.4	15.2	0.2	31.8
8.6	14.4	22.4	36.8	15.2	0.2	52.2
14.0	30.2	31.2	61.4	15.3	0.2	76.9
17.0	46.6	39.4	86.0	15.4	0.2	101.8
22.0	87.0	52.3	139.5	15.2	0.2	154.6
90% HNO_3 at -10°C						
7.0	4.3	4.6	8.9	4.5	0	13.4
10.4	7.2	5.8	13.0	4.0	0	17.0
14.0	10.9	7.3	18.2	4.0	0	22.1
18.2	17.5	9.3	26.8	3.9	0	30.7
22.0	27.8	11.6	39.4	4.0	0	43.4

[continuation of table I-40]

		80% HNO ₃ at 20 °C				
4,1	41,0	56,0	97,0	13,0	1,3	111,3
6,6	75,0	75,0	150,0	12,8	1,3	164,1
11,2	140,0	103,0	243,0	12,9	1,3	257,2
14,0	176,0	113,0	289,0	12,7	—	—
18,0	229,0	132,0	361,0	13,0	1,3	375,3
20,8	275,0	143,0	418,0	12,6	1,3	431,9
22,1	291,0	148,0	439,0	12,8	1,3	453,1

Key:

1. N₂O₄ content in solution, weight. %
2. Pressure, mm Hg

TABLE I-41. VAPOR PRESSURE³² ABOVE HNO₃-N₂O₄-H₂O SYSTEM

(1) Температура °C	(2) Давление паров, атм				
	P _{HNO₃}	P _{NO₂}	P _{N₂O₄}	P _{H₂O}	P _{общ.}
(3) 16,45 вес. % HNO ₃ , 74,7% N ₂ O ₄ , 8,84% H ₂ O					
40	0,31	1,13	0,97	0,03	2,44
50	0,63	1,51	1,23	0,04	3,69
58	0,77	1,93	1,68	0,05	4,93
(3) 45,38 вес. % HNO ₃ , 50,57% N ₂ O ₄ , 4,05% H ₂ O					
40	0,87	0,51	0,28	—	1,66
50	1,27	0,98	0,42	—	2,65
60	1,83	1,39	0,47	—	3,69
66	2,25	1,76	0,57	—	4,57
(3) 65,8% вес. % HNO ₃ , 32,02% N ₂ O ₄ , 2,18% H ₂ O					
30	—	—	—	—	1,55
40	0,94	0,39	0,210	—	1,57
50	1,02	0,47	0,215	—	1,74
60	1,24	1,05	0,490	—	2,78
75	2,10	1,90	0,620	—	4,62

Key:

1. Temperature, °C
2. Vapor pressure, atm.
3. weight. %

Figure I-16 shows the total pressure of vapors N₂O₄ + NO₂ + HNO₃ above N₂O₄ solutions in 100% nitric acid.

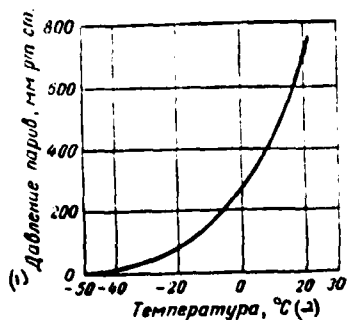


Figure I-14. Vapor Pressure above Nitric Tetroxide

Key:

1. Vapor pressure, mm Hg
2. Temperature, °C

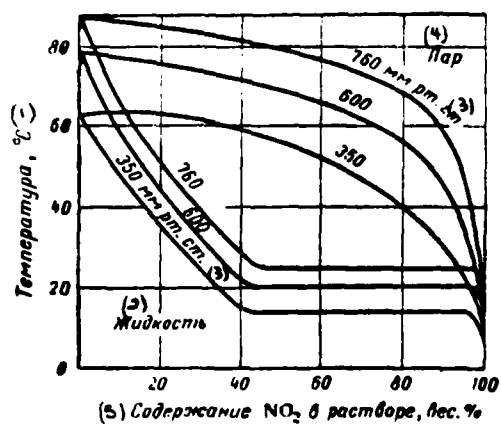


Figure 15. Diagram of Boiling of $\text{HNO}_3\text{-N}_2\text{O}_4$ System at Different Pressures

Key:

1. Temperature, °C
2. Liquid
3. mm Hg
4. Vapor
5. NO_2 content in solution, weight. %

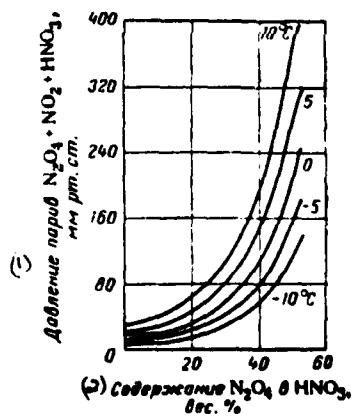


Figure I-16. Total Vapor Pressure of $\text{N}_2\text{O}_4 + \text{NO}_2 + \text{HNO}_3$ above Solution of N_2O_4 in 100% Nitric Acid

Key:

1. Vapor pressure of $\text{N}_2\text{O}_4 + \text{NO}_2 + \text{HNO}_3$, mm Hg
2. Content of N_2O_4 in HNO_3 , weight. %

1. Production of Diluted (Weak) Nitric Acid

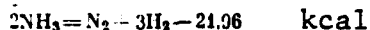
Oxidation (Conversion) of Ammonia into Nitric Oxide

Gaseous ammonia and air are separately purified from mechanical admixtures, heated and mixed in a strictly assigned ratio. The obtained ammonia-air mixture is further exposed to fine purification from residual contaminants and is sent to the contact apparatus for oxidation by air oxygen. Depending on the conditions for conducting

this process, NO, N₂O and N₂ can be obtained in different ratios according to the reactions:



Elementary nitrogen can be formed in the absence of a catalyst, for example, as a result of thermal dissociation of ammonia when an ammonia-air mixture comes into contact with the very heated walls of piping and equipment:



According to the studies conducted in recent years, 1.5-3% of the supplied ammonia can be lost in the contact equipment that is operating under pressure, even before it reaches the catalyzer, since the inner surface of the upper conical part of the equipment is heated strongly as a consequence of the thermal emission of the catalyzer grids.

If the ammonia breaks through the layer of catalyst, formation of elementary nitrogen is also possible:



Breakthroughs of ammonia are observed when the ammonia-air mixture exceeds the assigned linear velocity, with low contact temperature, and especially when the catalyst is poisoned by toxins.

The heat that is released during the oxidation reaction of ammonia is quite sufficient for the process to occur auto-thermally. The ammonia oxidation reactions with the formation of nitric oxide and elementary nitrogen are accompanied by a considerable loss of free energy, and occurs at a great rate, practically irreversibly (to the end).

There is currently no generally accepted concept regarding the mechanism for the contact process of ammonia oxidation. The basic reactions given above are summary, and as many researchers

assume, do not reflect the actual course of the process of ammonia oxidation.

Different hypotheses³³⁻³⁵ have been advanced regarding the mechanism for and features of the process of ammonia oxidation. The majority of them are reduced to hypotheses on the formation during the oxidation of NH_3 of unstable intermediate compounds, which as a result of breakdown and regrouping yield nitric oxide and elementary nitrogen. Almost all the researchers share the viewpoint that the rate of ammonia oxidation is determined by its diffusion to the surface of the catalyst as the slowest stage that limits the entire process as a whole.³³

The output of NO during catalytic oxidation of ammonia is characterized by the degree of its conversion, or the percentage of contact. These terms mean the ratio of the quantity of ammonia converted into nitric oxide to its original quantity that is assumed to be 100%. In contact equipment that operates at atmospheric pressure, the degree of conversion of ammonia must be 97-98% in equipment operating under pressure of 5 atm. and higher, 95-96%.

One of the most important conditions for achieving a high degree of conversion of ammonia into nitric oxide is the activity of the catalyst. This depends on its composition, characteristics of the grid and the operating conditions.

Catalysts

The oxidation of ammonia uses as catalysts, grids that are made of alloys of platinum with rhodium or with rhodium and palladium.* These catalysts (they are called platinoids) maintain high activity and good mechanical strength for a long time at temperatures to 880°C and pressure to 10 atm. They are easily regenerated.

Attempts to replace the expensive platinoid catalysts with nonplatinum did not yield positive results. Within 15-20 days, the

* In recent years, catalytic grids made of other platinoid alloys have been used in oxidizing ammonia into NO.

output of NO in the presence of nonplatinum catalysts, even operating under atmospheric pressure, was irreversibly reduced by several percents. A feature of all the nonplatinum catalysts (even the best of them, like, for example, $\text{CoO}_3 \times \text{CoO}$ or $\text{Fe}_2\text{O}_3 \times \text{Bi}_2\text{O}_3$) is their high sensitivity to admixtures that are practically always contained in the ammonia-air mixture.

Grids made of platinum-rhodium alloys (5-10% Rh) with wire diameter 0.05-0.07 mm are usually used abroad.

In the domestic nitric acid systems, whose contact sections operate at atmospheric and higher pressure, grids made of GIAP-1 alloy are used that contain 92.5% Pt, 3.5% Rh and 4% Pd. Grids made of platinum-rhodium-palladium alloy are made of wire 0.092 mm in diameter. They have 1024 holes (networks, cells) per 1 cm^2 . The quality of the catalyst grids is controlled by GOST [state standard] 3193-59, the wires for the platinoid grids are controlled by GOST 8395-57 and 8397-57.

The activity of the GIAP-1 catalyst is 0.5-1.0% higher than the platinum-rhodium (7% Rh) with the same mechanical strength.

When contact equipment operates at atmospheric pressure, it is loaded with three (less often four) catalyst grids, while the equipment that operates under pressure of 5-7 atm, 12-16 grids, under pressure of 8-9 atm.--a set made of 18-20 grids.

Table I-42 presents the basic characteristics of the platinoid grids; table I-43 presents the permissible deviations of the weight of the platinoid grids that differ in shape and diameter.

The new platinoid grids display weak catalytic activity. At the end of roughly 24 h of operation, the NO output in the ammonia oxidation process reaches the maximum amount.

The term "active surface of the grid" is used in practice. It means the surface of all the longitudinal and transverse wires per

unit of area or weight of grid. With wire diameter 0.009 cm and 1024 hole/cm², the active surface of the platinoid grid is

$$2 \cdot 3.14 \cdot 0.009 \sqrt{1024} = 1.809 \text{ cm}^2$$

The active surface of the grid is really much larger than the geometric surface of its wires. The threads of the grid during NH₃ oxidation are thickened and break up. Unique growths are formed on their surface, and enormous number of the smallest crystals are released of those metals that are included in the composition of the alloy. This feature of the platinoid catalysts is taken into consideration in the production practice: a grid that has previously been operating is set first on the course of the ammonia-air mixture. This makes it possible to considerably reduce the time for activation of the catalyst.

The USSR makes the most frequent use of the following platinoid grids:

Diameter, mm	540	1150	2100	2900
Approximate weight, g	237	990	3200	6200

The grids must have a shiny surface. There must be no cracks or oxide films on the wires. The damage places on the grid of total area under 5 cm² per 1 kg of grid may be fixed. Large grids from 2050 to 2915 mm in diameter may consist of two parts connected by a seam.

In certain contact sections that operate at atmospheric pressure, a two-stage (combined) catalyst is used to oxidize the ammonia. It consists of one platinum grid (first stage) and a layer of nonplatinum catalyst (second stage).³⁵ At the first stage of the catalyst, 88-92% of the ammonia is oxidized. The total output of nitric oxide in this catalyst corresponds to the output when three platinoid grids are used. The use of the two-stage catalyst reduces the one-time expenditures for the platinoid grids roughly three-fold, and decreases the platinum losses during the oxidation of ammonia by 10-15%.

TABLE I-42. CHARACTERISTICS OF PLATINOID GRIDS³

(1) Диаметр проволоки мм	(2) Число проволок на 1 см ²	(3) Число отверстий на 1 см ²	(4) Примерная масса 1 см ² сетки, г	(5) Активная поверхность сеток	
				м ² /м ²	см ² /г
0,06	32	1024	0,0389	1,206	31,0
0,07	32	1024	0,0529	1,407	26,6
0,08	32	1024	0,0691	1,808	23,2
0,09	32	1024	0,0875	1,809	20,7
0,04	60	3600	0,0324	1,507	46,5
0,05	60	3600	0,0506	1,884	37,2
0,06	60	3600	0,0729	2,251	31,1
0,07	60	3600	0,0995	2,638	26,5

Key:

1. Diameter of wire, mm
2. Number of wires per 1 cm²
3. Number of holes per 1 cm²
4. Approximate weight of 1 cm² of grid, g
5. Active surface of grid
6. cm²/g

TABLE I-43. PERMISSIBLE LIMITS OF DEVIATIONS IN WEIGHT OF PLATINOID ROUND GRIDS FROM CALCULATED MASS G

(1) Диаметр сетки мм	(2) G, g	(3) Пределы отклонений г	(4) Форма раскроя	(1) Диаметр сетки мм	(2) G, g	(3) Пределы отклонений г
540	237	218—256	Круг ⁽⁵⁾	2050	3383	3112—3653
830	556	511—600	"	2100	3549	3265—3832
880	624	574—674	"	2150	3718	3420—4015
1050	892	820—983	"	2900	6722	6184—7280
1080	943	867—1018	Квадрат ⁽⁶⁾	—	96	88—104
1150	1067	981—1152	Шестиугольник ⁽⁷⁾	475	158	149—165

Key:

1. Grid diameter, mm
2. G, g
3. Limits of deviations, g
4. Shape of cutting
5. Circle
6. Square
7. Hexagon

Physical-Chemical Bases of the Process

In addition to the activity of the catalyst which depends on its composition, the degree of conversion of ammonia into nitric oxide is also determined by other factors. The most important of them are: contact temperature, NH₃:O₂ ratio in the ammonia-air mixture, purity of the gas mixture that comes for contact, and

intensity of the catalyst.

Effect of Temperature

During contact oxidation of ammonia, a noticeable quantity of nitric oxide is formed already at 300°C. With an increase in temperature, the degree of conversion increases, reaching the maximum (roughly 98%) at 800-900°C. In practice, the temperature conditions of ammonia oxidation are adopted depending on the systems for production of nitric acid with regard for the complications that are associated with the creation of high temperatures in the catalyst zone.

In contact equipment that operates at atmospheric pressure, one tries to maintain a temperature of 770-820°C in the catalyst, and in equipment that operates under pressure of 6-9 atm, 880-900°C. The highest degree of ammonia conversion is achieved at these temperatures. It is not expedient to increase the temperature above 900°C, despite a certain rise in the degree of conversion, since in this case, the losses of catalyst are drastically increased.

It is computed that a theoretical increase in temperature is about 70°C for each percentage of ammonia in the ammonia-air mixture that is converted into nitric oxide. The quantity of heat that is released during oxidation of ammonia often does not guarantee maintenance of the indicated temperatures on the catalyst. In order to reach the assigned temperature of contact, air or (less often) an ammonia-air mixture is preheated, or its content of ammonia is increased. The modern systems of nitric oxide production combine all these methods. In the units which operate at atmospheric pressure, the air is heated to 110°C, and on units operating at increased pressure--to 250-300°C.

Conducting of the process at increased temperatures, besides increasing the output of nitric oxide, has other advantages as well: the rate of the ammonia oxidation reaction increases and the time required for contact is reduced. Thus, at 650°C, the contact time is 5×10^{-4} s, and at 900°C, is reduced to 1.1×10^{-4} s.

Effect of O₂:NH₃ Ratio in Ammonia-Air Mixture

Oxidation of ammonia almost always uses only air. The NH₃ concentration in the ammonia-air mixture is therefore determined by the oxygen content in air. According to the equation $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$, for complete oxidation of 1 mole of ammonia, 1.25 moles of oxygen are required. In this case, the NH₃ content in the ammonia-air mixture is:

$$\left[\frac{21}{1.25} : \left(100 + \frac{21}{1.25} \right) \right] 100 = 14.4 \quad \text{volume.}\%$$

However, with a ratio of O₂:NH₃=1.25, the degree of conversion of NH₃ into NO is comparatively low since a surplus of oxygen is required. In addition, with a content in the mixture of 14.4% NH₃, one would have to work in the region of explosion-dangerous concentrations. The lower limit of explosiveness of the ammonia-air mixture at atmospheric pressure is roughly 13.8 volume.% NH₃. At pressure 5 and 8 atm. this limit is reduced respectively to 13 and 12.4 volume.%. Consequently, the ammonia concentration in the mixture with air must be below 14.4%. The limits of explosiveness of the ammonia-air mixtures are shown in fig. I-17.

The upper and lower limits of explosiveness of the ammonia-oxygen mixtures significantly depends on the direction of the gas stream (upwards, downwards, horizontally), its moisture content, pressure and other conditions.

In selecting the optimal concentration of NH₃ in the ammonia-air mixture, and consequently, the O₂:NH₃ ratio, one should take into consideration the operating conditions of the catalyst (temperature, pressure, purity of the original gases, etc.). It is presently preferable to work with an O₂:NH₃ ratio in limits of 1.65-1.8. The degree of conversion is considerably reduced with (O₂:NH₃)<1.6.

If there is waste oxygen, it is used to enrich the air, and the NH₃ content in the ammonia-air mixture is increased to 12-12.5%. In this case, the high output of nitric oxide is maintained without

preheating of the air. The intensifying effect of oxygen on the processes of oxidation of ammonia and absorption of nitric oxides is examined in a number of publications. 36-40

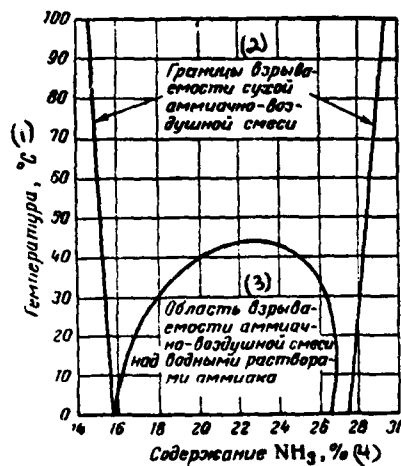


Figure I-17. Limits of Explosiveness of Dry and Water-Vapor-Saturated Ammonia-Air Mixture

Key:

1. Temperature, °C
2. Boundaries of explosiveness of dry ammonia-air mixture
3. Region of explosiveness of ammonia-air mixture above aqueous solutions of ammonia
4. NH_3 content, %

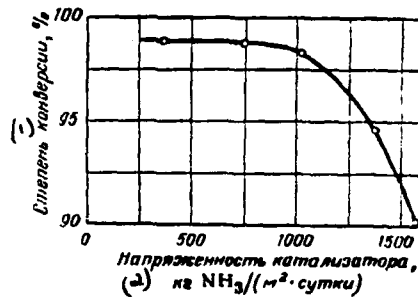


Figure I-18. Dependence of Degree of Conversion of Ammonia into Nitric Acid on Intensity of Catalyst (Grids Made of GIAP-1 Alloy, Contact Temperature 700-700 °C.)

Key:

1. Degree of conversion, %
2. Intensity of catalyst, $\text{kg NH}_3/(\text{m}^2 \times \text{day})$

Effect of Intensity of Catalyst

The degree of conversion of the ammonia is very dependent on the intensity of the catalyst. This term means the quantity of ammonia that can be oxidized in a unit of time, per active surface of the catalyst or unit of its mass. The intensity of the catalyst is usually expressed in kg/day of NH_3 per 1 m^2 of active surface of the grid or 1 g of platinoids.

The contact equipment that operates at atmospheric pressure

maintains intensity in limits of 550-700 kg/(m² x day), and equipment that operates under pressure of 8-9 atm.--in limits of 2800-3500 kg/(m³ x day). With a deviation from the assigned intensity towards any side, there is an inevitable reduction in the degree of conversion because of conversion of part of the ammonia into elementary nitrogen. Figure I-18 presents the dependence of the degree of conversion of ammonia³ on the intensity of the GIAP-1 catalyst. The data were obtained during operation at atmospheric pressure with an ammonia-air mixture that is practically completely purified of chemical and mechanical admixtures.

The intensity of the catalyst can also be characterized by the stream of the ammonia-air mixture, or its inverse quantity, the time of contact (stay) of the reacting mixture and the surface of the grids (contact time). This time τ (in s) is computed from the ratio of free volume of catalyst to the volumetric velocity of the ammonia-air mixture under conditions of contact (temperature and pressure).

The free volume of catalyzer grids (in m³), i.e., the difference in their total volume and the total volume of the platinoid wires, is computed from the formula⁴¹:

$$1.15 \cdot \frac{d}{100} \cdot n (1 - 1.57 d \sqrt{m})$$

where S--area of grid, m²;

d--diameter of grid wire, cm;

n--number of grids in catalyzer group;

m--number of holes per 1 cm² of grid area.

The velocity of the gas mixture (in m³/s) under working conditions of contact equals:

$$\frac{V_0 (273 + t)}{273 P}$$

where V₀--velocity of gas mixture with 0°C and 760 mm Hg, m³/s;

t--contact temperature, °C;

P--working absolute pressure, atm.

From here we find the contact time:

$$\tau = \frac{1.15 \ln P (1 - 1.57 d \sqrt{m}) 273}{100 V_0 (273 - t)}$$

Effect of Admixtures in Ammonia-Air Mixture

The most important condition for achieving a high degree of ammonia conversion is sufficient purity of the ammonia-air mixture that is sent to the contact equipment. The filtering devices that are used in the production of nitric acid make it possible to purify the gaseous mixture only from mechanical admixtures (silicate dust, scale, etc.), but the chemical admixtures remain almost completely in the ammonia-air mixture. They are the strongest toxins for the platinoid grids. The catalysts are poisoned especially often with admixtures of sulfur compounds (H_2S , SO_2 , SO_3 , etc.). Aerosols of oils and different salts, acetylene, hydrogen phosphide and hydrogen fluoride are also strong toxins for the platinoid catalyst.

Falling on the grids, the oil burns and "carbonizes" part of their surface. As a result, the degree of ammonia conversion is diminished by 2-3%. The presence in the ammonia-air mixture of an admixture of acetylene results in a drastic decrease in the activity of the catalyst. However, if a pure ammonia-air mixture begins to come to the catalyst, its activity is rapidly restored. Admixtures of chlorine and carbon dioxide almost have no effect on the catalytic activity of the catalyst grids.

Losses, Service Life and Regeneration of Platinoid Catalyst

The reactions which occur on the surface of the catalyst when it is operating induce physical changes in the structure of the grids. When the grids are operating, their surface is broken up and nonuniform growths appear on it, the diameter of the wires becomes unequal, etc. As a result of these changes, there is a gradual reduction in the mechanical strength of the grids, the separation of the metal particles by the gas flow from their surface increases. This causes losses of catalyst and significantly reduces the service life of the catalyst grids.

Direct and irreversible losses of catalyst are distinguished. Direct losses mean the loss of grid weight in a definite time of their operation. Irreversible losses are smaller than the direct by that quantity of catalyst (dust, bits of catalyst grid, etc.) which are collected from the filters and other apparatus, as well as on the piping and storage tanks for nitric acid. The service life of the catalyst grids is expressed as the quantity of oxidized ammonia or (more often) spent nitric acid (in kg) that is attributed to 1 g of grid during their operation from the moment of loading in the equipment to the refining (melting) in the form of scrap.

A number of factors³ affect the amount of losses and the service life of the catalyst grids: composition and intensity of the catalyst, pressure of the gas mixture, contact temperature, duration of operation, contamination of the ammonia-air mixture, design of the contact equipment, etc. Below is an examination of the effect on the losses of the catalyst of only the main listed factors.

With an increase in pressure, direct losses rise, and for the GIAP-1 catalyst comprise (in g/m HNO₃):

At atmospheric pressure	0.045-0.055
At 5-6 atm.	0.13-0.16
At 7.5-8 atm. (without consideration for return)	0.24-0.28

Similar losses are observed when working with platinum-rhodium catalyst. An increase in the losses of platinoids in the equipment which operates under pressure is explained by the fact that in them the velocity and density of the gas mixture are considerably greater, while the temperature is higher than necessary to obtain the same degree of conversion of ammonia in the equipment which operates at atmospheric pressure.

An increase in the contact temperature from 780 to 850°C results in an increase in the direct losses of catalyst by almost double. With a further increase in temperature to 900-920°C, the

losses of catalyst rise several times. Experience has shown that the higher the intensity of the catalyst grids, the smaller their losses (with other conditions equal). However, one should take into account that with intensity over 750 kg/m^2 of the active surface per day, the degree of conversion is reduced. In addition, the increased intensity at temperatures above $820\text{-}830^\circ\text{C}$ reduces the service life of the grids.

When solid admixtures of the ammonia-air mixture (for example, silicate dust that is formed as a result of wiping porolite tubes) fall on the grids, there is a very strong effect on the increase in losses of the catalyst. On the first grid in the course of the gas, several times greater losses of metal are generally observed than in the next grids. This is not only explained by the fact that on the first grid, the main quantity of ammonia is oxidized, but also by the greatest contamination of the mixture which enters the first grid. When operating at atmospheric pressure, 65-67% of the metal from the total is lost in the first grid on the course of the gas *on the second 20-25% and on the third 5-10%.* Consequently, with each regeneration of the catalyst, the grids change places in the set: the lower grid is usually set first in the gas course. The grids are usually refined after their weight has been reduced by 10-15% from the initial.

An increase in the duration of operation of the grids results in an increase in the losses of metal. The service life of the grids that operate under pressure of 8-9 atm must therefore be limited to 2-3 months; at atmospheric pressure, 12 months. On the catalyst GIAP-1 that operates at atmospheric pressure and temperature of $770\text{-}820^\circ\text{C}$, for 1 g of grid (before it is refined), 2000-2400 kg of nitric acid (100% HNO_3) are produced. The service life of this catalyst at pressure 7-9 atm. and temperature $880\text{-}900^\circ\text{C}$ must correspond to generation of 1650-1800 kg of nitric acid per 1 g of grid.

The finely-dispersed particles of platinoid alloys that are removed by the gas stream settle in the equipment and piping. Some of them remain in the production acid, and roughly 15-20% of the total losses of metal are discharged with the exhaust gases.

In the units operating at atmospheric pressure, part of the platinum dust is removed from the acid (on filters with adapter made of glass wool) and from sludge which is accumulated in the nitric acid tanks.

It is best to set up trapping of the platinum dust on units which operate under pressure. Here it is filtered out from the nitrous gases, acid which is formed in the cooling units-condensers, and their production acid which is sent to the tank (glass wool is also used as the filter attachment). In addition, the platinum dust is periodically collected from the equipment and gas lines by wiping their inner surfaces with moisture-absorbing cotton moistened with alcohol. A small quantity of platinum dust is taken from the hydrochloric acid used to regenerate the grids. Thanks to these measures, the irreversible losses of platinum catalyst are successfully reduced by 30-50%.

New methods have been sought in recent years for trapping the platinum dust. Crushed limestone of definite chemical composition ($\sim 1.5\% \text{SiO}_2$), quartz wool in combination with an absorbent mass based on calcium oxide, etc. have been tested as the filtering materials. Judging from certain foreign data, as a result of filtering the hot nitrous gases directly after the contact equipment, roughly 85-90% of all the platinum lost in the process of oxidizing ammonia are successfully trapped.

The duration of operation of the catalyst grids until the degree of conversion of ammonia in the contact equipment operating at atmospheric pressure is reduced is 5-7 months; on units which operate at increased pressure, 20-45 days. The standards for the degree of conversion of ammonia have been set with regard for the operating conditions of the unit (purity of gases, method of production, etc.).

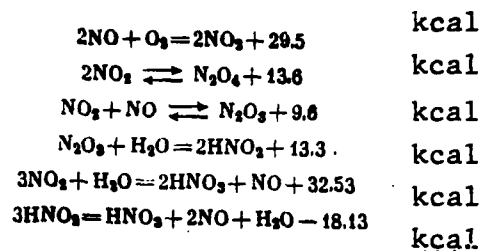
Restoration of the activity of the catalyst, regeneration of the grids, is done as follows. The grids taken from the contact equipment are washed in water and placed in a quartz bath filled

with a 12-15% solution of chemically pure hydrochloric acid. Then the solution of hydrochloric acid is heated to 60-70°C and the grids are kept at this temperature for 2 h. After this, the acid solution is poured out, the grids are thoroughly washed in distilled water (until there are no chlorine ions in the wash water), dried and they are calcined in alcohol or a hydrogen flame. If necessary, before regeneration the grids are repaired by replacing the damaged sections with whole pieces of spent grids intended for refining.

Processing of Nitric Oxide into Nitric Acid

In nitrous gases that are obtained by contact oxidation of ammonia, NO is oxidized by the oxygen present in the gas to higher oxides of nitrogen which form nitric acid during the interaction with water.

When nitrous gases are processed into nitric acid, the following reactions occur:



The process of producing diluted (weak) nitric acid can be presented as the successive occurrence of the following stages:
 1) diffusion of nitric acids from gas to liquid phase; 2) absorption of nitric oxides by water with the formation of nitric and nitrous acid; 3) breakdown of nitrous acid.

Of the reactions presented above, the slowest is the first. On the whole, it limits the entire process of reprocessing nitric oxides into diluted nitric acid. The reaction of nitric oxide oxidation is accelerated with a drop in temperature, and with an increase in temperature is slows down all the way to almost complete halting.

The dependence of the equilibrium constants of the reaction $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ on temperature can be computed from the equation:

$$K_1 = \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2}$$

where K_1 --equilibrium constant with given temperature;

P_{NO} , P_{NO_2} , P_{O_2} --partial pressures of gas mixture components, atm.

Below are the computed constants for equilibrium of the oxidation reaction of NO into NO_2 at different temperatures:

Temperature °C	lgK ₁	K ₁	Temperature °C	lgK ₁	K ₁
0	-14.093	8.07·10 ⁻¹⁴	400	-1.091	8.11·10 ⁻²
50	-10.732	1.85·10 ⁻¹¹	450	-0.472	0.337
150	-3.368	4.29·10 ⁻⁷	600	+0.963	9.180
200	-4.871	1.35·10 ⁻⁶	700	+1.673	47.100
300	-2.854	2.22·10 ⁻³	800	+2.247	177.00
350	-1.810	1.55·10 ⁻²	900	+2.821	662.00

The equilibrium constant of the oxidation reaction of NO for other temperatures can be computed from the formula:

$$\lg K_1 = \frac{5749}{t+273} + 1.75 \lg(t+273) - 0.0005(t+273) + 2.839$$

where K_1 --equilibrium constant at t ;

t --temperature, °C.

Since the reaction of oxidation of NO into NO_2 occurs slowly, then we do not strive to reach an equilibrium composition of the nitrous gases to be processed. Usually with assigned conditions, we are limited to a definite degree of oxidation. The rate of oxidation of NO into NO_2 strongly depends on the concentration of components in nitrous gases, temperature and pressure. The equation for the reaction rate $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ can be presented in a general form by the formula:

$$Z = k \cdot e^{at}$$

where Z --rate of reaction of NO oxidation;

k --constant of the reaction rate;

- a--concentration of NO in the gaseous mixture;
 b--concentration of O₂ in the gaseous mixture.

Table I-44 presents the constants for the rate of the nitric oxide oxidation rate at absolute pressure 1 atm. and different temperatures. If the NO oxidation reaction is done under pressure above 1 atm., then the corresponding rate constant is multiplied by the square of pressure.

TABLE I-44. CONSTANTS OF REACTION RATE OF OXIDATION AT DIFFERENT TEMPERATURES^{12,41} (ABSOLUTE PRESSURE 1 ATM.)

(1) Темпера- тура, °C	(2) Константы скорости реакции			(1) Темпера- тура, °C	(2) Константы скорости реакции		
	$k_a \cdot 10^{-4}$	k_p	$k_{\%} \cdot 10^8$		$k_a \cdot 10^{-4}$	k_p	$k_{\%} \cdot 10^8$
0	3.48	69.3	6.930	200	1.31	8.71	0.871
30	2.65	42.8	4.280	241	1.21	6.80	0.680
60	2.18	29.2	2.920	300	1.12	5.13	0.513
90	1.87	21.0	2.100	340	1.10	4.84	0.434
100	1.80	19.5	1.9500	389	1.08	3.67	0.367
141	1.54	13.3	1.330				

Key:

1. Temperature, °C
2. Constants of reaction rate

Here k_c --values of constants with concentration of nitric oxide and oxygen expressed in mole/l;

k_p --values of constants with concentrations of nitric oxide and oxygen expressed through partial pressures in atm. (concentration of components may be expressed also in molar fractions of a unit);

$k_{\%}$ --values of constants with concentrations of nitric oxide and oxygen expressed in percents by volume with absolute pressure 1 atm.

The presented data demonstrate that the quantity k diminishes with a rise in temperature. It follows from here that the rate of NO oxidation by oxygen changes depending on the temperature of the gas mixture, proportionally to the change in the rate constant.

The rate constants for oxidation of NO into NO₂ diminish with an increase in pressure. For example, at 20°C, they have¹² the following values:

Absolute pressure, atm.	1	2	3	4	5	6
k_p	55.9	51.0	45.9	41.4	36.6	31.1

The time required for oxidation of NO into NO₂ to the assigned degree is determined from the equation:

$$k\tau = \frac{1}{(b-a)^2} \left[\frac{(b-a)x}{(a-x)a} + 2.3 \lg \frac{(a-x)b}{(b-x)a} \right]$$

where k--constant of reaction rate;

τ--reaction time, s;

a--half of the initial NO concentration, volume %

b--initial concentration of O₂, vol. %

x--consumption of O₂ to oxidize NO, vol. %.

With an increase in pressure, the reaction rate of NO oxidation into NO₂ rises in direct proportion to the square of pressure, while the time required for reaching the assigned degree of oxidation is changed in inverse proportion to the square of pressure. With an increase in pressure, it becomes possible to reduce the specific volumes of the equipment for oxidation of NO into NO₂ not only because of the increase in the rate of this reaction, but because of a reduction in the physical volume of the gas mixture that changes in inverse proportion to pressure. Thus, the required reaction volume of the equipment is inversely proportional to the cube of pressure (reduction in the second degree because of the increase in the rate of NO oxidation into NO₂, and in the first degree because of the reduction in the total volume of gases).

Processing of nitrous gases into diluted acid is usually done at 10-50°C. A lower temperature has recently been maintained in individual cases. At these temperatures, part of the nitrogen peroxide is polymerized into N₂O₄. In nitrous gases, NO₂ and N₂O₄ are practically always in a state of equilibrium. The equilibrium constant K₂ of the reaction $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ is expressed through partial pressures of NO₂ and N₂O₄, equal to

$$K_2 = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

Below are the values for the constant K₂ for certain temperatures t:

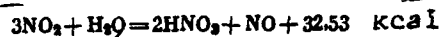
$t, ^\circ\text{C}$	0	20	40	60	80	100	120	150
K_2	0.0178	0.0886	0.4345	1.6070	5.129	14.26	35.32	114.60

The equilibrium constant K_2 can be computed according to the formula:

$$\lg K_2 = -\frac{2692}{t+273} + 1.75 \lg(t+273) + 0.00483(t+273) - 7.144 \cdot 10^{-6}(t+273)^2 + 3.062$$

By knowing the quantity K_2 for this temperature, one can compute the degree of dissociation of N_2O_4 and the equilibrium quantities of nitrogen peroxide and tetroxide in the gas phase.

Absorption of nitrogen peroxide by water occurs according to the following summary reaction:



By ignoring the small content of N_2O_3 in the gases, all the calculations of the process of absorbing nitric oxides are made based on this equation. It follows from the reaction equation, that of the three NO_2 molecules, two are converted into nitric acid, while one into NO which again must be oxidized according to the known reaction:



The formed nitrogen peroxide again reacts with water and is converted by 2/3 into nitric acid and by 1/3 into nitric oxide, etc. Thus, no matter how many absorption cycles are made, it is impossible to convert all the nitrogen peroxide into nitric acid: 1/3 of the nitric oxides will always be released in the gas phase in the form of NO . It is also taken into consideration that with a decrease in the total concentration of nitric oxides, the process of NO oxidation is drastically slowed down, and practically complete processing of the oxides into acid would require enormous volumes of reaction equipment. Consequently, we are limited to a definite degree of absorption of nitric oxides: in the systems operating at atmospheric pressure, 92-94% and in the systems operating at increased pressure, 98-99.5%.

The nitric oxides that remain in the gases are partially trapped by the alkali solutions (in systems without pressure) or are released into the atmosphere. Certain active units that operate under increased pressure have recently been neutralizing the exhaust gases by catalytic breakdown of the nitric oxides.

The process of interaction of NO_2 with water is done in towers arranged in series with a ceramic packing (in systems without pressure) and in columns with bubble-cap plate or sieve-plate (in pressurized systems). Close contact between the gases and the solution is guaranteed in the absorption equipment. Almost always, even with low concentrations of nitric oxides, the process of acid formation occurs more rapidly than oxidation of NO into NO_2 . One can consequently consider that the reaction of NO_2 absorption by water reaches the state of equilibrium, and acid formation occurs only as NO is oxidized into NO_2 .

The equilibrium constant of the reaction $3\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HNO}_3 + \text{NO}$

$$K_3 = \frac{P_{\text{HNO}_3} P_{\text{NO}}}{P_{\text{NO}_2}^3 P_{\text{H}_2\text{O}}}$$

can be presented as the product of two particular constants:

$$K_3' = \frac{P_{\text{NO}}}{P_{\text{NO}_2}^3}$$

$$K_3'' = \frac{P_{\text{HNO}_3}^2}{P_{\text{H}_2\text{O}}}$$

The constant K_3' expresses the ratio of NO and NO_2 in the gas phase, or the degree of oxidation of the nitrous gases, while the constant K_3'' expresses the ratio of partial pressures of vapors of HNO_3 and H_2O above an aqueous solution of nitric acid.

The constants K_3' , K_3'' and their product K_3 which depend on the temperature and concentration of nitric acid irrigating the tower (or column) are presented in table I-45 and I-46.

The effect of individual factors on the processes occurring in the absorption part of the nitric acid system, as well as certain

relationships that characterize these processes are presented in fig. I-19-I-22.

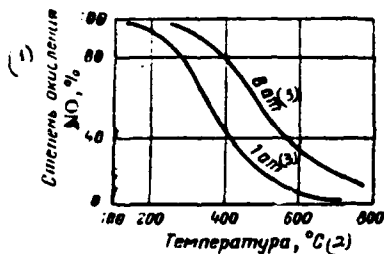


Figure I-19. Dependence of Equilibrium Degree of NO Oxidation on Temperature and Absolute Pressure (initial composition of gas mixture: 9.92 vol.% of nitric oxide, 5.68% oxygen).

- Key:
1. Degree of oxidation of NO. %
 2. Temperature, °C
 3. Atmospheres

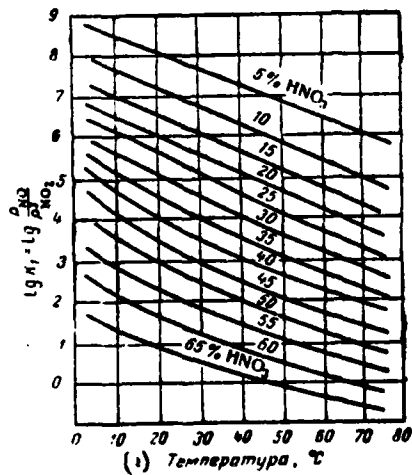


Figure I-20. Dependence of Partial Constants of Equilibrium on Temperature and Concentration of Nitric Acid

- Key:
1. Temperature, °C.

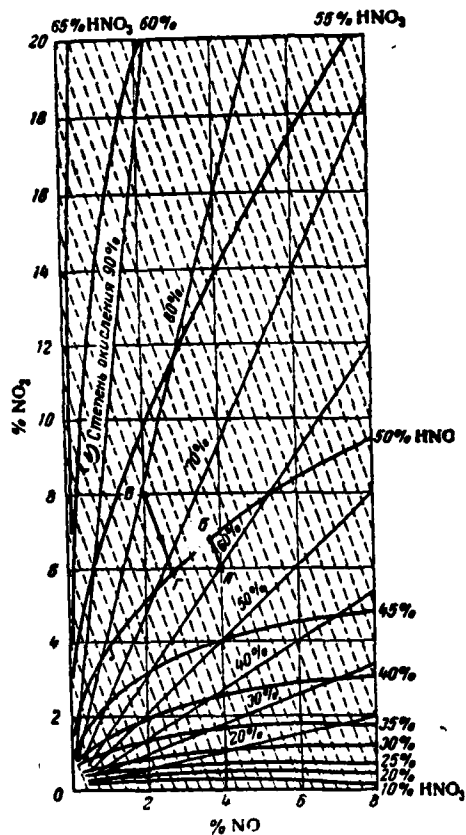


Figure I-21. Nomogram to Determine Ratio of NO and NO₂ above Nitric Acid under Conditions of Equilibrium at 25°C (dotted line shows the lines for change in gas composition during its transition to the equilibrium state with acid).

- Key:
1. Degree of oxidation **90%**.

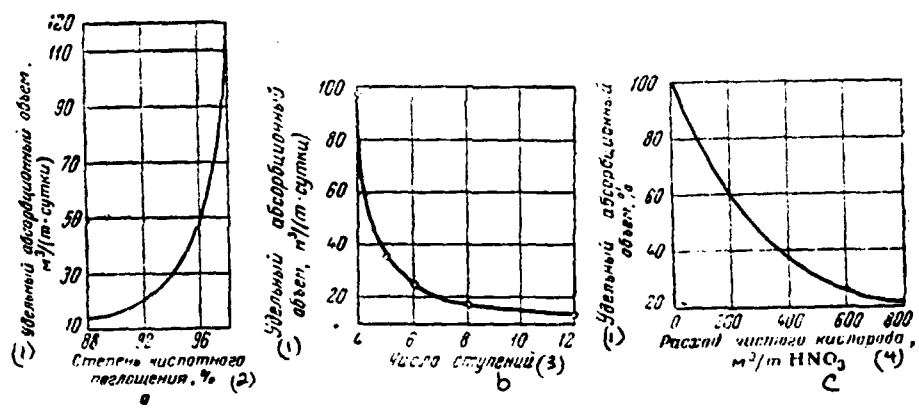
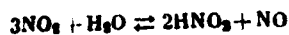


Figure I-22. Dependence of Specific Absorption Volume on Different Factors

Key:

- a. On degree of acid absorption of nitric oxides (system made of six towers, acid content in gases 5.5%, absorption temperature 30°C, acid concentration 50% HNO₃)
 - b. On number of stages of tower system (without consideration for volume occupied by packing)
 - c. On consumption of pure oxygen per 1 m of 100% HNO₃ (specific absorption volume without addition of oxygen is taken as 100%).
1. Specific absorption volume, m³/(m x day)
 2. Degree of acid absorption, %
 3. Number of stages
 4. Consumption of pure oxygen, m³/m HNO₃

TABLE I-45. CONSTANTS OF REACTION EQUILIBRIUM¹²



(1) Концентрация HNO ₃ вес. %	$\lg K_1' = \lg \frac{p_{\text{HNO}_3}}{p_{\text{NO}_2}}$			$\lg K_2' = \lg \frac{p_{\text{HNO}_3}}{p_{\text{H}_2\text{O}}}$			$\lg K_3 = \lg K_1' + \lg K_2'$		
	(2) Температура, °C								
	25	50	75	25	50	75	25	50	75
24.1	+5.37	4.20	+3.17	-7.77	-6.75	-5.66	-2.40	-2.55	-2.49
33.8	+4.36	+3.18	+2.19	-6.75	-5.65	-4.66	-2.39	-2.47	-2.47
40.2	+3.70	+2.58	+1.68	-5.91	-4.86	-3.97	-2.21	-2.28	-2.35
45.1	+3.20	+2.10	+1.18	-5.52	-4.44	-3.50	-2.30	-2.34	-2.32
49.4	+2.75	+1.67	+0.77	-5.12	-3.99	-3.11	-2.38	-2.28	-2.34
59.9	-0.13	-0.69	-1.12	-2.12	-1.69	-1.27	-	-	-

(3) Среднее -2.24 | -2.38 | -2.39

- Key:
1. HNO₃ concentration, weight. %
 2. Temperature, °C
 3. Average

TABLE I-46. PARTIAL CONSTANTS $\lg K_2' = \lg \frac{P_{NO}}{P_{NO_2}^2}$

Температура, град. °C (1)	Концентрация HNO ₃ , вес. % (2)												
	5	10	15	20	25	30	35	40	45	50	55	60	65
10	8,45	7,58	7,00	6,50	6,07	5,62	5,17	4,68	4,15	3,55	2,92	2,20	1,37
25	7,90	6,87	6,25	5,75	5,25	4,75	4,25	3,73	3,18	2,66	2,08	1,42	0,70
50	6,90	5,85	5,20	4,64	4,09	3,55	3,08	2,60	2,10	1,60	1,10	0,55	-0,05
75	5,93	4,77	4,12	3,55	3,03	2,55	2,09	1,65	1,17	0,71	0,24	-0,25	-0,75

Key:

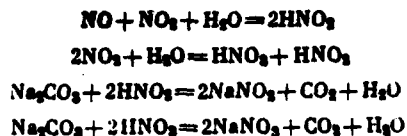
1. Temperature, °C
2. HNO₃ concentration, weight. %

The degree of absorption of nitric oxides, i.e., their conversion into nitric acid, depends on many factors: temperature conditions of the process, composition of nitrous gases, surface and density of spraying, quality of the packing, design of the column plates, pressure, specific volume of absorption equipment, etc.

Absorption of Nitric Oxides of Low Concentration by Alkali Solutions⁴²⁻⁴⁷

On the units operating at atmospheric pressure, as indicated, we are limited to processing into nitric acid of 92-94% of the nitric oxides. The remaining quantity of nitric oxides in the nitrous gases (about 1% NO + NO₂) is absorbed by solutions of calcined soda, less often, by milk of lime or solutions of caustic soda.

The plan for the process of absorption of nitric oxides of low concentration by solutions of calcined soda can be presented by the following equations:



Oxidation of nitric oxide occurs simultaneously according to the reaction: $2\text{NO} + \text{O}_2 = 2\text{NO}_2$. Usually absorption of the nitric oxides by alkali solutions is done in towers with ceramic packing made of rings no more than 150 x 150 mm in size. This makes it possible to

create a large contact surface between the liquid and gas phases.

The degree of absorption by alkali solutions of the residual nitric oxides depends on the composition and concentration of nitric oxides in the gas, density of sprinkling during circulation of the alkali solutions, the content in them of nitrites, nitrates and free alkali, as well as the quantity of admixtures suspended in the gas (oxides and hydroxides of heavy metals, silicates, etc.).

The nitric oxides are absorbed from the gas mixture in which nitric oxide dominates over peroxide, in the form of N_2O_3 . The rate of NO_2 absorption by the alkali solution is lower than the rate of N_2O_3 absorption. It is consequently expedient to preliminarily completely transform NO into NO_2 , also taking into consideration that for this process, with general low concentration of nitric oxides, greater volumes of oxidation towers would be necessary. It has been established that the oxidizing rate of absorption of nitric acids with their low concentration in gas reaches the maximum already with a ratio of $NO_2: NO = 1$.

After acid absorption of the nitric acids, the $NO_2:NO$ ratio in the gas does not exceed 0.25-0.3, therefore the gases should be preliminarily additionally oxidized to the assigned quantity. This process usually occurs in an empty tower which is placed before the alkali part of the absorption system. The density of tower sprinkling by alkali solutions is kept in limits of $5-6 \text{ m}^3/\text{m}^2$ of the surface. With lower density of sprinkling, the degree of absorption of nitric oxides is considerably impaired.

With an increase in the total content of salts in the circulating alkali solutions above 400 g/l , and a surplus of free Na_2CO_3 of $10-12 \text{ g/l}$, the degree of absorption of the nitric oxides (initial content 0.9% of $NO + NO_2$) is decreased by 8-9% because of the increase in the viscosity of the solutions, and for other reasons. Consequently, for greater completeness of absorption of the nitric oxides, it is more expedient to remove the production nitrite-nitrate solutions with total salt content of $400-420 \text{ g/l}$ with invariable presence of free Na_2CO_3 in a quantity of $\sim 15 \text{ g/l}$. In

this case, solutions are obtained with NaNO_2 : NaNO_3 ratio equal to (6-7):1. This makes it possible, when they are concentrated by evaporation and crystallization, to separate into the precipitate no less than 30% of the standard sodium nitrite.

Suspended admixtures have a great effect on the degree of absorption of the nitric oxides by alkali solutions. Their source in the sprinkling cycle of the towers is calcined soda which often contains over 1% insoluble compounds. In addition, poorly soluble sodium bicarbonate is constantly formed in the solutions. In a comparatively short time (roughly in 3 years), a considerable quantity of insoluble admixtures is formed on the tower packing, especially in its upper part. This results in a deterioration of sprinkling, and as a consequence, a decrease in the degree of absorption of the nitric oxides. It is expedient to filter the soda solutions before nitric oxide is supplied for absorption.

The degree of absorption increases with a rise in pressure and concentration of nitric oxides in the gas. A change in temperature in limits of 20-60°C has almost no effect on the degree of absorption.

It is fairly difficult to dissolve soda in water^(p. 17). Absorption of nitric oxides previously employed 20-22% aqueous solutions of soda. In this case, nitrite-nitrate solutions were obtained with total salt concentration no higher than 300 g/l. In order to attain a higher concentration of them, it is preferable to dissolve the soda in part of the circulating solution and return it to the cycle of tower sprinkling. Good joint solubility of NaNO_2 and Na_2CO_3 , as well as NaNO_3 and NaCO_3 (table I-47, I-48) makes it possible to prevent the precipitation of salts from the circulating solutions in the process of nitric acid absorption.

For normal conducting of the process of alkaline absorption of nitric acids, their content is successfully reduced in the exhaust gases roughly to 0.12%. The fundamentals of the process of nitric

acid absorption from nitrous gases by milk of lime, solutions of caustic soda and other alkalis do not differ from those described.

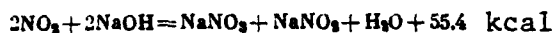
TABLE I-47. JOINT SOLUBILITY OF NaNO_2 AND Na_2CO_3 IN WATER AT 30°C

(1) Растворимость, вес. %			(2) Плотность раствора g/cm^3	(1) Растворимость, вес. %			(2) Плотность раствора g/cm^3
NaNO_2	Na_2CO_3	$\text{NaNO}_2 + \text{Na}_2\text{CO}_3$		NaNO_2	Na_2CO_3	$\text{NaNO}_2 + \text{Na}_2\text{CO}_3$	
0	29.62	29.62	1.345	27.27	12.91	40.18	1.360
7.33	26.86	34.19	1.353	35.10	7.98	43.08	1.366
8.55	25.25	34.80	1.356	43.80	1.79	45.59	1.376
16.82	19.92	36.74	1.351	46.20	0.0	46.20	1.372

Key:

1. Solubility, weight. %
2. Density of solution, g/cm^3

By knowing the heat of formation of nitrous and nitric acids (p. 27, 34) and the heats of their neutralization by alkalis, one can compute the total thermal effect of the reactions of salt formation in solutions. During absorption of nitric oxides by solutions of caustic alkalis, the thermal effect is:



9 Inversion of Nitrites into Nitrates^{48,49}

← Nitrite-nitrate solutions that are obtained in alkaline absorption of nitric oxides from nitrous gases, as well as mother liquors which are formed in the production of crystalline NaNO_2 are reprocessed into the appropriate nitrates (p. 168). During conversion (inversion) of nitrites into nitrates by nitric acid, chlorides are broken down (p. 184) and the chloride compounds are removed from the system (fig. I-23).

The rate of the inversion process is determined by the rate of breakdown of nitric acid that is formed intermediately during the

TABLE I-48. JOINT SOLUBILITY OF NaNO_2 and NaNO_3 IN WATER

Растворимость (1)				Растворимость (1)			
г в 100 г воды (2)		вес. % (3)		г в 100 г воды (2)		(3) вес. %	
NaNO_2	NaNO_3	NaNO_2	NaNO_3	NaNO_2	NaNO_3	NaNO_2	NaNO_3
(4) При 0 °C				(4) При 52 °C			
68	19	36.4	10.2	104.3	20.6	46.6	9.2
67	36.3	33	17.85	99.5	43.2	41.0	17.8
64.9	41.7*	31.3	20.2	98.8	82*	35.2	29.2
50.3	48.8	25.5	23.8	65.2	88	25.8	34.8
30.2	55.4	16.3	29.8	44.2	92.9	18.7	39.2
				27.2	101.4	11.9	44.5
				14.7	109	6.6	48.8
(4) При 21 °C				(4) При 103 °C			
81.1	9.6	42.5	5.03				
79.7	23.5	39.3	11.6	153.3	33.2	53.5	11.6
73.8	50.8	32.8	22.6	148.9	58.8	48.2	19.1
73.1	54.5*	32.1	24.0	142.4	116*	39.7	32.4
64.2	56.7	29.1	25.7	100	128.8	30.8	38.8
46.8	62.8	22.4	30	60.1	142.9	19.8	47.1
21.6	74.7	11	38.2				

Key:

1. Solubility
2. g in 100 g of water
3. weight. %
4. at

* Both salts precipitate out of the supersaturated solution.

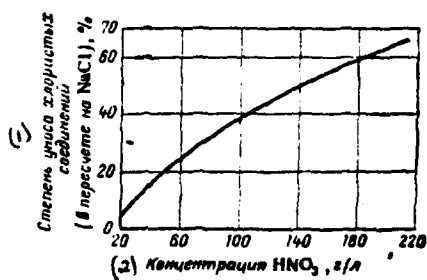


Figure I-23. Dependence of Degree of Removal of Chloride Compounds with Nitric Oxides during Inversion of Nitrites into Nitrates on the HNO_3 Concentration

Key:

1. Degree of removal of chloride compounds (in conversion for NaCl), %
2. HNO_3 concentration, g/l

interaction of nitrites with nitric acid. The solutions that are exposed to inversion are very supersaturated with nitric acid which slows down the breakdown of nitric acid and results in a decrease in the rate of the reaction of nitrate formation. The rate of the inversion process of nitrites significantly rises with an increase in the temperature of the solutions, increase in them of nitric acid, and with the supply of large quantities of air.

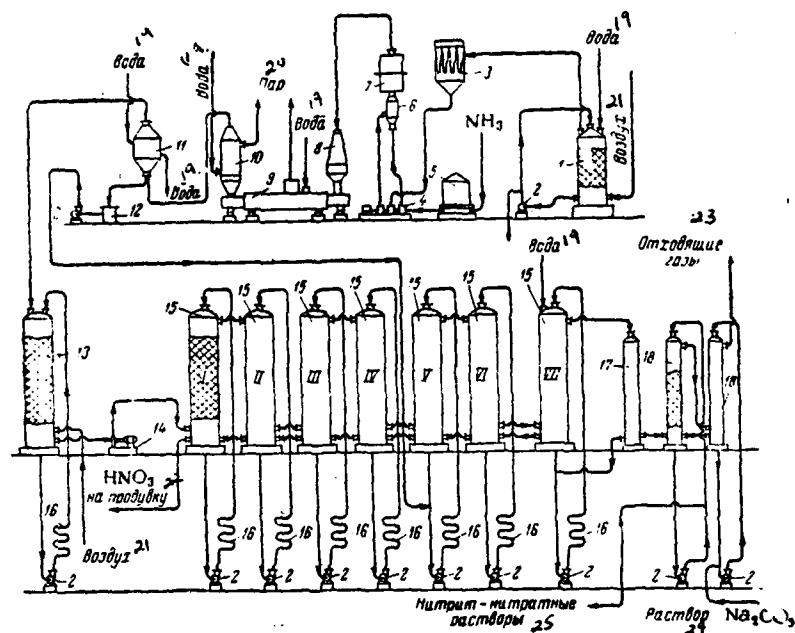


Figure I-24. Plan of Production of Diluted Nitric Acid at Atmospheric Pressure

1. Scrubber for water rinsing of air
 2. Pumps
 3. Sleeve filter
 4. Ammonia-air ventilator
 5. Ammonia filter
 6. Mixer of ammonia and air
 7. Porolite filter
 8. Contact apparatus
 9. Boiler-recovery unit
 10. Water evaporator
 11. Bubbling cooler
 12. Tank
 13. Washing absorption tower
 14. Ventilator-gas blower of nitrous gases
 15. Acid absorption towers
 16. Acid cooler
 17. Oxidizing tower
 18. Alkali absorption towers
- Key:**
19. Water
 20. Steam
 21. Air
 22. To blower
 23. Exhaust gases
 24. Solution
 25. Nitrite-nitrate solutions

Industrial Plans for Production of Diluted Nitric Acid

The theoretical principles for the process of forming diluted (weak) nitric acid are stated in a number of works^{12, 50-54}.

Different systems are currently used for producing diluted nitric acid.⁵⁵⁻⁶³ Some of them have been updated in recent years. This significantly improved the technical-economic indices of their operation.

The systems that operate under increased pressure have to be equipped with apparatus to trap the nitric oxides^{64,65,94} that are contained in the exhaust gases, or for their catalytic breakdown.^{66-68,95}

Systems Operating at Atmospheric Pressure

Oxidation of ammonia (fig. I-24) is done in contact equipment 1, 1.2 and 2.9 m in diameter. Absorption of nitric oxides is done in 6-8 paired towers made of chrome-nickel steel of brand Kh18N9T. In the production of 45-49% nitric acid and degree of acid absorption 92%, the volume of the tower for 1 T/day of acid (100% HNO₃) is 20-29 m³, including the product of the system of alkali trapping of nitric acid from the exhaust gases (in conversion for acid). The density of sprinkling of the circulating acid in the first two towers (on the gas course) is assumed to be equal to 10-12, in the third and fourth 8, and in the last towers, 4-5 m³/(m³ x h).

The systems operate at rarefied, or more often, at low pressure. In the latter case, the gas blowers which are installed in the beginning of the system, create gas pressure on the approximate order of 1000-1200 mm wat. col. The reaction heat is removed by water-cooling of the acid circulating in the towers. Shell-and-tube, or less often, sprinkling coolers are used for this purpose.

Nitric acids are trapped from the nitrous gases by solutions of alkalis in the system consisting of one oxidizing (hollow) and two absorption towers. For 1 T^{tr} of daily output (with regard for the

product of alkali absorption in conversion for 100% HNO_3 , the oxidizing volume is assumed to be equal to 3.5 m^3 , and the absorption volume 5 m^3 .

The system is distinguished by simplicity of the equipment. its simple maintenance, low consumption of catalyst and electricity. The shortcomings of the system include : large capital outlays for construction, mainly as a consequence of a considerable consumption of special steels; production of nitric acid of reduced concentration; impossibility of operating the system until it is completely built (in contrast to the systems that are built on the aggregate principle); need to build a section for alkali trapping of the nitric oxides even in those cases where it is not advantageous to produce technical-grade nitrates for economic considerations.

In addition, in the systems operating at atmospheric pressure, it is almost impossible to reach the sanitary standard for the nitric acid content in the exhausts.

Below are the main indicators of the technological regime:

Content of mechanical admixtures in air, mg/m^3 , not more	0.007
NH_3 content in ammonia-air mixture, %	10.5-11.5
Contact temperature, $^{\circ}\text{C}$	about 800
Intensity, kg NH_3 per 1 m^2 of active surface of catalyst per day	550-650
Degree of ammonia conversion, %	96.5-97.5
Temperature of nitrous gases at inlet to absorption part of system, $^{\circ}\text{C}$	45-55
Pressure of nitrous gases at inlet to absorption part of system, mm wat. col.	1000
Temperature of acid in towers, $^{\circ}\text{C}$	30-40
Concentration of production acid, %	45-49
Content in exhaust gases, %	
of nitric acids	0.1-0.15
of oxygen	4-5
Composition of solutions of alkali absorption of nitric oxides, g/l	
NaNO_2	320-350
NaNO_3	to 50
$\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$	10-15

The consumption coefficients per 1 t of nitric acid are:

Ammonia (100% NH ₃), kg	287-290
Platinoid catalyst (irreversible losses), g	0.045-0.049
Calcined soda (100% Na ₂ CO ₃), kg:	
in production of sodium nitrate only	77.0
in the production of sodium nitrite and sodium nitrate	69.0
Electricity for production needs, kW x h	
average annual consumption	115
in summer	125
Water for cooling, m ³	
average annual consumption	150
in summer	190

Main Equipment*

Scrubber for water rinsing of air. The diameter of the scrubber is 5.6 m, height 9.5 m. It is made of carbon steel and is covered on the inside with anticorrosion composition. The scrubber adapter is ceramic rings, 50 x 50 x 3 or 80 x 80 x 8 mm which can be loaded by heaving.

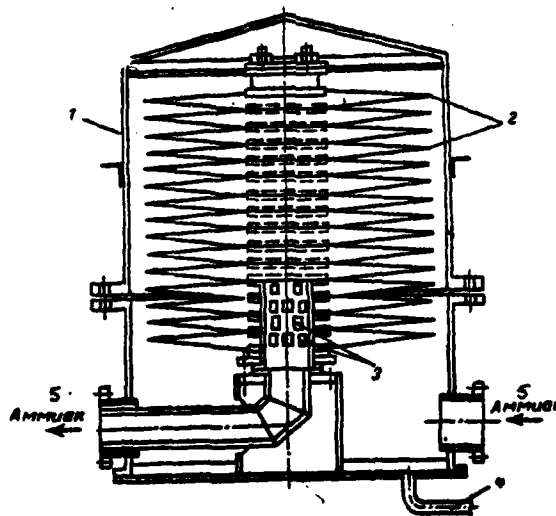


Figure I-25. Filter for Purifying Gaseous Ammonia

Key:

- | | |
|------------|---------------------------------------|
| 1. Housing | 4. Coupling for draining contaminants |
| 2. Cells | 5. Ammonia |
| 3. Windows | |

* Here and in the description of other systems brief characteristics of the equipment are given which are used most often in the production of nitric acid.

Linear air velocity of up to 0.5 m/s is maintained in the scrubber. The density of sprinkling with water is 4-5 m³/h per 1 m² of section.

Cloth filter for air cleaning consists of cells, sleeves, that are assembled into sections on common wooden frames. The filtering material is coarse wool broadcloth that meets the requirements of GOST 6621-53.

The cell-sleeve dimensions are: diameter of the upper part 280 mm, lower 200 mm, length 2410 mm. The surface of the sleeve is 1.84 m². The load on 1 m² of the filtering surface is equal to 60-80 m³/h of air.

Cloth filter for ammonia purification (fig. I-25). There are 15 sections, cells made of aluminum, in the cylindrical housing (made of carbon steel) 1600 mm in diameter and 2250 mm in height. The cells are covered with cotton chamois. Their total filtering surface equals 50 m³. The load of the gaseous ammonia is 60-80 m³/(m² x h).

Porolite filter for purifying the ammonia-air mixture (fig. I-26). The vertical cylindrical housing of the filter is made of aluminum. Porous ceramic tubes numbering 421, 586 or 1257 are attached to the tubular grid. The diameter of the tubes is 50/30 mm, and length is 760 mm. Depending on the purity of the mixture, the load on 1 m² of the filtering surface is from 60 to 110 m³/(m² x h) of mixture.

Cardboard filter for purifying the ammonia-air mixture. Within the vertical cylindrical housing of the filter made of aluminum, less often of stainless steel, there is a group of metal rings with disks placed on them made of filtering cardboard brand FMP-1 and VMK. The filtering surface of the cardboard filter is 50 m² and more.

The contact equipment consists of two truncated cones whose larger bases are connected by a cylindrical part made of stainless steel (abroad it is often made of aluminum alloy). The lower cone

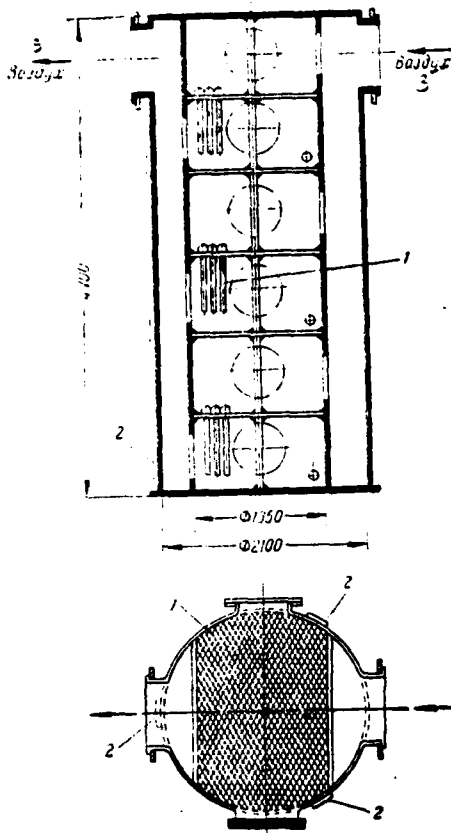


Figure I-26. Porolite Filter for Purifying Ammonia-Air Mixture

Key:

1. Porolite tubes
2. Viewing windows
3. Air

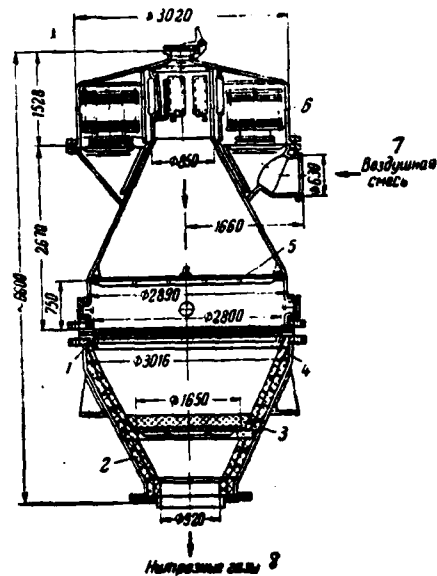


Figure I-27. Contact Equipment with Two-Stage Catalyst for Ammonia Oxidation

Key:

1. Platinoid catalyst grid
2. Lining
3. Metal Raschig rings
4. Basket with non-platinum catalyst
5. Distributor grid
6. Cardboard filter
7. Air mixture
8. Nitrous gases

made of carbon steel is lined with refractory brick. The output of the contact equipment 2000 mm in diameter and ~ 5000 mm high, calculating for nitric acid, is 27-35 $\frac{t}{day}$, and of an apparatus 1100 mm, 8-10 $\frac{t}{day}$.

Contact equipment with two-stage catalyst. In the middle of this contact equipment, between the cylindrical part and the upper cone, a platinum grid is attached with the help of rings. A basket made of heat-resistant alloyed steel is placed under it. Tablets of nonplatinum catalyst are loaded into it. The bottom of

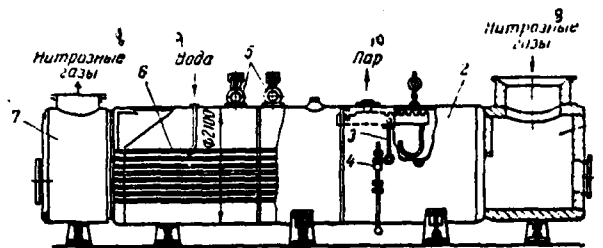


Figure I-28. Boiler-Recovery Unit

Key:

1. Input chamber
2. Housing
3. Water gage
4. Ejector
5. Safety valves
6. Piping (water) part
7. Outlet chamber
8. Nitrous gases
9. Water
10. Steam

the basket is a nichrome grid with openings less than 4 mm. Under the grid, there are grate bars which are placed on brick arches. In order to prevent sagging of the platinoid grid which must be arranged at a definite distance from the nonplatinum catalyst, cross braces made of nichrome wire are stretched under the grid.

One of the versions of contact apparatus with two-stage catalyst is presented in fig. I-27.

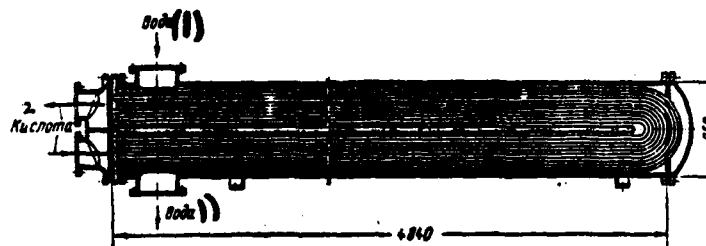


Figure I-29. Cooler of Nitric Acid

Key:

1. Water
2. Acid

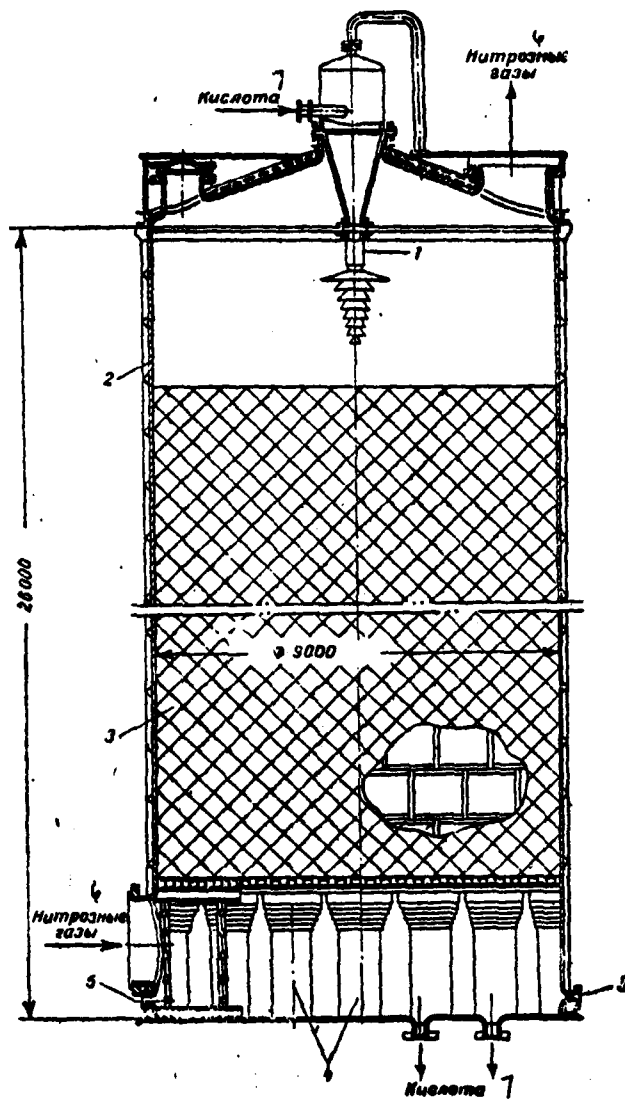


Figure I-30. Tower of Acid Absorption

Key:

1. Sprayer
2. Housing
3. Adapter--Ceramic rings
4. Supports under adapter
5. Coupling pipe for acid overflow
6. Nitrous gases
7. Acid

Gas bubbling cooler with surface 80 m^2 , diameter 2.2 m and height 3.16 m is made of stainless steel. There are five sieve plates with openings 2 mm in diameter operating in parallel in the

welded housing. Under the plates there are false bottoms to prevent liquid from falling through. The removal of heat is done by water which is circulating in the coils (pipes 38 x 2.5 mm in diameter). The surfaces of the coils are established from a calculation of 1.1-1.25 m² per 1 $\frac{t}{m}$ /day of 100% HNO₃.

Gas tubular cooler is a vertical shell-and-tube apparatus made of stainless steel. The main dimensions are: surface of cooling 300 m², diameter 1.3 m, height 9.1 m. There are 367 tubes installed with diameter of 44 x 2.5 mm.

About 7 m² of cooling surface is provided for 1 $\frac{t}{m}$ of daily output of acid (100% HNO₃).

The boiler-recovery unit (fig. I-28) consists of two gas chambers and a middle heat-exchange part. The chambers are lined with acid-resistant brick. The boiler housing is welded, made of carbon sheet steel 14 mm thick. The heat-resistant boiling pipes (412) 44 x 3 mm in diameter are also made of carbon steel. The thickness of the pipe grids is 30 mm. The heat transmission surface is 330 m². Nitrous gases pass on the pipes. The interpipe space is the water part of the boiler. The working pressure of vapor is 10-12 atm and the temperature of the nitrous gases at the outlet from the boiler must not be lower than 150-160°C.

The acid cooler (fig. I-29) is a heat-exchange apparatus of shell-and-tube type with cooling surface 50 m². The diameter of the tubes (57 of them) is 32 x 2.5 mm.

Combined ammonia-air ventilator combines the ammonia and air ventilators that are installed on a common shaft. The output of the ventilator for air is 30,000 m³/h, and for ammonia 4100 m³/h. The pressure equals 700 mm wat. col. Ventilators with output of 27,500 m³/h for ammonia-air mixture are also used. The rate of shaft rotation of these ventilators is 2950 rpm. The total drop in pressure equals 800 mm wat. col. (p. ~~99~~⁷³ and fig. I-43).

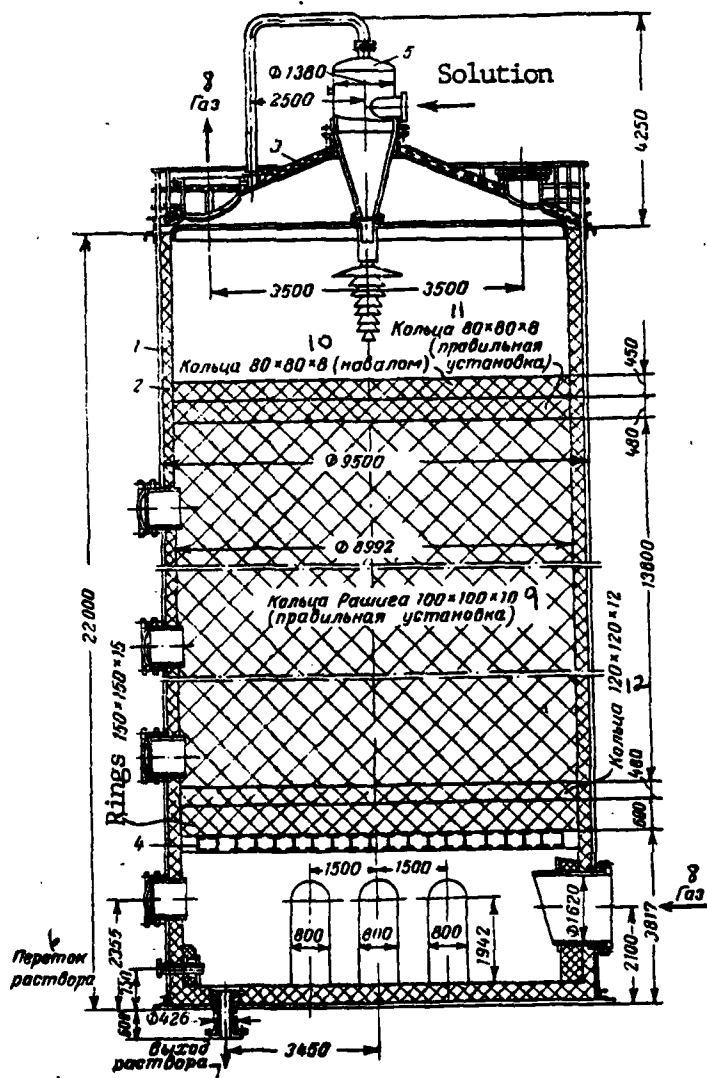


Figure I-31. Tower of Alkaline Absorption of Nitric Oxides (Placement of adapter rings, except for upper layer, is in regular rows)

Key:

1. Tower housing
2. Lining
3. Cover
4. Metal support beams
5. Spraying devices
6. Solution overflow
7. Exit of solution
8. Gas
9. Raschig rings 100 x 100 x 10 (regular installation)
10. Ring 80 x 80 x 8 (heaped)
11. Rings 80 x 80 x 8 (regular installation)
12. Rings 120 x 120 x 12

The tower of acid absorption is designed to operate at rarefaction up to 500 mm or at pressure of 1000 mm wat. col. It is made of stainless steel (welded). Figure I-30 presents a tower 9 m in diameter and 26 m high.

The tower of alkali absorption is made of carbon or stainless steel. The tower made of carbon steel is lined with acid-resistant materials. The tower dimensions are: diameter 6-10 m, height 19-26 m. The adapter is acid-resistant ceramic rings 150 x 150 mm in size (lower layer is 2-3 m high), 100 x 100 (second layer is 14-18 m high), 80 x 80 and 50 x 60 mm (third and fourth layers) placed in regular rows. Only the most upper layers of rings are loaded in heaps.

Figure I-31 presents a tower 9.5 m in diameter and 22 m high (to the roof).

Systems Operating under Pressure of 8-9 Atmospheres

The systems that operate under pressure (fig. I-32) are built on the aggregate principle. They operate on atmospheric air, and air that is enriched with oxygen. Oxidation of ammonia uses contact equipment 310, 520 and 540 mm in diameter. Absorption of nitric oxides uses columns 1.7 m in diameter and 13 m high with bubble-cap plates (less often with sieve-plates).

The reaction heat is removed by water that is circulating in the coils placed between the bubble-cap plates. Additional air for oxidation of NO into NO₂ is supplied to the cooler-condenser, or to the lower part of the absorbing column. The volume of the column is 0.5-0.6 m³ per 1 T/day of nitric acid. The power used for compression of the gases is recuperated by 30-40% in the turbine that sits on the common shaft with the air compressor.

Catalytic breakdown of nitric oxides that are contained in the exhaust gases has been partially introduced in recent years in these systems.

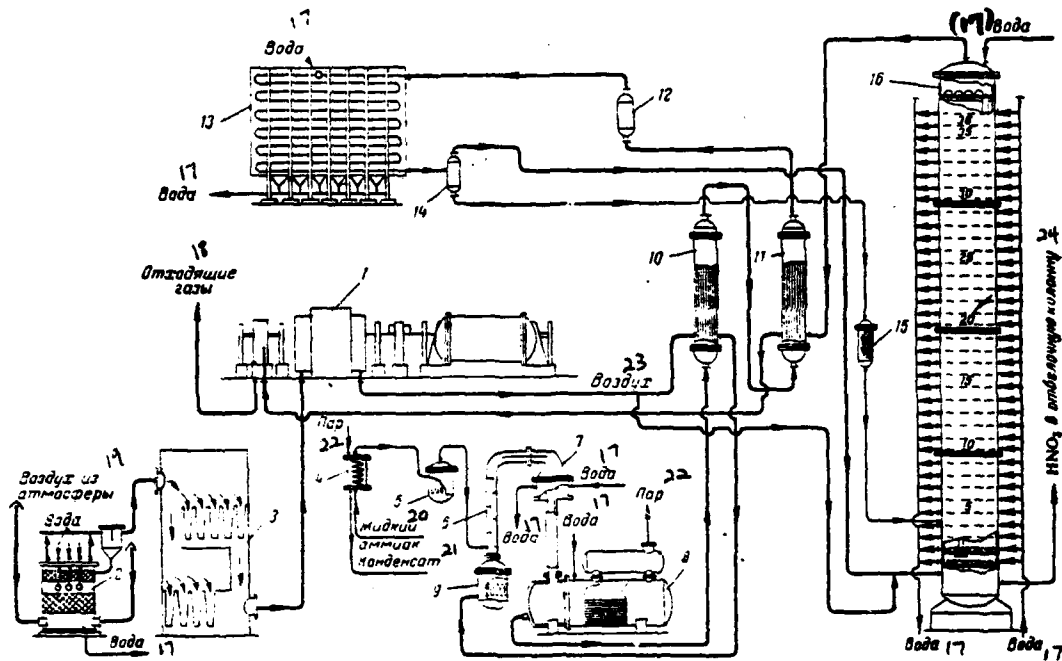


Figure I-32. Plan for Production of Diluted Nitric Acid under Absolute Pressure of 8-9 Atmospheres

Key:

1. Turbocompressor
2. Scrubber
3. Cloth air filter
4. Liquid ammonia evaporator
5. Filter
6. Mixer
7. Contact apparatus
8. Boiler-recovery unit
9. Porolite filter for air
10. Air heater
11. Exhaust gas heater
12. Filter to trap platinum from gas phase
13. Cooler-condenser of nitrous gases
14. Separator
15. Filter to trap platinum from liquid phase
16. Absorption column
17. Water
18. Exhaust gases
19. Air from atmosphere
20. Liquid ammonia
21. Condensate
22. Steam
23. Air
24. HNO_3 to whitening column

The systems operating under pressure are characterized by lower capital outlays for construction as compared to the capital investments to the systems that operate at atmospheric pressure; the possibility of obtaining acid with less than 56% concentration; and the aggregate principle of construction which is especially important for multiple-tonnage production.

Shortcomings of these systems are: high consumption of electricity; increased outlays of ammonia (degree of conversion is 2-3% lower than in systems with contact assemblies operating at atmospheric pressure); increased shop expenditures for maintenance of the unit, and losses of platinoid catalyst which are greater (2.5-3-fold) than on the units operating at atmospheric pressure.

Below are the main indicators of the production regime:

Content of mechanical admixtures in the air, mg/m ³ , no more	0.007
Temperature of gaseous ammonia after evaporator, °C	65 - 68
Temperature of ammonia-air mixture, °C	
with the use of atmospheric air	200 - 250
with the use of air enriched with oxygen	80 - 90
NH ₃ content in ammonia-air mixture, volum. %	
with the use of atmospheric air	10.5-11.5
with the use of air enriched with oxygen	11.5-12.5
Intensity of catalyst, kg NH ₃ per 1 g of platinoids	4-5
Degree of ammonia conversion, %	94-95
Contact temperature, °C	880-900
Temperature of nitrous gases after exhaust gas heater, °C	300-320
Pressure (absolute) at end of absorption system, atm.	5.5-6.5
HNO ₃ concentration in production acid, %	56-58
Temperature (average) of acid in column, °C	30-40
Content in exhaust gases, volum. %	
of nitric oxide	0.15-0.25
of oxygen	2.0-2.5

Consumption coefficients for 1 T of nitric acid:

Ammonia(100% NH ₃), kg	292-295
Electricity for production needs, kW x h	360-380
Platinoid catalyst (irreversible losses), g	0.155-0.170
Water for cooling, m ³	110-130
Steam, t	0.3-0.5

Basic Equipment

Contact apparatus (fig. I-33) consists of two main parts: upper, head and lower, housing (basins). The head is made from chrome-nickel steel (less often from nickel), and the housing is made

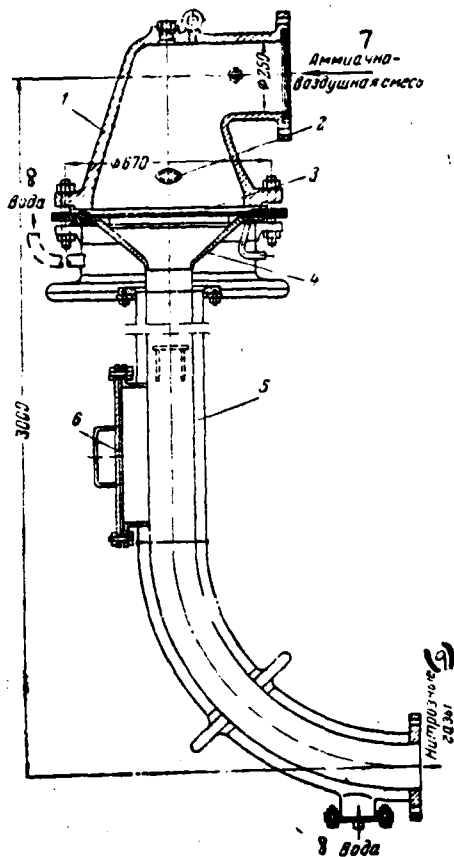


Figure I-33. Contact Apparatus Operating at Absolute Pressure of 8-9 Atmospheres

Key:

1. Head
2. Hole for firing grid
3. Group of platinoid grids
4. Housing (basin)
5. Water sleeve
6. Trap door for cleaning sleeve
7. Ammonia-air mixture
8. Water
9. Nitrous gases

sheet chrome or chrome-nickel steel 12 mm thick. There is a group of platinoid grids on the grate bars between the head and the housing on a lattice. The grate bars and the lattice are made of chrome-nickel alloy (20% Ni and 80% Gr).

There is a water sleeve in the lower part of the housing to protect the apparatus from burning through. The output of the contact apparatus with internal diameter of 500 mm in conversion for nitric acid is 58-63 $\frac{\text{t}}{\text{day}}$.

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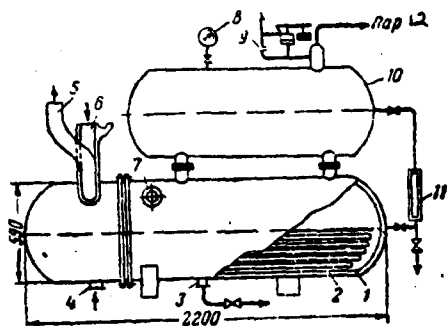


Figure I-34. Boiler-Recovery Unit (New Type)

Key:

1. Lower shell
2. Pipe still
3. Coupling for blowing through boiler from contaminants
4. Coupling for water supply for cooling boiler head
5. Outlet of nitrous gases
6. Inlet of nitrous gases
7. Coupling for supplying condensate for feeding the boiler
8. Manometer
9. Safety valve
10. Upper shell
11. Water gage
12. Steam

Boiler -recovery units. The boiler-recovery unit presented in fig. I-34 has been utilized in recent years. The boiler consists of two shells horizontally arranged on each other. Within the lower shell (590 mm in diameter, 2200 mm long) there is a two-way pipe still made of U-shaped pipes. The upper shell which is the separator-steam-collector, is made of seamless steel pipe 495 mm in diameter. Pressure to 14 atm. is maintained in the boiler.

In addition, boiler-recovery units of another type are in operation (fig. I-35). The housing of this boiler has bent pipes 57 mm in diameter. The boiler is made of carbon sheet steel 15 mm thick. The heating surface of the boiler equals 18.5 m^2 and the output is $2 \frac{\text{t}}{\text{h}}$. Pressure to 12 atm. is maintained in the boiler.

Exhaust gas heater (fig. I-36) is a vertical heat exchanger made of chrome-nickel steel. The heater shell has a pipe still 3 m long that consists of 37 pipes $21/25 \text{ mm}$ in diameter. The pipes are rolled in thick-walled pipe boards. There is a compensator in the upper part of the heater.

Cooler-condenser (fig. I-37). In the housing-container made of carbon steel 7 m long and 0.8 m wide and 2.7 m high there are coils made of stainless steel (pipes 57 mm in diameter). The

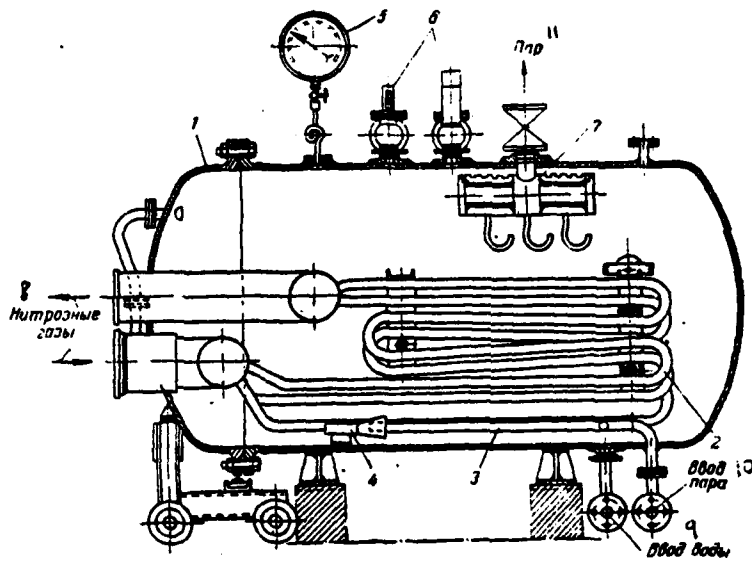


Figure I-35. Boiler-Recovery Unit (Old Type)

Key:

1. Boiler housing
2. Heating pipes
3. Pipe to feed steam during warm-up of boiler
4. Injector
5. Manometer
6. Safety valves
7. Dehumidifier
8. Nitrous gases
9. Steam input
10. Water input
11. Steam

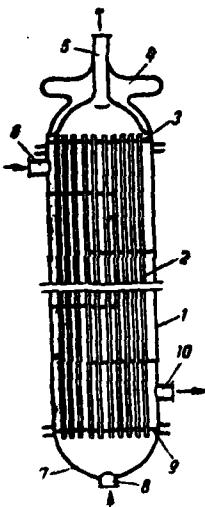


Figure I-36. Exhaust Gas Heater

Key:

1. Shell
2. Pipe still
3. Rear pipe board
4. Compensator
5. Coupling for outlet of nitrous gases
6. Coupling for inlet of exhaust gases
7. Front cover of shell
8. Coupling for inlet of nitrous gases
9. Front pipe board
10. Coupling for outlet of exhaust gases

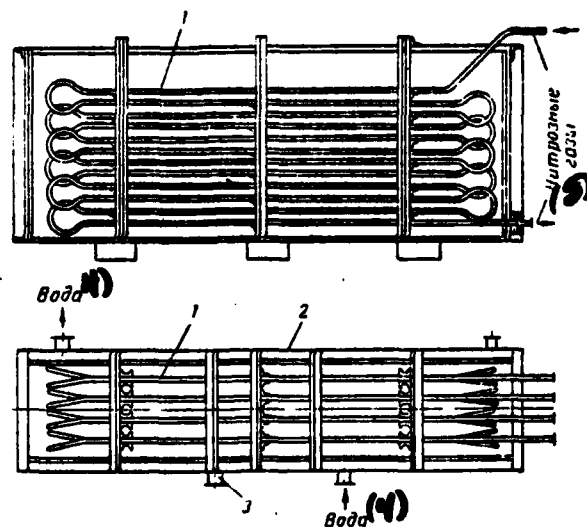


Figure I-37. Cooler-Condenser of Submersible Type

Key:

1. Coils
2. Shell
3. Coupling for water drainage and silt discharge
4. Water
5. Nitrous gases

container is covered on the inside with acid-resistant varnish.

Absorption column. One of the column designs is shown in fig. I-38. The column housing often consists of four sheet-steel cylinders with flanges that are tightened by bolts. The height of the sheet-steel cylinder is 3 m, the inner diameter is 1.68 m. The total height of the column is 13 m, and its full volume is about 30 m^3 . The column has 38 plates that are located a distance of 300 mm from each other. Each plate has 37 bubbling caps with cuts in the lower part and connecting pipes for overflow of the liquid to the lower plate. The gas velocity in the free column section equals 0.2-0.3 m/s.

Acid enters the 7th-8th plate (below) from the cooler-condenser. The nitrous gases are sent to the first plate of the column. The acid exits through the coupling located in the lower part of the column. The reaction heat is removed by water through the coils made of pipes 25 mm in diameter. The total surface cooled in the

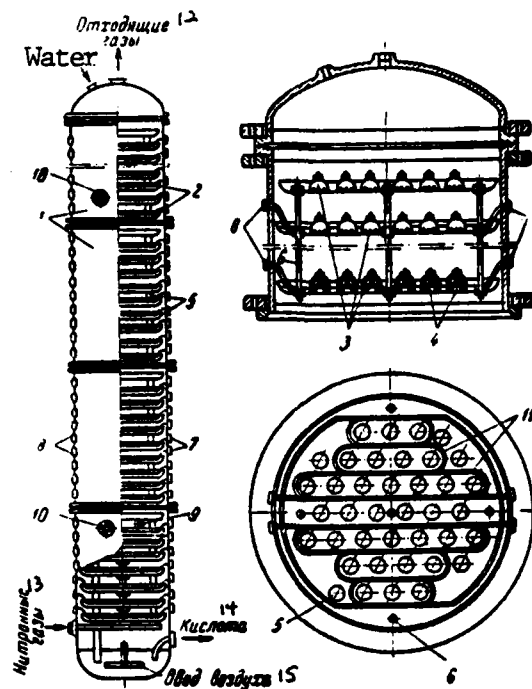


Figure I-38. Absorption Column

- Key:
1. Sheet-steel cylinders
 2. Plates
 3. Bubbling caps
 4. Hole for gas passage
 5. Overflow pipes
 6. Rod for plate attachment
 7. Input of cooling water
 8. Output of cooling water
 9. Input of separator acid
 10. Coupling for removal of acid sample
 11. Cooling coils
 12. Exhaust gases
 13. Nitrous gases
 14. Acid
 15. Air input

column is about 60 m².

Industry also uses other types of columns that operate under pressure of 8-9 atmospheres. They are mainly distinguished by the design of the caps, their number and attachment to the plates.

Systems Operating under Pressure of 7.3 Atmospheres

The most important feature of the system for nitric acid production under absolute pressure of 7.3 atmospheres* is the presence of a gas-turbine drive. In such systems, (fig. I-39), the air after purification from mechanical admixtures is compressed in the compressor of the gas-turbine unit to 3.5 atmospheres, and after cooling, is additionally compressed in a centrifugal supercharger to 7.3 atm. The air heated in compression is additionally heated by nitrous gases to 270°C and is sent to the combined unit that consists of a mixer and porolite filter. At the same time, gaseous ammonia enters the mixer after purification and warming. The ammonia-air mixture that is formed is purified in a porolite filter from residual mechanical admixtures and enters the contact apparatus.

The nitrous gases from the contact apparatus successively pass through the boiler-recovery unit, oxidizer, air-heater and cooler-condenser. The oxidized, cooled and considerably dried nitrous gases are sent through the separator to the lower part of the absorption column.

Nitric acid that is formed in the cooler-condenser, after separation of the nitrous gases from it by gravity flow, enters the plates of the column where there is acid of the same concentration. The production nitric acid at the outlet from the column is blown through with hot air from the dissolved nitric oxides and is sent to a storehouse.

The gases emerging from the absorption column, passing the separator for separation of the acid spray, enter the assembly of catalytic cleansing from nitric oxides that are reduced to elementary nitrogen here. The gas-reducer is products of methane-hydrogen oxidation and carbon monoxide. The ratio of methane and oxygen in the gas is kept in limits of 0.6-0.65. Palladized aluminum oxide is used as the catalyst.

Before catalytic purification, the exhaust gases are heated

*The absolute pressure is given here and further.

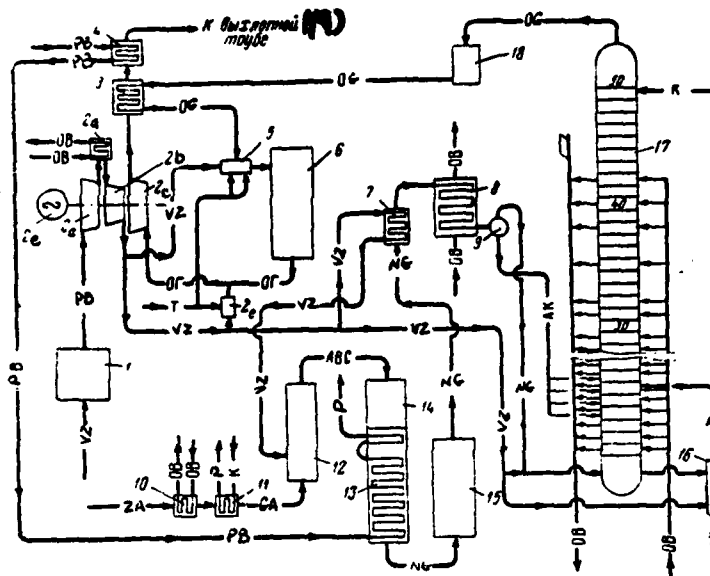


Figure I-39. Plan for Production of Diluted Nitric Acid under Absolute Pressure of 7.3 Atm.

Key:

1. Apparatus for air purification
2. Gas-turbine aggregate GTT
 - a. Compressor
 - b. Supercharger
 - c. Gas turbine
 - d. Air cooler
 - e. Engine-generator
3. Start-up combustion chamber
3. Exhaust gas heater
4. Water economizer of boiler
5. Chamber of water preparation
6. Reactor of catalytic purification
7. Air heater
8. Cooler-condenser
9. Acid separator
10. Ammonia evaporator
11. Ammonia heater
12. Combined apparatus (mixer and porolite filter)
13. Boiler-recovery unit
14. Contact apparatus
15. Oxidizer
16. Whitening (blow-through) column
17. Absorption column
18. Separator

Designations:

- VZ. Air
 NG. Nitrous gases
 OG. Exhaust gases
 AK. Nitric acid
 ZA. Liquid ammonia
 GA. Gaseous ammonia

[continuation of key]

- ABC. Ammonia-air mixture
- T. Fuel gas
- P~~X~~.V Feed water for boiler
- P. Steam
- K. Condensate
- OB. Cooling water
- 19. To exhaust pipe

by natural gas combustion products (furnace gases) to the temperature necessary for igniting the gas-reducer in the presence of the catalyst.

The mixture of gases (exhaust, furnace, natural) is sent to the reactor where reduction of nitric oxides occurs with an increase in temperature to 730°C. After the reactor, the purified gases are mixed with air and the furnace gases of the combustion chamber of the gas-turbine unit. This gas mixture enters the gas turbine at a temperature of 700°C under pressure of 5.4-5.7 atm. Here the gases are expanded to pressure of 1.06 atm. Their temperature is reduced to 400°C. In this case, electricity is generated in the gas-turbine unit which is needed to compress the air to 7.3 atm.

The purified exhaust gases are sent from the gas turbine to the boiler-recovery unit with economizer where the heat of these gases is used to generate steam at pressure of 13 atm. The exhaust gases from the economizer at temperature about 180°C and gage pressure of 120 mm wat. col. are sent into the atmosphere through a high pipe.

The gas-turbine unit is automated. It is started up by remote control from the machine room. Devices and instruments are provided for which make it possible to synchronize the course of the processes in the gas-turbine unit and in the sections for the production of nitric acid. Because there is a gas-turbine unit in the systems operating under pressure of 7.3 atm., the outlays of electricity for the production of nitric acid are completely compensated for. The energy surplus is used in the general plant network. These systems are also distinguished by a high degree of neutralization of the exhaust gases by catalytic breakdown of the nitric oxides they

contain; increased concentration of production nitric acid; high level of automation of all processes; lower capital investments for construction, and 2.5-3-fold greater output of the units as compared to the combined system (absorption under pressure of 3.5 atm.).

The shortcomings of the described system include: increased specific consumption of ammonia and platinoid catalyst; need to use natural or another fuel gas which does not allow us to consider the system universal for all areas of nitric acid production.

Below are the main indicators of the production regime:

Content	
of mechanical admixtures in air, mg/m ³ , not more	0.007
of ammonia in ammonia-air mixture, volum. %	10
Pressure (absolute) of air at outlet, atm.	
from compressor	3.53
from supercharger	7.3
Air temperature at outlet, °C	
from compressor	to 130
from supercharger	125-135
from air cooler	42
from heater	to 270
Temperature, °C	
of ammonia-air mixture	220
of contact	890-900
Temperature of nitrous gases, °C	
at outlet from boiler-recovery unit	230
the same of oxidizer	to 310
the same from absorption column	40
Pressure (absolute) atm.	
of steam at outlet from boiler-recovery unit	13
of gases at inlet to gas turbine	to 5.7
Concentration of production acid, %	56-58
Content in exhaust gases, volum. %	
of nitric oxides	0.005-0.03
of oxygen	to 3

Approximate consumption coefficients per 1 ^t of nitric acid:

Ammonia (100% NH ₃), kg	290
Platinoid catalyst, g	0.159
Palladized catalyst, g	0.05
Water for cooling, m ³	
average annual consumption	151
in summer	170
Natural gas for catalytic purification, m ³	135

The waste that is obtained is 1-2 T of steam (13 atm.) per 1 T of acid.

Basic Equipment

Apparatus for air purification. The apparatus of similar design is depicted in fig. I-41. The diameter of the upper part (water washer is 4 m, the diameter of the sleeve filter is 9.1 m. Three heating elements are installed to dry the cloth sleeves when they are moistened on the air intake apparatus.

Air heater is a shell-and-tube heat exchanger with U-shaped pipes 25 mm in diameter. The total heat-exchange surface of the heater is 617 m^2 . The air passes on pipes.

Combined apparatus, mixer and porolite filter are united in design in a common housing. Ammonia passes on the mixer pipes. At the outlet from the pipes, it is mixed with air that is fed into the interpipe space and emerges through the holes in the pipe lattice. The forming ammonia-air mixture enters the porolite filter that is located in the upper part of the apparatus. The total height of the combined apparatus is 6.46 m.

Contact apparatus. The diameter of the cylindrical part of the apparatus is 2.2 m. Twelve platinoid grids 1600 mm in diameter are clamped in a special holder that is placed on the lattice which rests on metal beams. A layer of ceramic rings serving to stabilize the heat regime on the catalyst grids and for partial trapping of platinoid dust is placed in regular rows under them on the grid bar lattice. The grid bar lattice rests on the arches made of refractory brick.

The ammonia-air mixture enters the apparatus from the side, passes on the guide walls to the upper part of the apparatus, and from here enters for contact.

The oxidizer is a cylindrical apparatus 2.8 or 3.2 m in diameter and about 10 m high. In the upper part of the oxidizer there

is a filter for trapping the platinoid dust from the hot nitrous gases. The surface of the filter is about 9 m^2 . The housing of the oxidizer is covered with insulation on the outside to reduce the losses of heat into the environment.

Submersible cooler-condenser consists of four coolers, each of which has 14 rows of coils. The heat-exchange surface of one cooler is 237 m^2 . The design of the cooler-condenser is similar to that depicted in fig. I-37. ^(p. 65) The possibility of using a shell-and-tube heat exchanger is also provided instead of it.

The absorption column, 45.3 m high and 3.2 m in diameter is separated into two parts. The lower part which has 3 sieve plates serves as the preliminary oxidizing vessel. The upper part which consists of 47 plates is designed for simultaneous oxidation and absorption of the nitric oxides. A small quantity of acid for creation of a foam regime of absorption on the plates is fed to the upper plate of the oxidizing part of the column from its absorption part. Cooled vapor condensate is supplied to sprinkle the column.

Water coils with cooling surface of about 700 m^2 are arranged on the plates. A large part of the finished acid is removed from the column from the fourth plate, and a smaller part from the cube. The temperature of the nitrous gases at the column inlet is 79°C , and 40°C at the outlet. The specific absorption volume of the column is roughly $1 \text{ m}^3 / (\frac{1}{2} \times \text{day})$ of 100% HNO_3 .

The reactor of catalytic gas purification operates under pressure of 6 atm. The height of the apparatus is about 7 m, the diameter is 3.8 m. The tablets of palladized catalyst are placed on the floors.

The gas-turbine aggregate GTT-3 consists of an axial compressor, centrifugal supercharger, gas turbine, intermediate air-cooler, reducer and combustion chamber. The aggregate includes an engine-generator type ATMF with output of 850 kW that is connected through the reducer to the gas turbine and is designed to start up the turbine and feed surplus power into the circuit.

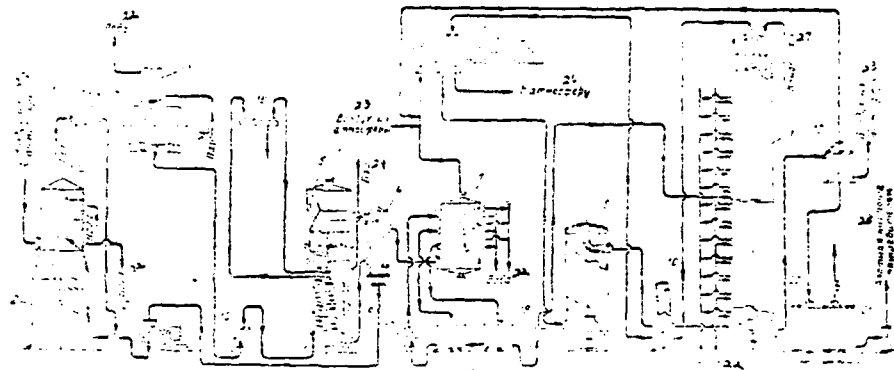


Figure 1-40. Plan for Unit to Produce Diluted Nitric Acid by Combined Method under Absolute Pressure of 3.5 Atm. in Absorption Part of System

- | | |
|--|-----------------------------------|
| 1. Cloth filter for ammonia purification | 14. Dearator tank |
| 2. Apparatus for air purification | 15, 17, 19, 21. Centrifugal pumps |
| 3. Ammonia-air ventilator | 16. Separator |
| 4. Ammonia-air mixture heater | 18. Tanks for acid condensate |
| 5. Contact apparatus with cardboard filter | 20. Storage of nitric acid |
| 6. Boiler-recovery unit | 22. Water |
| 7. Gas cooler-washer | 23. Air from atmosphere |
| 8. Turbocompressor for nitrous gases with regeneration turbine | 24. Steam |
| 9. Oxidizer | 25. Gas |
| 10. Exhaust gas heater | 26. To atmosphere |
| 11. Absorption column | 27. Condensate |
| 12. Blow-through column | 28. Nitric acid to consumers |
| 13. Deaeration column | |

The gas turbine and compressor are mounted in one housing and are seated on a common shaft. The rotor rotation is 5100 rpm. The compressor has 16 stages of compression and the gas turbine has 7 stages of expansion. The one-cylinder separator supercharger has 2 stages of compression. The combustion chamber operates only when the unit has been started up.

When the technological load is completely disconnected, the gas turbine can be put on an energy operating regime.

Combined System with Pressure of 3.5 Atmospheres in the Absorption Part

The systems that operate by the combined method (fig. I-40)* under pressure of 3.5 atm. at the stage of nitric oxide absorption, are built on the aggregate principle. Ammonia is oxidized at atmospheric pressure in contact apparatus which is combined with a cardboard filter and boiler-recovery unit. The nitric oxides are absorbed in the column with sieve-plates that operate on a highly productive foam regime. The reaction heat is removed by water, and in individual cases, by cooling liquor that circulates in the coils laid in the form of packets on a certain part of the plates. The specific absorption volume of this column is 2.3-2.5 m³/(2 x day) of 100% HNO₃. Nitrous gases are compressed in the compressors which are equipped with a recuperation turbine. The nitric acid content in the exhaust gases is 0.11-0.16% in the winter and somewhat higher in the summer.

The system is characterized by roughly 40% lower capital investments for construction (on the whole for installation) as compared to the system that operates at atmospheric pressure, the use of columns with sieve-plates, comparatively low consumption of ammonia and platinoid catalyst, improved apparatus, in particular, for purification of the air and ammonia of admixtures, use of ammonia oxidation heat to produce superheated steam (pressure to 40 atm.,

*

For the flowsheet of automatic regulation of the system see p.

temperature to 450°C), and the use of the heat of oxidation of NO into NO₂.

Shortcomings of the system are: increased specific consumption of electricity; need to compress the nitrous gases into expensive turbocompressor; high capital outlays for construction of sections to convert ammonia; difficulties in creating apparatus of high productivity and aggregates with output over 50,000 ~~z~~ per year.

Below are the main indicators for the production regime:

Content	
of mechanical admixtures in air, mg/m ³ , no more	0.007
of ammonia in ammonia-air mixture, vol.%	10.5-11.5
Pressure of ammonia-air mixture after ventilator, mm wat. col.	400-650
Temperature, °C	
of ammonia-air mixture	65-75
of contact	800-820
Rarefaction on catalyzer grids of contact apparatus, mm wat. col.	to 10
Temperature of nitrous gases, °C	
at inlet to boiler-recovery unit	~800
at outlet from boiler-recovery unit	160-180
Pressure (absolute) of superheated steam obtained in boiler-recovery unit, atm.	to 40
Temperature of steam emerging from boiler-recovery unit, °C	to 450
Temperature of nitrous gases at outlet, °C	
from warmed ammonia-air mixture	100-110
from gas cooler-washers	35-40
Temperature of acid at outlet from gas cooler-washers	40-45
Concentration of acid at outlet from gas cooler-washers, %	10-20
Temperature of nitrous gases at outlet, °C	
from turbocompressor	120-130
from oxidizer	200-220
from heaters of exhaust gases	90-100
Rarefaction of nitrous gases at outlet to turbocompressor, mm Hg	550-650
Pressure (absolute) of nitrous gases at outlet from turbocompressor, atm.	3.6-3.8
Temperature of exhaust gases at inlet, °C	
to preheater	35
to recuperation turbine	170-180
Pressure (absolute) of exhaust gases, atm.	
at outlet from absorption column	3.0-3.2
at inlet to recuperation turbine	2.9-3.1
Concentration of production acid, %	47-49
Content in exhaust gases, vol.%	
of nitric oxides	0.11-0.16
of oxygen	to 3

Consumption

Consumption coefficients per 1 T of nitric acid:

Ammonia (100% NH ₃), kg	287-290
Platinoid catalyst (irreversible losses), g	0.045-0.049
Chemically purified water and condensate of steam, m ³	2.1
Water for cooling, m ³	180-200
Electricity for production needs, kW x h	230-260

Basic Equipment

Apparatus for purification of air from mechanical admixtures (fig. I-41). The housing is made of aluminum. Within the apparatus there are three sieve plates of the distillation type (discharge section of the sieve plate is 0.9 m²) and sleeve cloth filter. The quantity of air that passes through the apparatus is 17,000 m³/h. The consumption of water for washing air is 80 m³/h. The air velocity in the washing section of the apparatus is 0.7 m/s. The filtering material in the sleeve filter is coarse wool broadcloth. The surface of the filtering material is 220 m². In order to slow down the water droplets that are carried away by the air, a layer of ceramic rings 25 x 25 x 4 mm in size is laid in the apparatus.

Mixer of ammonia and air (fig. I-42) is made of aluminum. It is 1480 mm long with diameter of 820 mm. Within the mixer there is a vortex generator and 121 aluminum pipes 22 x 2 mm in diameter.

Ammonia-air ventilator (fig. I-43) with output of 27,500 m³/h is designed to feed an ammonia-air mixture into the system with assigned ammonia concentration.

Cloth filter for cleaning the ammonia is shown in fig. I-25.

The ammonia-air mixture heater is made of stainless steel. It is a vertical shell-and-tube apparatus 1120 mm in diameter and 5150 mm high. The diameter of the tubes is 32 x 2.5 mm. The heat transmission surface is 140 m². The mixture of air and ammonia passes on tubes while the nitrous gases pass in the intertube space.

Combined contact apparatus (fig. I-44) consists of a cardboard filter and the contact apparatus proper. It is located directly

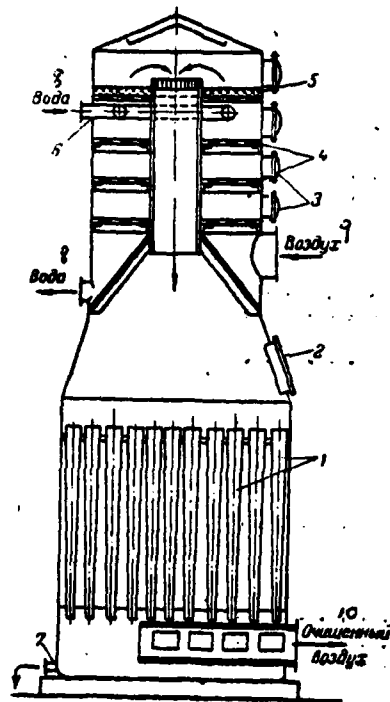


Figure I-41. Apparatus for Purifying Air of Mechanical Admixtures

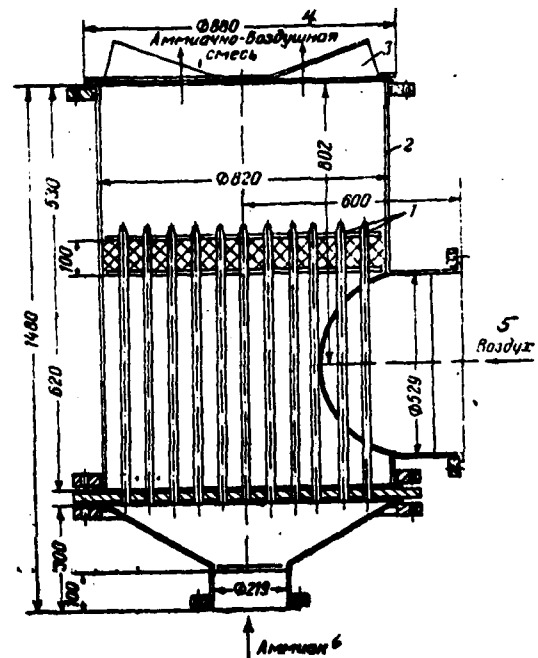
Key:

1. Cloth sleeves
2. Main manhole
3. Manholes
4. Sieve-plates
5. Entrainment layer of rings
6. Spraying device
7. Drainage connection pipe
8. Water
9. Air
10. Purified air

Figure I-42. Mixer of Air and Ammonia

Key:

1. Aluminum pipes
2. Housing
3. Vortex generator
4. Ammonia-air mixture
5. Air
6. Ammonia



on the direct-flow steam boiler-recovery unit.

The cardboard filter is installed on the upper cone of the contact apparatus and consists of five filtering blocks. Each block is assembled from 56 cardboard discs (FMP-1 or VMK brand cardboard 0.9-1.25 mm thick) with rigid metal framework. The filtering blocks

are in an aluminum housing 3020 mm in diameter and 1528 mm high. The surface of one block is 24 m^2 . Passing through the blocks, the ammonia-air mixture enters at a temperature to 70°C through the inner cylinder to the upper cone of the contact apparatus.

The contact apparatus proper consists of two truncated cones and a cylindrical part. At the site of transition of the upper cone into the cylindrical part, there is a lattice that creates a uniform stream of gas mixture to the catalyst. Three platinoid grids are attached on rings between the cylindrical part and the lower cone of the apparatus. The lower cone which is lined with refractory brick is equipped with a lattice on which there is a layer (250 mm high) of rings made of stainless steel $32 \times 32 \times 1$ mm in diameter. There are hermetically sealed holes for firing the contact apparatus, observing the condition of the grids and measuring the temperature in the apparatus.

Direct-flow boiler-recovery unit (fig. I-45), 5750 mm high has a heat transmission surface of 366 m^2 . The output of the boiler of steam with pressure 40 atmospheres is up to 2.8 T/h.

The gas cooler-washer (fig. I-46) consists of three sieve-plates that are contained in a housing 2800 mm in diameter and 5470 mm high. There are cooling coils (tubes 38 mm in diameter) with total surface of 110 m^2 on the plates for removal of the reaction heat.

Absorption column (fig. I-47) 3000-3200 mm in diameter and 46.8 m high has 40 sieve-plates with holes 2 mm, and 9 mm spacing between them. The total weight of the column is 58 T. The plates are arranged at a distance of 1200 and 1000 mm from each other along the height of the column. The permissible velocity of nitrous gases in the free section of the column is 0.3-0.4 m/s. In order to drain the liquid from plate to plate, each of them has two overflow pipes 57 mm in diameter. Their ends are lowered into the receiving vessel (recess) of the lower plate. The liquid passes from the vessel on the plate to the overflow pipe that is located on the

opposite side from the liquid entrance.

In order to remove the heat of reactions that occur in the column, cooling coils are placed on the plates. They are made of pipes 38 x 2.15 mm in diameter with total surface of 500 m². The cooling coils are distributed according to the height of the column in the following order:

No. of plate (counting from below)	1-3	4-8	9-11	12-21	22-25	26-27	28-29	30-4
	4	3	2	2	1	—	2	—
Number of coil rows	42	31.5	21	11	55	—	11	—
Cooling surface, m ²								

The oxidizer (fig. I-48) is a stout cylindrical apparatus made of stainless steel with volume about 50 m³. It is designed to oxidize NO into NO₂ with the oxygen of the nitrous gases.

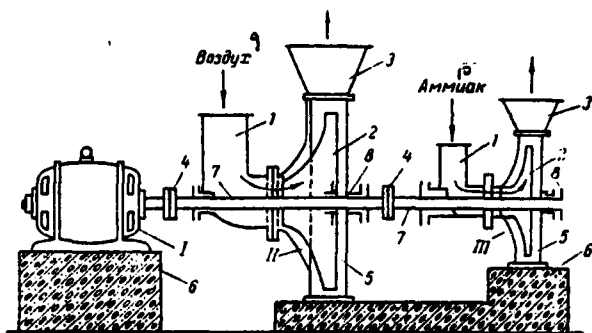


Figure I-43. Ammonia-Air Ventilator (Combined)

Key:

- I. Electric engine
- II. Air ventilator
- III. Ammonia ventilator
- 1. Absorption connection pipes
- 2. Rotors
- 3. Supercharger connection pipes
- 4. Connections
- 5. Ventilator housing
- 6. Foundations
- 7. Shaft
- 8. Bearings
- 9. Air
- 10. Ammonia

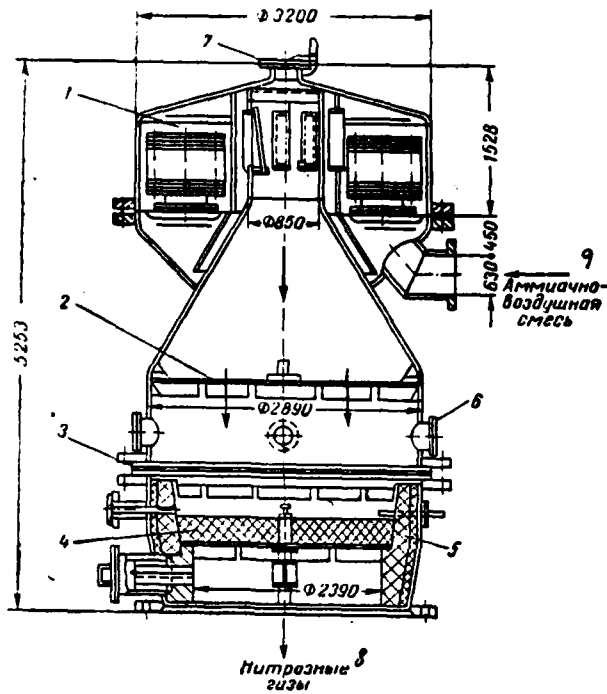


Figure I-44. Combined Contact Apparatus for Ammonia Oxidation

Key:

1. Blocks of cardboard filter
2. Distributor lattice
3. Platinoid catalyst
4. Metal Raschig rings
5. Lining
6. Viewing window
7. Safety valves
8. Nitrous gases
9. Ammonia-air mixture

Exhaust gas heater (fig. I-49) is also made of stainless steel.

The blow-through column (fig. I-50) of the bubbling type with 3-4 bubble-cap plates used to blow off the nitric oxides dissolved in the nitric acid often has a diameter of 800 and 1500 mm and height of 2445 and 2750 mm.

The characteristics of the compressor (supercharger) are given on p. 334*

*This pertains to the Russian page number.

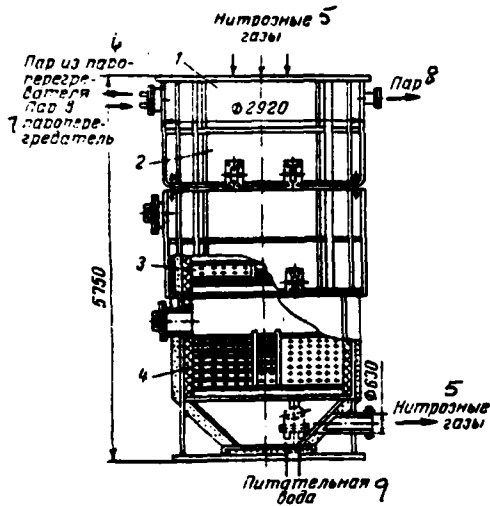


Figure I-45. Direct-flow Boiler-Recovery Unit

Key:

1. Block of steam-heater
2. Boiler block
3. Block of economizer II
4. Block of economizer I
5. Nitrous gases
6. Steam from steam-heater
7. Steam to steam-heater
8. Steam
9. Feed water

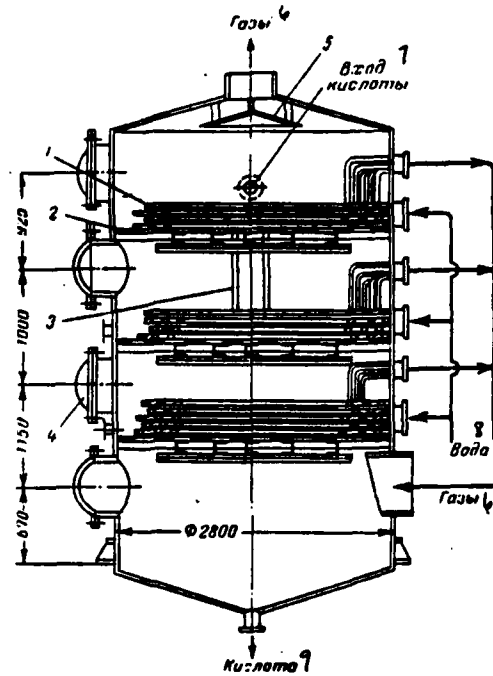


Figure I-46. Gas Cooler-Washer

Key:

1. Cooling block of coils
2. Sieve-plate
3. Overflow pipes
4. Manhole
5. Splash-catching deflectors
6. Gases
7. Acid input
8. Water
9. Acid

The specific loads on the main apparatus are:

Apparatus	Loads
Filtering, $m^3/(m^2 \times h)$ surfaces	
apparatus for cleaning air of mechanical admixtures (cloth filter)	60-80
filter for ammonia purification	60-80
filter (cardboard) for purifying ammonia-air mixture of mechanical admixtures	60-90
Contact apparatus (intensity of platinoïd catalyst, $kg/(m^2 \times day)$)	550-650
Heat exchange $m^2/(T \times day)$	
ammonia-air mixture heater	1.0-1.15
steam boiler-recovery unit	6.0-7.0
gas cooler-washer	1.6-1.8
exhaust gas heater	2.8-3.2
cooling coils of absorption column	3.6-4.0

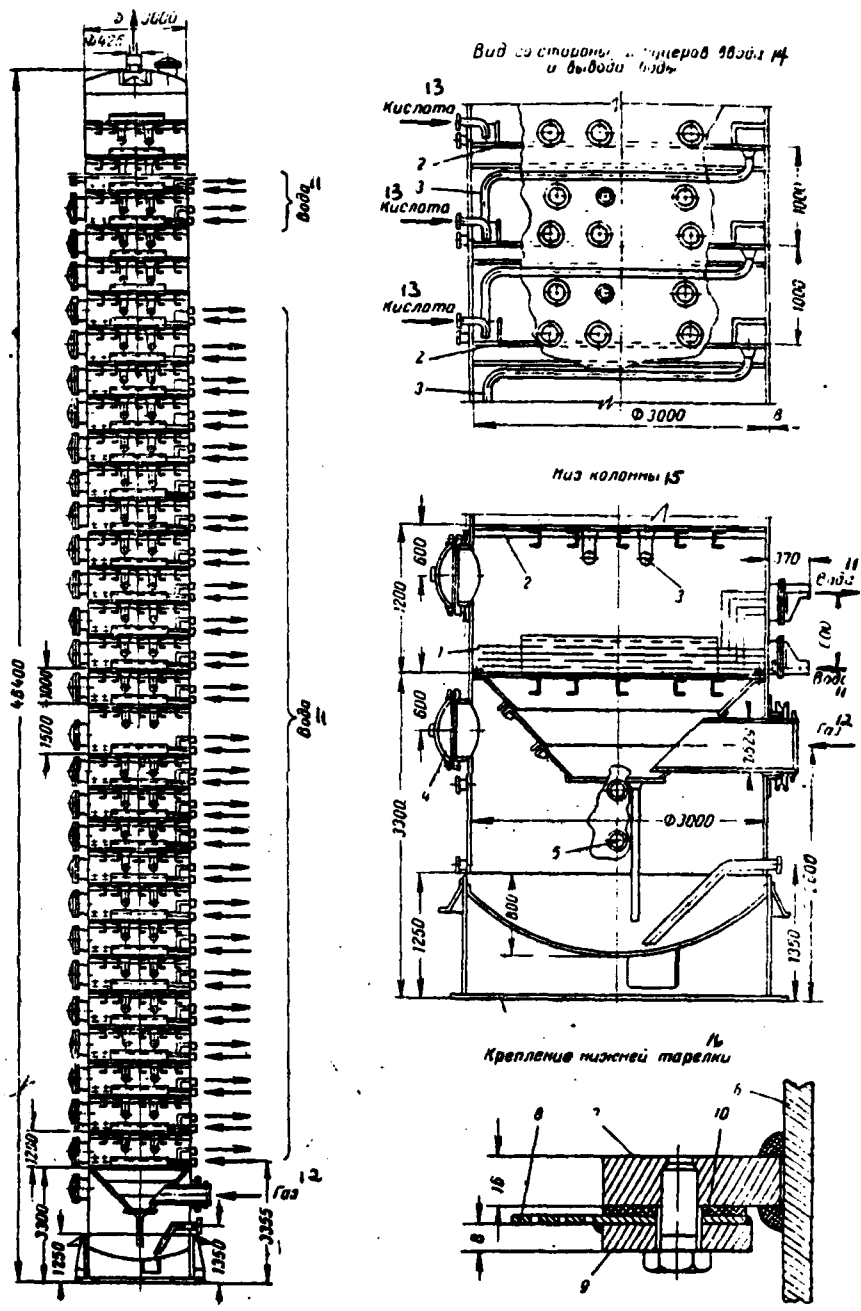


Figure I-47. Absorption Column with Sieve Plates

Key:

- | | |
|---------------------------------|--|
| 1. Cooling coil | 7. Bands |
| 2. Sieve-plate | 8. Sieve-plate |
| 3. Overflow pipes (connections) | 9. Bands |
| 4. Manhole | 10. Gasket made of polytetrafluoroethylene |
| 5. Viewing glass | |
| 6. Wall of column housing | |

[continued on next page]

[continuation of key]

- | | |
|-----------|--|
| 11. Water | 14. View from side of connecting pipes for input and output of water |
| 12. Gas | 15. Bottom of column |
| 13. Acid | 16. Attachment of lower plate |

Figure I-48. Oxidizer

Key:
1. Nitrous gases

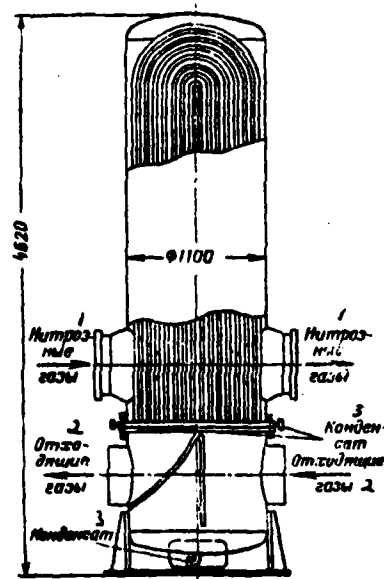
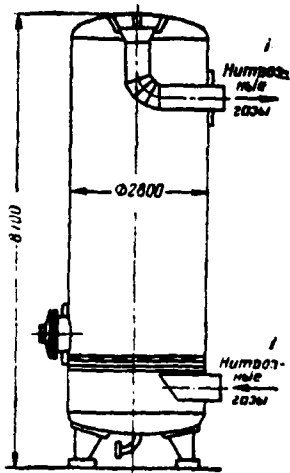


Figure I-49. Exhaust Gas Heater

Key:
1. Nitrous gases
2. Exhaust gases
3. Condensate

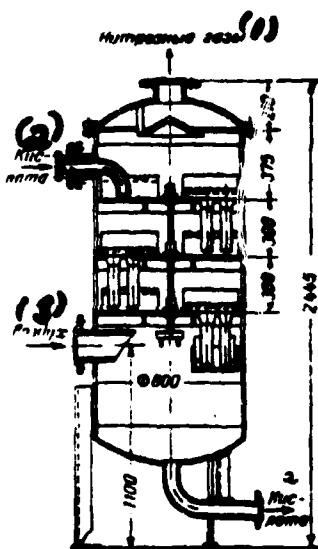


Figure I-50. Blow-through Column for Whitening Nitric Acid from Dissolved Nitric Oxides

Key:
1. Nitrous gases
2. Acid
3. Air

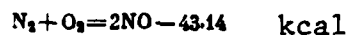
Preliminary standards of product output (in fractions of a unit):

Output for ammonia when it is converted into nitric oxide	0.97-0.975
Output for nitric oxides when processed into nitric acid	0.985
Total output for production without regard for mechanical losses (random leaks of gas, acid, etc.), no less	0.95
The same with regard for mechanical losses, no less	0.94

New Methods of Producing Diluted Nitric Acid

We have searched for many years for direct methods of producing nitric oxide, by fixation of nitrogen and oxygen of atmospheric air. These attempts were halted because it was impossible at that time to solve the problem of producing NO of sufficient concentration.

It has been established by calculations and experiments that in order to obtain acceptable concentrations of nitric oxide according to the reactions



it is necessary to maintain temperature above 2400°K in the reaction zone.

Equilibrium concentrations of NO when this reaction occurs correspond to the following values:

Temperature, °K	2000	2200	2400	2580	2700	3000	3200
Concentration of NO, vol. %	0.59	0.98	1.5	2.05	2.31	3.57	4.39

It was also established that in order to prevent a decrease in NO (as a consequence of its breakdown) to equilibrium corresponding to a lower temperature, instant cooling of the gas mixture removed from the reaction zone is required.

Fixation of atmospheric nitrogen at high temperatures in the flame of the electric arc did not yield positive results, since, in particular, rapid cooling of the gas mixture and production of an NO concentration over 1.2 volum. % were not successful. This low NO concentration created a complication in processing the gas mixture

into nitric acid and determined the inefficiency of the process as a whole. For 1 T of nitric acid that was obtained by the methods of electric synthesis (according to different versions), 12,000-16,000 kW x h of electricity was consumed, while, with indirect methods of nitrogen fixation (through ammonia), even with insufficiently complete plans, only about 1500 kW x h was required.

Based on the achievements of modern science and technology, extensive research has been renewed in recent years in the area of direct fixation of the atmospheric nitrogen. Thermal, plasma and radiation methods are currently being developed especially intensively.

The thermal method is based on a combination of thermal fixation of atmospheric nitrogen with processes of producing steam and electricity on high output power plants. The high temperatures which are needed to form nitric oxide from nitrogen of the atmospheric air are obtained by burning gaseous fuel in a high-pressure generator. The nitric oxide in this method is seemingly a by-product.

The plasma method⁶⁹ is based on complete or partial transition of air into the ionized state in which it contains not only neutral molecules and atoms, but also ions and electrons.^{70,71}

The gas-discharge plasma is created, for example, in an electrode plasmotron. Synthesis of nitric oxide from atmospheric air in the plasma stream occurs in negligible fractions of a second. During the development of the plasma method for production of nitric oxide, new procedures were sought for cooling ("hardening") of the gas mixture in which the high content (roughly 6-7%) of the nitric oxide in the gas mixture could be completely preserved.

The radiation method is based on bonding of nitrogen and oxygen of atmospheric air by the effect of ionizing radiation of uranium-235 on them.

Certain direct methods for production of nitric oxide for the manufacture of nitric acid stipulate verification on large experimental units. The latter also include apparatus to study the processes of enrichment of the obtained nitric oxide and its processing into nitric acid.

At the same time, development and introduction of new systems for producing diluted nitric acid based on synthetic ammonia are intensively continuing. Both in the USSR and abroad, a trend has been noted towards the use of aggregates of high output (700-1200 T/day of 100% HNO_3).

On high-output aggregates that are made on the basis of the current achievements of equipment and machine building, one can reduce the specific outlays of ammonia and platinoid catalyst, operate without supplying electricity from outside, comprehensively automate all processes and guarantee the sanitary standard for the content of nitric oxides in the exhaust gases. These and certain other advantages of the high output aggregates (for example, production of nitric acid of increased concentration, no less than 60%, production of water vapor, about 1.5 ^{t/t} ~~FA~~ HNO_3 , etc.) make it possible to reduce by roughly 30% the specific capital investments for the production of diluted nitric acid and decrease by 15% the net cost of the product as compared to the active units operating under increased pressure.

The foreign systems for producing nitric acid from synthetic ammonia in high output aggregates are based on different fundamentals of the production processes. Certain systems operate under pressure in the entire production line (loop), others, the combined, operate at different increased pressure at the stages of conversion and absorption. In the second case, the process occurs according to the following plan.

1. Oxidation of ammonia into nitric oxide is done at a moderate moderate pressure (for example, 3.5-4 atm.), while absorption of nitric oxides is done at a relatively high pressure (for example, 10 atm. and higher).

2. The process of acid formation is done in two successively operating absorption columns. In the first (on the gas course) column, the main quantity of nitric oxides is absorbed, and in the second, their remaining quantity. In this case, nitric acid of low concentration (1-3% HNO_3) is formed in the second column. It is transferred by pump to sprinkle the first column.

3. The heat which is released during ammonia oxidation, and the heat from oxidizing NO into NO_2 is used to produce electricity that is necessary to compress air and nitrous gases to the pressures indicated above.

Figure I-51 presents one of the foreign plans for producing nitric acid with concentration of 65-69% in a unit with output of 1000 t /day, counting on 100% HNO_3 .

This plan guarantees the following basic consumption coefficients for 1 t of nitric acid:

Ammonia, kg	280-282
Platinoid catalyst, g	0.09-0.10
Water for cooling, m^3	
$t < 20^\circ\text{C}$	130
$t > 20^\circ\text{C}$	200
Electricity, kw x h	8

Of the other peculiarities of the plan, we note the following: the output of the contact apparatus is 350 t /day (counting on 100% HNO_3); the content in the exhaust gases (before their dilution with air) to 0.05 vol.% of nitric oxides; all the machines are installed on one shaft; the planned repair of machines is done every 18-24 months (coefficient of use of the equipment is about 97%); operation and repair of the unit requires few service personnel.

Foreign practice is making more extensive use of systems that produce 65-70% nitric acid. The absorption columns of these systems are equipped with plates of special design. Thus, one foreign firm⁶³ has developed and is widely introducing into industry the method of

producing 69-70% nitric acid in a system that operates under pressure of 4 atm. at the stage of nitric oxide absorption. The design of the plates of the absorption column of this system is known under the common name of "fat absorber."

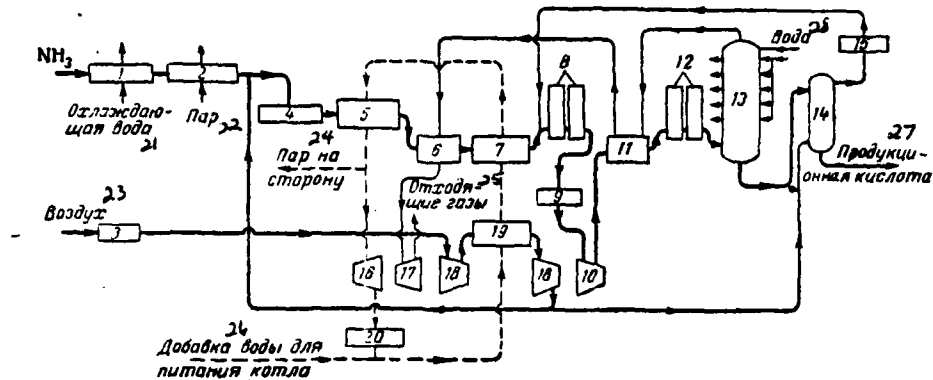


Figure I-51. Plan for Unit to Produce Diluted Nitric Acid by Combined Method under Increased Pressure

Key:

1. Evaporator
2. Ammonia heater
3. Filter to purify air
4. Contact apparatus
5. Boiler-recovery unit
6. Secondary heater of exhaust gases
7. Heat exchanger
8. Oxidation towers
9. Cooler
10. Compressor of nitrous gases
11. Primary heater of nitrous gases
12. Oxidizing towers
13. Absorption column
14. Blow-through column
15. Cooler
16. Steam turbine
17. Recuperation turbine
18. Air compressor
19. Heat exchanger
20. Condenser
21. Cooled water
22. Steam
23. Air
24. Steam to side
25. Exhaust gases
26. Addition of water to feed boiler
27. Production acid
28. Water

According to the patent description and the published data, the column consists of 16 plates with continuous bottom. Each plate is separated above with partitions into sectors which are designed to oxidize NO into NO₂ and into adjacent sectors in which the nitrogen peroxide is absorbed. Notches are made in the partitions of the sectors for passage of liquid and nitrous gases. The acid solutions circulate only in the absorption sectors. In the isolated sectors of NO oxidation, the nitric acid concentration corresponds to the condition of equilibrium with the gas mixture, or close to it. Towards the top of the column, as the nitric oxides in the gas mixture diminish, the oxidizing sectors of the plates significantly increase. The plates have cooling devices (for example, of the plate-type) through which the cooling liquor or cooled water circulates. With this design of the plates, the most favorable conditions are created for NO oxidation in the liquid phase. Almost completely oxidized NO, i.e., essentially only nitrogen peroxide, enters the adjacent sectors of the plates for absorption.

In standard absorption columns, even with sieve-plates, the process of NO oxidation into NO₂ occurs to a considerable measure in the gas phase and is uncontrollable. The column with "fat absorber" that operates under pressure of about 4 atm. in the output of 69-70% acid has productivity of 200 T/day (counting on 100% HNO₃). The gases escaping from the column contain 0.05 vol.% of NO + NO₂ and are diluted with an air stream before they are discharged into the atmosphere.

Automation of Production of Diluted Nitric Acid

Figure I-52 presents the flowsheet for automating the production of diluted nitric acid under pressure of 3.5 atm. The main element in the plan is regulation of the ratio of the quantity of air and ammonia entering the contact apparatus.

The regulator of the P₁ ratio acts on the actuating mechanism on the ammonia line according to loading the unit for air (basic air). The pressure in the contact apparatus is regulated by changing

the supply of the ammonia-air mixture by regulator P_2 depending on the operating regime of the ventilator and the degree of blockage of the cardboard filters.

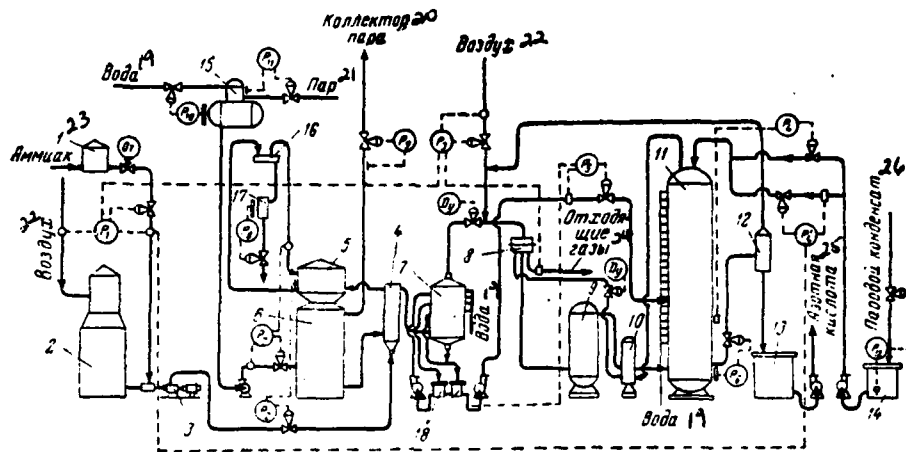


Figure I-52. Flowsheet of Automatic Regulation of Process of Obtaining Diluted Nitric Acid by Combined Method with Absolute Pressure 3.5 atm. in Absorption Part of System

Key:

1. Cloth filter for purification of ammonia
2. Apparatus for purification of air
3. Ammonia-air ventilator
4. Heater of ammonia-air mixture
5. Contact apparatus
6. Boiler-recovery unit
7. Gas cooler-washer
8. Turbocompressor of nitrous gases
9. Oxidizer
10. Heater of exhaust gases
11. Absorption column
12. Blow-through column
13. Nitric acid storage
14. Steam condensate tank
15. Deaerator
16. Separator
17. Receptacle
18. Nitric acid condensate tank
19. Water
20. Steam collector
21. Steam
22. Air
23. Ammonia
24. Exhaust gases
25. Nitric acid
26. Steam condensate

Regulators:

- P₁. of ratio of quantity of air and ammonia
- P₂. of pressure on grids of contact apparatus
- P₃. of oxygen content in exhaust gases
- P₄. of concentration of production acid
- P₅. of supply of nitric acid condensate for sprinkling absorption acid
- P₆, P₈, P₁₀, P₁₂. of level
- P₇. of ratio of quantity of steam and water
- P₉. of steam pressure
- P₁₁. of pressure in deaerator column
- D₁. remote control
- O₁. cutter

The normal operation of the boiler-recovery unit is guaranteed by the regulator of ratio P₇ which measures the supply of feed water depending on the quantity of generated steam. The constant level in the receptacle of the separation device of the boiler is regulated by changing the discharge of water from the receptacle (regulator P₈). Safe operating regime of the boiler-recovery unit is attained by installing regulating valves with remote manual control on by-pass lines for feeding supply water into the boiler and discharging condensate. The pressure of the overheated steam (40 kg-f/cm²) in the collector after the boiler-recovery unit is maintained constant with the help of pressure regulator P₉.

The operating regime of the deaeration unit in order to prepare the nutrient water for the boiler-recovery units is regulated by stabilizing the pressure in the deaeration column (regulator P₁₁) and water level in the deaeration tank (regulator P₁₀).

For more complete oxidation of the nitrous gases obtained in the contact apparatus, regulation is provided for the ratio of the quantity of basic and additional air that is sucked up by the turbo-compressor, with correction for the oxygen content in the exhaust gases by influencing the regulating baffle P₃ which is installed on the additional air pipeline. Certain plants only use remote control by a slide valve on the line to feed additional air.

The assembly for regulating the concentration of production acid consists of two parallel operating regulators. The first, main regulator P₄ controls the supply of steam condensate into the

absorption column depending on the ammonia load on the system. The second regulator corrects the quantity of supplied steam condensate according to the concentration of obtained nitric acid (regulator P₄). The regulating valves of both regulators are installed in parallel on the supply line for steam condensate into the absorption column.

The quantity of condensate of nitric acid that enters the absorption column is regulated with correction for the level of acid condensate in the tank (regulator P₅). A constant level of acid in the absorption column is maintained by the level regulator P₆ which changes the supply of acid from the column. The level of steam condensate in the tank is regulated by changing the supply of steam condensate to the tank (regulator P₁₂).

For start-up operations, except for the baffles on the lines for supply of additional air and ammonia-air mixture, a baffle is used at the entrance of nitrous gases into the turbocompressor. If a pre-emergency regime develops, protective blocking and emergency-production signalling are provided for.

2. Production of Concentrated Nitric Acid

Direct Synthesis of Nitric Acid

The process of producing concentrated nitric acid from liquid nitric oxides, oxygen and water occurs with the formation of unstable intermediate compounds. The total reaction of direct synthesis of concentrated nitric acid is depicted by the following equation:



There are known industrial methods for producing concentrated nitric acid which are mainly distinguished by the technology for producing liquid nitric oxides. The process of interaction of the liquid nitric oxides, the oxygen and water (in practice, diluted nitric acid is used instead of water), and subsequent processing of the obtained solutions into the finished product are the same in all methods of producing concentrated nitric acid.

Liquid nitric oxides are obtained from nitrous gases that are formed during the oxidation of ammonia by air oxygen and during inversion of nitrites into nitrates (this method has limited application).

The process of producing concentrated nitric acid proper consists of the following main stages:

preparation of a mixture of liquid nitric oxides with diluted nitric acid in assigned ratios $N_2O_4:H_2O$ (so-called raw mixture);

interaction of raw mixture with oxygen in autoclaves at pressure of 50 atm. and temperature of 70-85°C (production of autoclave acid);

separation of nitric oxides from concentrated solutions of nitric acid (production of finished product and liquid nitric oxides which can be returned to the production cycle).

The literature cites fairly detailed data on the absorption of nitric oxides of concentrated nitric acid^{12, 72, 73}, condensation of nitric oxides from nitrous gases^{3, 12, 74, 75}, on conditions for the formation^{3, 12, 76-80} and technology for producing concentrated nitric acid^{3, 12}, physical properties of diluted and concentrated nitric acid which contains dissolved nitric oxides³¹⁻⁸⁴, as well as methods for computing certain stages in the process of direct synthesis of concentrated nitric acid.⁸⁵

Below is the basic information on the production of liquid nitric oxides and their processing into concentrated nitric acid.

Production of Liquid Nitric Oxides

There are two popular methods in industry for obtaining nitric oxide: by absorption of NO_2 from nitrous gases by concentrated nitric acid^{72,73} with subsequent separation of the liquid nitric oxides from the obtained solution; condensation of NO_2 from nitrous

gases at increased pressure. Selection of the method for producing liquid nitric oxides is determined to a considerable measure by the system of producing diluted nitric acid.

Absorption of nitric oxides from nitrous gases by concentrated nitric acid. This method is based on the high solubility of NO_2 in concentrated nitric acid at low temperatures. For example, the solubility of nitric oxides in 97% nitric acid at -10°C and atmospheric pressure is:

NO_2 content in gases, vol. %	10	15	20	25	30
NO_2 content in solutions ($\text{HNO}_3 + \text{N}_2\text{O}_4$), weight. %	29.4	34	37.2	41	45

One can almost completely extract the nitric oxides from the nitrous gases that are obtained by any method with the help of concentrated nitric acid. Before absorption of the nitric oxides by concentrated nitric acid, the gas mixture must be prepared in the appropriate manner.

The surplus reaction water (this surplus is roughly $\frac{2}{3}$ of its total quantity in the gas mixture) is first removed from the nitrous gases by cooling. In cases where the gases are cooled at atmospheric pressure, an acid condensate is formed which contains 2-4% HNO_3 , and at higher pressure, 25-30% HNO_3 . These acid condensates are usually used in the production of diluted nitric acid. After the water is removed from the gaseous mixture, the NO is oxidized into NO_2 by oxygen, and then by 97-98% nitric acid.

In the systems which produce concentrated nitric acid and operate at atmospheric pressure, NO is oxidized by oxygen that is contained in the nitrous gases, in two oxidation towers which are installed in series. The oxidizing towers are sprinkled with 54-56% nitric acid. In this case, only a small part of the nitric oxides is absorbed. The released heat of the NO oxidation reaction is removed by the acid that is circulating between the oxidizing tower and the water cooler.

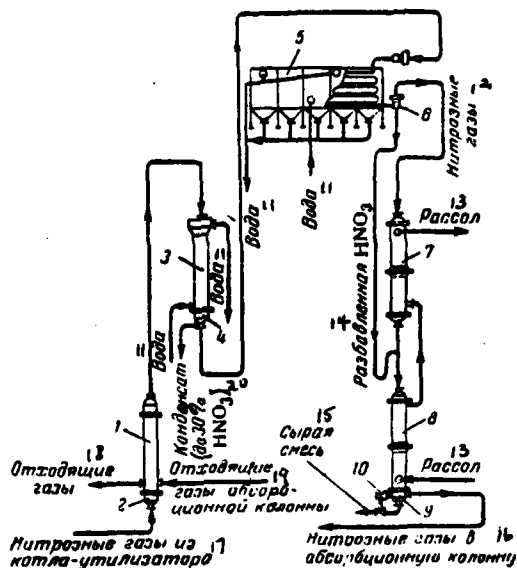


Figure I-53. Plan of Assembly for Obtaining Liquid Nitric Oxides by Condensation Method

Key:

1. Exhaust gas heater
2. Filter for trapping platinum
3. High-speed cooler
- 4, 6, 9. Separators
5. Condenser-cooler
7. Liquor condenser of the I stage
8. Liquor condenser of the II stage
10. Level regulator
11. Water
12. Nitrous gases
13. Liquor
14. Diluted HNO_3
15. Raw mixture
16. Nitrous gases to absorption column
17. Nitrous gases from boiler-recovery unit
18. Exhaust gases
19. Exhaust gases of absorption column
20. Condensate (to 30% HNO_3)

The degree of NO oxidation by air oxygen or of nitrous gases usually does not exceed 93%. Complete NO oxidation is not achieved under these conditions because of the drastic slowing down of the reaction as the concentration of nitric oxide drops. Its additional oxidation by concentrated nitric acid occurs according to the reaction $\text{NO} + 2\text{HNO}_3 = 3\text{NO}_2 + \text{H}_2\text{O} - 17.58 \text{ kcal}$. Its rate increases with a rise in temperature.

The oxidized nitric oxides are absorbed by 98% nitric acid at a temperature of about -10°C . The solution that is obtained in this case (it is sometimes called nitroleum) contains 25-35% of dissolved nitric oxides. With an increase in the NO_2 content in the solution, the rate of its absorption is noticeably reduced. The constant for the rate of NO_2 absorption by concentrated nitric acid is determined by the equation:

$$\lg k = 1.655 + 0.3 \lg V - 1.37 \lg T + 0.0149z$$

where V --linear velocity of gas (0.2-0.6 m/s);
 T --temperature (263-283°K);
 z --concentration of nitric acid (85-98%).

The obtained solutions of nitric acid that contain nitric oxides are reprocessed to remove them (whitening). This process is done at the boiling temperature of the solutions. It depends on the pressure and their content of nitric oxides. The released vapors of nitric oxides condense at a temperature of -10°C .

Release of nitric oxides from nitrous gases under pressure.

This method is based on a considerable change in the pressure of saturated vapor of nitric oxides depending on the temperature. The nitrous gases are prepared in the same way as in the release of nitric oxides under atmospheric pressure. In order to dehydrate the gas mixture, the nitrous gases are cooled in a high-speed cooler (to $55-65^{\circ}\text{C}$), and then in a cooler-condenser (to $30-40^{\circ}\text{C}$). The gas mixture (degree of NO oxidation 93-94%) is further sent to the coolers (fig. I-53) where nitric oxide condensation occurs in two stages. In the first stage (upper cooler) the cooling is often done not by liquor, but by water to 10°C , and in the second stage (lower cooler) to -15°C .

In order to avoid blockage of the lower (liquor) cooler with solid N_2O_4 , the temperature of the condensate at the exit from it is maintained at roughly -15°C . With a content in the gas mixture

of 2% water vapors, the freezing temperature of the formed liquid (raw mixture) equals -13.4°C , and with 5.5% water vapors, it is reduced to -16°C . Precipitation of solid N_2O_4 is practically excluded if there is 6-8% N_2O_3 in the nitrous gases.

The rate of reaching equilibrium with a decrease in NO_2 is comparatively high. It is mainly determined by the rate of removal of heat of the condensing gas. With optimal temperature of condensation (from -10 to -15°C), the time for stay of the gas stream in the cooler-condensers of nitric oxides generally does not exceed 5 s. If ammonia is oxidized by air oxygen, the content of nitric oxides in the nitrous gases is often 11%. At atmospheric pressure this corresponds to their partial pressure of 83.5 mm Hg. The pressure of the vapors above the liquid N_2O_4 at -10°C equals 150 mm Hg. Thus, without using increased pressure, it is practically impossible to condense the nitric oxides. At absolute pressure of 5 atm., temperature of -10°C and content in the gases of 10% NO_2 , the degree of its condensation can reach 45%.

It is comparatively rare under industrial conditions to obtain a degree of nitric oxide condensation from the diluted gases higher than 35%. This is explained by the reduced pressure of the nitrous gases in the liquor coolers; the partial freezing of the liquid nitric oxides with a shortage of N_2O_3 in the gas mixture; increased temperature of the nitrous gases after the high-speed cooler and the cooler-condenser, etc. Fairly good removal of the liquid nitric oxides during condensation of nitrous gases requires burning of the ammonia-air mixture which contains 11.5-11.7% NH_3 , maintenance in the ammonia-air mixture of the ratio $\text{O}_2:\text{NH}_3=1.65$, addition to the second stage of nitrous gas cooling of a certain quantity of diluted acid, etc. It is not always possible in production to maintain these conditions, therefore, removal of the nitric oxides generally is 25-35%.

The raw mixture formed in the liquor coolers is separated from the gases in the separator and sent to the mixer of the autoclave division. The gas mixture which contains uncondensed nitric oxides, water vapors, nitrogen, nitric acid vapors is reprocessed into

diluted nitric acid.

Below are the basic indicators for the technological regime of removing nitric oxides from nitrous gases during operation under pressure:

Ammonia content in the ammonia-air mixture, %	11.5
O ₂ :NH ₃ ratio in ammonia-air mixture	1.6-1.65
Temperature of nitrous gases at outlet from high-speed cooler, °C	55-60
HNO ₃ concentration at outlet from high-speed cooler, %	25-30
Temperature of nitrous gases at outlet from cooler-condenser, °C	30-40
Degree of oxidation of NO into NO ₂ in gases after cooler-condenser, %	93-94
HNO ₃ concentration at outlet from cooler-condenser, %	56-60
Temperature of liquor at inlet to liquor cooler-condensers, °C	20-22
Temperature of gases at outlet from liquor coolers, °C	
of first stage (upper)	10
of second stage (lower)	-15

Production of Concentrated Nitric Acid

The rate of the process of nitric acid formation is drastically slowed down as the concentration of 47-50% HNO₃ is reached on units operating at atmospheric pressure, and 55-58% HNO₃ on units operating under pressure of 6-9 atm. One can obtain nitric acid with concentration all the way to 100% only with a considerable increase in the partial pressure of NO₂ and O₂ with the use of high pressure. Concentrated nitric acid is produced in autoclaves of the periodic-action or continuous-action type that operate under pressure of 50 atm.

Synthesis of concentrated nitric acid from liquid nitric oxides uses 56-60% nitric acid that is formed in the oxidizing towers or in the cooler-condensers. The concentration of nitric acid is roughly the same in the raw mixture obtained during condensation of nitric oxides from nitrous gases.

The rate of interaction of the liquid nitric oxides with aqueous solutions of nitric acid and oxygen is considerably accelerated with a rise in temperature and an increase in the surplus nitric

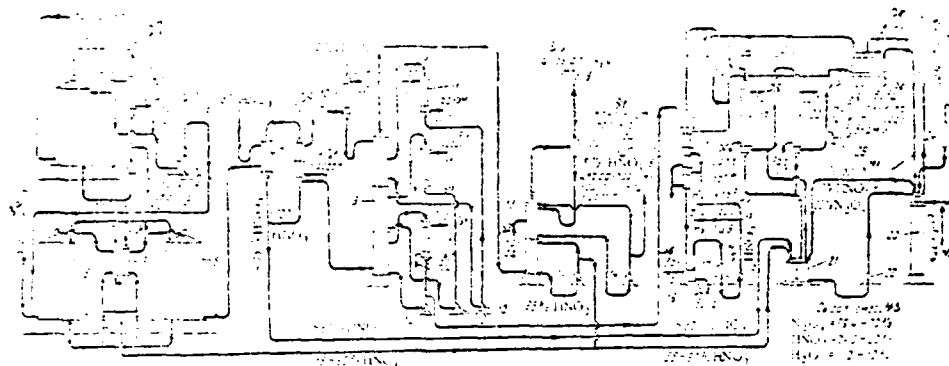


Figure 1-10. Plan for Production of Concentrated Nitric Acid by the Method of Direct Synthesis at Atmospheric Pressure

- | | |
|---|--------------------------------------|
| 1. Washing tower | 18. Reverse nitric oxide cooler |
| 2. Nitric acid coolers | 19. Nitric oxide condenser (aqueous) |
| 3. Incombinator | 20. Nitric oxide condenser (liquor) |
| 4. Nitric acid pumps | 21. Raw mixture mixer |
| 5. Oxidizing towers | 22. Furner for raw mixture |
| 6. Final oxidizer | 23. Autoclave |
| 7. Liquor gas cooler | 24. Receiver |
| 8. Absorbing tower | 25. Autoclave acid receiver |
| 9. Liquor cooler to concentrate nitric acid | 26. Hydraulic valve |
| 10. Liquor coolers for nitrooleum | 27. Nitrous gases from gas cooler |
| 11. Pumps | 28. Water |
| 12. Washing tower | 29. Nitrous gases |
| 13. Pumps for washing tower | 30. Liquor |
| 14. Whitening column | 31. HNO_3 to diluted acid shop |
| 15. Concentrated nitric acid cooler | 32. Blow-through gases |
| 16. Collector | |

[continued on next page]

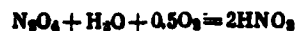
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33. To exhaust pipe
34. Water vapor condensate
35. 5% HNO₃ to diluted nitric acid shop
36. Vapor
37. To storehouse
38. To apparatus 7 and 9
39. Nitrous gases to turboblowers 3
40. Blow-through gases to apparatus 5
41. Overflow
42. Oxygen
- 43.. Raw mixture

oxides.^{79,80} The role of temperature in the process of formation of concentrated nitric acid is apparently reduced to acceleration of hydrolysis of N₂O₄ and breakdown of HNO₂ which is formed as an intermediate product in the process of producing HNO₃. However, an increase in temperature above 75-80°C is not permitted since it results in an intensification of corrosion of the aluminum reaction vessel (p141)^(R97) and removal of a large quantity of nitric oxides with the blow-through gases.

The surplus of liquid nitric oxides in the autoclave mixture mainly determines the rate of acid formation, i.e., the output of the autoclave. The larger the N₂O₄:H₂O ratio, the less time is required for reaching the assigned acid concentration.

In the raw mixture that is sent for autoclaving, the minimum ratio of components must correspond to the reaction:



$$92 + 18 + 16 = 126$$

or 730 kg N₂O₄ + 143 kg H₂O + 127 kg O₂ = 1000 kg (counting on 100% HNO₃).

The minimum weight ratio of N₂O₄:H₂O is 92:18=5.11. With this ratio, not only is the standard concentration of nitric acid not produced, but the process of acid formation is very elongated in time. A raw mixture is usually used in practice with a ratio of N₂O₄:H₂O=6.4-7. The composition of the raw mixture sometimes has to be "corrected," i.e., in order to obtain the assigned N₂O₄:H₂O ratio,

diluted nitric acid or nitrogen tetroxide are added. The presence of N_2O_3 in the raw mixture does not affect the rate of the process of acid formation, but increases the consumption of oxygen.

In autoclaves of periodic action with the indicated $N_2O_4:H_2O$ ratio, concentrated acid (98% HNO_3 and higher) is obtained in 3 h. The process of acid formation proper takes 30-60 min., and the rest of the time is spent on auxiliary operations (loading of the raw mixture into the autoclave 30 min., unloading the autoclave acid 30 min., etc.). The nitric acid obtained in the autoclaves with dissolved nitric oxides is sent for whitening.

Figure I-54 presents a plan for producing concentrated nitric acid by the method of direct synthesis at atmospheric pressure.

Below are the approximate indicators for the technological regime of direct synthesis of concentrated nitric acid from nitrous gases obtained at atmospheric pressure:

Oxidizing towers	
Acid temperature at outlet from second tower, °C	40-42
Acid concentration, %	56-60
Degree of oxidation of nitrous gases, %	92-93
Final oxidizer	
HNO_3 concentration in solution entering to sprinkle the final oxidizer, %	97-98
Acid temperature at outlet from final oxidizer, °C	25-27
Acid concentration at outlet from final oxidizer, %	70-74
Liquor gas cooler	
Gas temperature at outlet from cooler, °C	from -8 to -10
Nitric acid concentration, %	88-90
Absorption tower	
Temperature of circulating solution, °C	-10
NO_2 content in solution, %	
in upper stage	~5
in middle stage	10-15
in lower stage	25-30
Washing tower	
Solution temperature, °C	0
HNO_3 concentration, %	
in lower stage	56-60
in upper stage	~5
Content of nitric oxides after tower, %	~0.06

Autoclave

Approximate composition of raw mixture, %

N ₂ O ₄	66-70
HNO ₃	24.7-20
H ₂ O ³	9.3-10
Oxygen concentration, %	95-97
Pressure, atm.	50
Temperature of autoclave acid at outlet from autoclave, °C	70-85

Whitening column

Acid temperature, °C	
entering for whitening	45
at outlet from column	85

Nitric oxide condenser

Temperature, °C	
of gas at inlet to condenser	40
of liquid nitric oxides at outlet from condenser	from -8 to -9

The approximate consumption coefficients on units of direct synthesis of concentrated nitric acid from nitrous gases obtained at atmospheric ($P_{atm.}$) and increased (P_{136}) pressure:

	$P_{atm.}$	P_{136}
Ammonia (100% NH ₃), kg	294	297
Platinoid catalyst (irreversible losses), mg	45-55	150-170
Electricity, * kW x h	500	520
Steam, kg	1.0	0.3
Water for cooling, m ³	400	200
Oxygen**, m ³	150	140
Cold (need), thous. kcal	490	500

*With regard for the outlays for production of cold, as well as nitro-leum (at P_{136}); the consumption of electricity for production of oxygen is not taken into account.

** In the periods of start-up of the autoclave division, the consumption of oxygen at $P_{atm.}$ can reach 200 m³/T and 175 m³/T HNO₃ at P_{136}

The dependence of the concentration of obtained autoclave acid on the N₂O₄:H₂O ratio and the employed pressure is presented in fig. I-55.

Basic Equipment

High-speed gas cooler (fig. I-56) is a heat exchanger of the shell-and-tube type. The tube is made of stainless steel and the

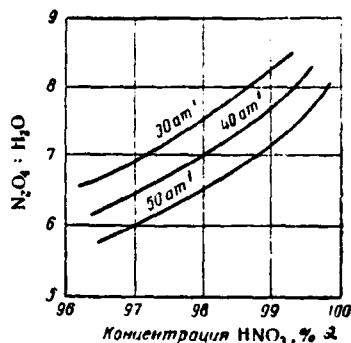


Figure I-55. Dependence of Concentration of Autoclave Acid on $N_2O_4:H_2O$ Ratio at Different Pressure (in autoclave of 11 plates, temperature 70-73°C).

Key: 1. atmospheres
2. HNO_3 concentration, %

shell is made of carbon steel. Nitrous gases flow on the pipes and cooling water flows in the interpipe space (by countercurrent to the gases). The tube consists of 1159 pipes 21 x 1.5 mm in diameter and 3060 mm long. The total surface of the tube is 200 m² and the time for stay of the gases in the pipes is 0.1-0.2 s. The specific surface of the high-speed cooler is about 5 m²/(T x day) of 100% HNO_3 .

High-speed coolers are also used with surface of the heat exchange 45 m² (fig. I-57). They have 128 pipes 25 x 2 mm in diameter and 5000 mm long.

The oxidizing towers (fig. I-58) are made of stainless steel. The towers are filled with piles of ceramic rings. The density of tower sprinkling is 8-10 m³/(m² x h). The specific volume of the tower is 11-12 m³/(T x day) HNO_3 . The specific surface of the acid coolers in the oxidizing towers is 3-4 m²/(T x day) HNO_3 .

The final oxidizer (fig. I-59) is a cylindrical tower that is made of stainless steel. The sites for input and distribution of the concentrated nitric acid are often lined with aluminum.

The final oxidizer has two-three layers of packing, piles of ceramic rings 25 x 25 and 50 x 50 mm in size. The lower layer that is sprinkled by the solution from the sprayer promotes an improvement in the contact between the acid and the nitrous gases fed from below. The upper layer of rings is designed to separate the sprays of liquid carried off by the gas stream. The specific volume of the

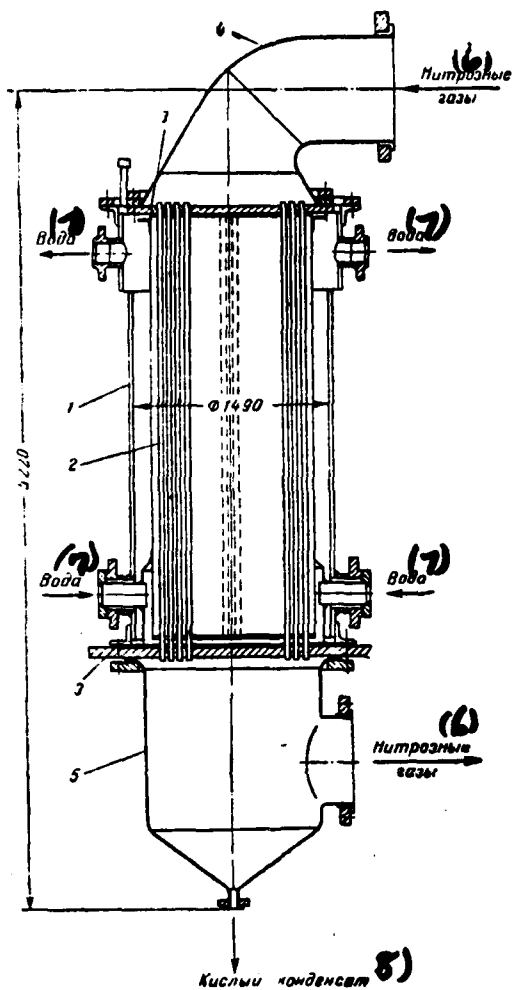


Figure I-56. High-speed Gas Cooler
($F=200 \text{ m}^2$)

Key:

1. Shell
2. Pipes
3. Pipe grids
4. Covers
5. Bottom
6. Nitrous gases
7. Water
8. Acid condensate

tower-final oxidizer equals $0.3 \text{ m}^3 / \tau$
(τ x day) HNO_3 .

Absorbing tower (tower of "nitroleum" absorption) with diameter 3020 and height 11,510 mm (or diameter 2424 and height 19,000 mm) is made of aluminum. The tower (fig. I-60) is separated by two partitions into 3 sections: stages of sprinkling with solutions. In the center of the partitions there are vents which are covered with cupolas for

transfer of the gases from one stage to another. At each sprinkling stage, there is independent circulation of the solution that is cooled in the extension shell-and-tube coolers.

Each section of the column has two layers of packing each, made of ceramic rings. The upper layer is sprinkled with acid with the help of sprayers. The acid passes by gravity flow from the upper stage. The lower layer is sprinkled with acid that flows from the upper layer, and the acid that is cooled to -10°C by circulation in the liquor coolers. In order to reduce the losses of cold into the surrounding medium, the absorption tower is covered with a thick

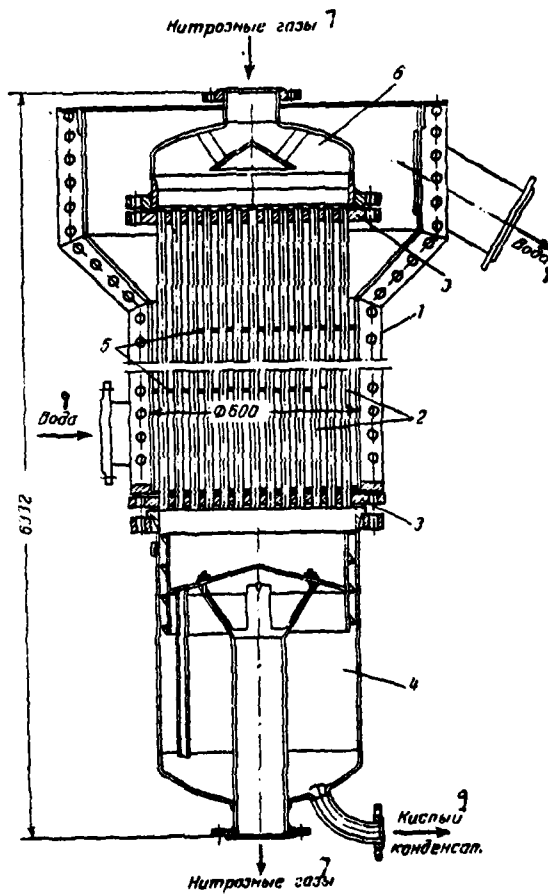


Figure I-57. High-Speed Gas Cooler
($F=45 \text{ m}^2$)

Key:

1. Shell
2. Pipes
3. Pipe grids
4. Separator
5. Partitions
6. Cover
7. Nitrous gases
8. Water
9. Acid condensate

layer of insulation.

Instead of one absorbing tower with three stages of absorption, sometimes two towers are installed in series. In this case the first tower on the gas course has two stages of sprinkling, while the second has one stage.

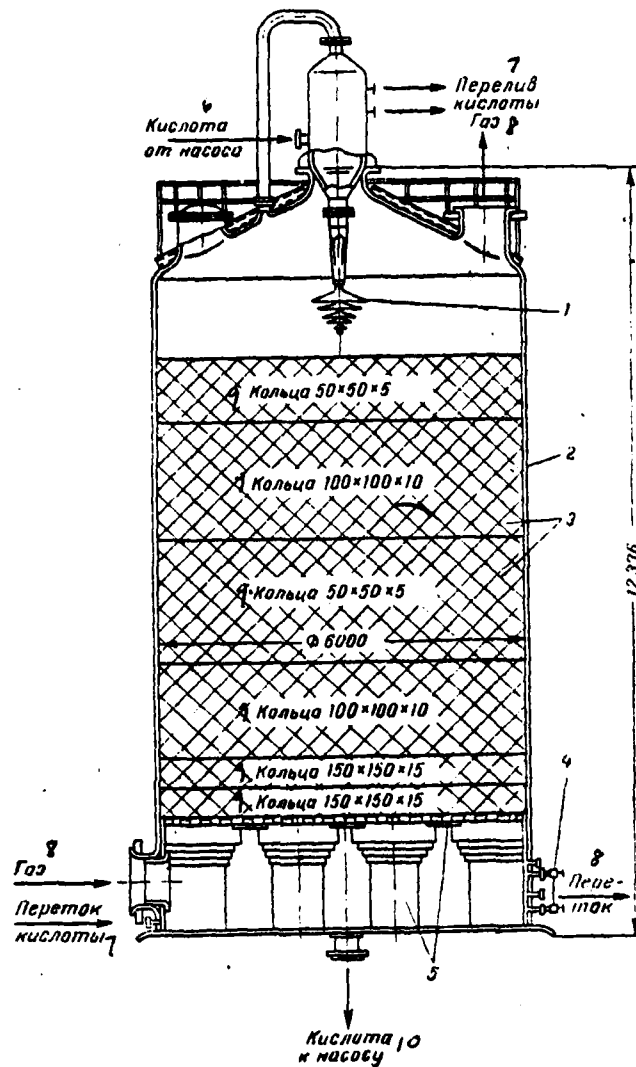


Figure I-58. Oxidizing Tower

Key:

1. Sprayer
2. Housing
3. Packing
4. Level indicator
5. Support under packing (pile of rings; lower row--regular placement)
6. Acid from pump
7. Acid overflow
8. Gas
9. Rings
10. Acid to pump

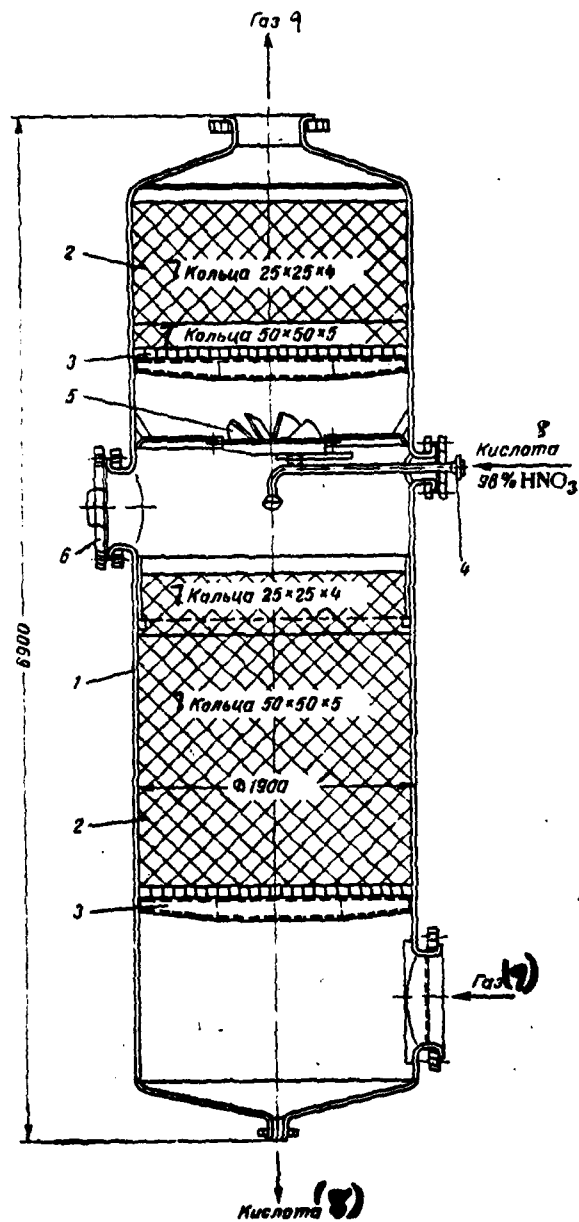


Figure I-59, Final Oxidizer

Key:

1. Housing
2. Packing (piled)
3. Support--grid under packing
4. Sprayer
5. Vortex generator
6. Manhole
7. Rings
8. Acid
9. Gas

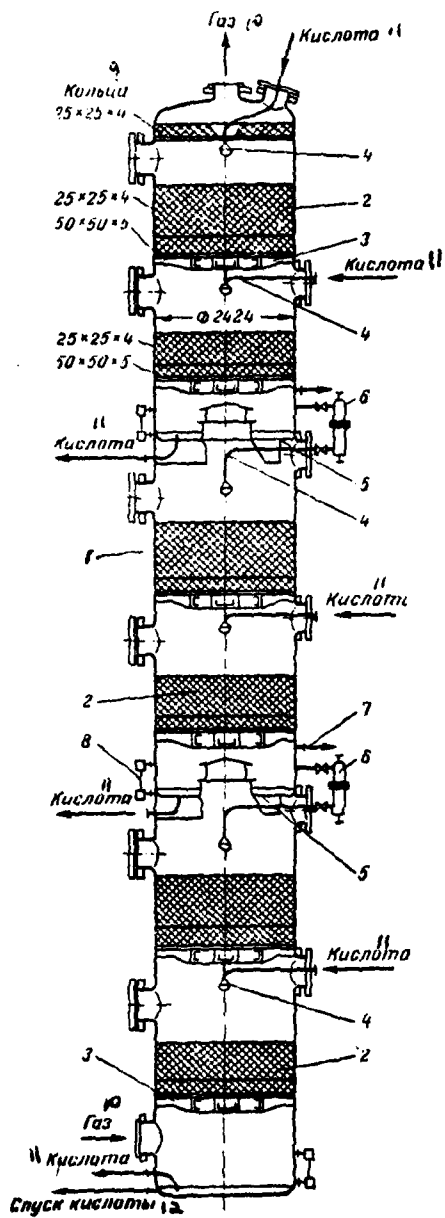


Figure I-60. Tower of Nitro-leum Absorption (Height 19 m)

- Key:
- | | |
|------------------------------|----------------|
| 1. Housing | 11. Acid |
| 2. Packing | 12. Acid drain |
| 3. Support under packing | |
| 4. Sprayer | |
| 5. Closed plate (for liquid) | |
| 6. Filter | |
| 7. Air pipe | |
| 8. Level indicator | |
| 9. Rings | |
| 10. Gas | |

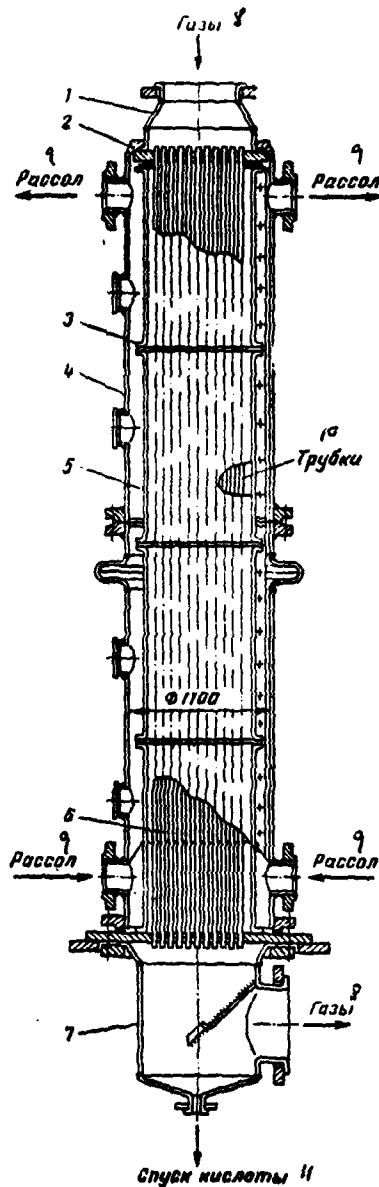


Figure I-61. Liquor Gas Cooler (Height ~7.7 m, F=145 m²)

- Key:
- | | |
|----------------------|----------------|
| 1. Upper cover | 11. Acid drain |
| 2. Pipe grid | |
| 3. Partition | |
| 4. Shell | |
| 5. Directional shell | |
| 6. Pipes | |
| 7. Lower cover | |
| 8. Gases | |
| 9. Liquor | |
| 10. Pipes | |

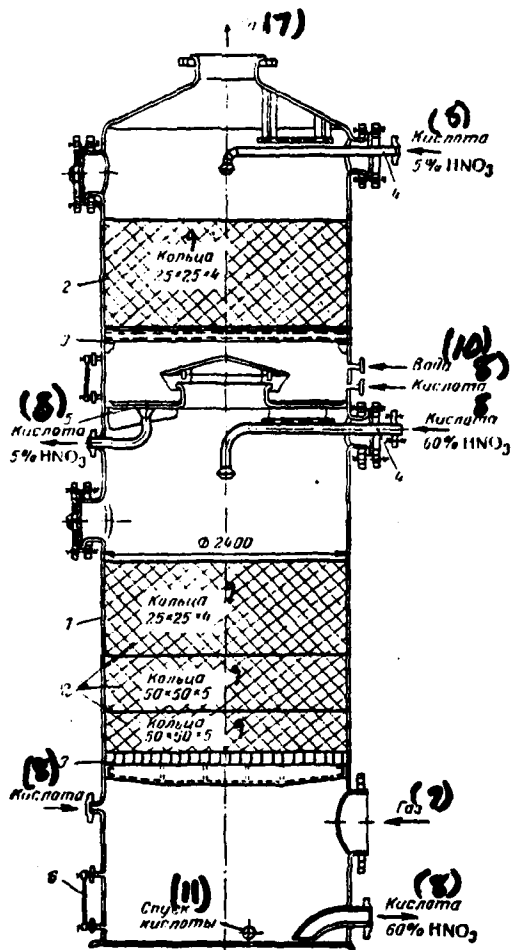


Figure I-62. Washing Tower (Height 10 m)

- Key:
1. Housing
 2. Packing (piled, lower row-- regular placement)
 3. Support under packing
 4. Sprayers
 5. Closed plate (for liquid)
 6. Level indicator
 7. Gas
 8. Acid
 9. Rings
 10. Water
 11. Acid drain

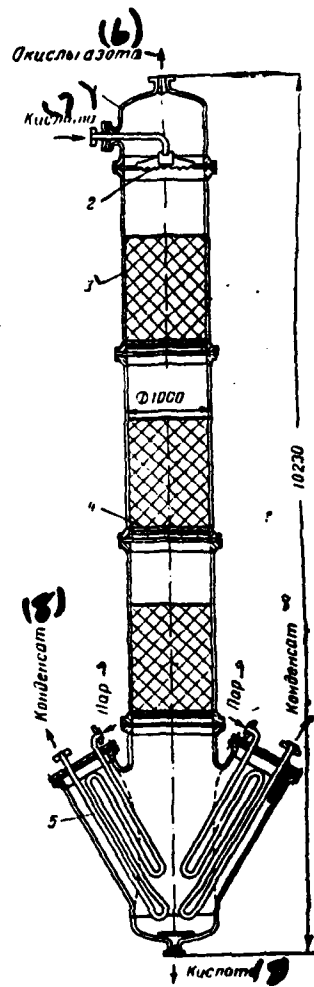


Figure I-63. Whitening Column with Packing Made of Ceramic Raschig Rings

- Key:
1. Cover
 2. Sprayer device
 3. Shell
 4. Grid
 5. Boiler
 6. Nitric oxides
 7. Acid
 8. Condensate
 9. Steam

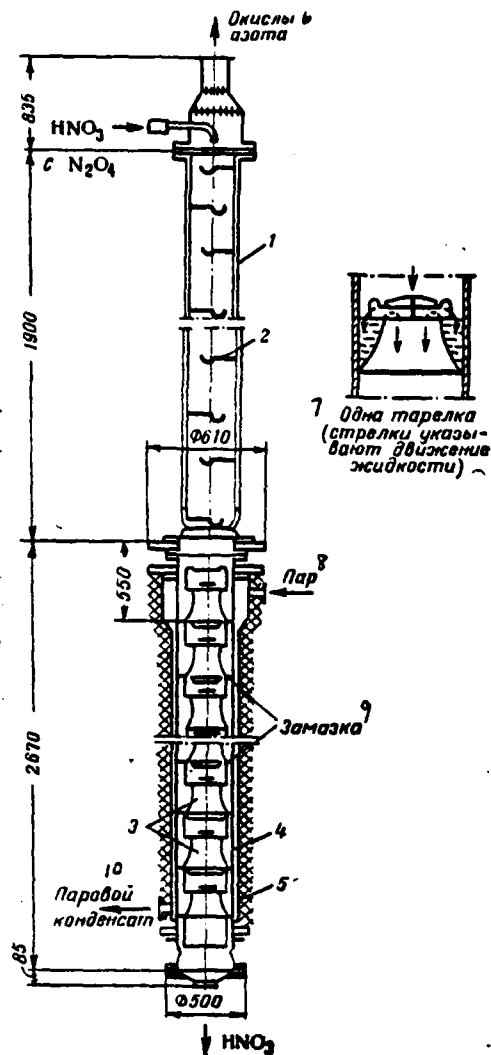


Figure I-64. Whitening Column of Plate-Cascade Type

Key:

1. Upper pipe
2. Cascade semiplates
3. Plates
4. Lower pipe
5. Steel sleeve for steam
6. Nitric oxides
7. One plate (arrow indicates movement of liquid)
8. Steam
9. Paste
10. Steam condensate

The first tower has five layers of packing made of ceramic rings of total height 3750 mm.

The specific volume of the absorbing system equals $1.25-1.50 \text{ m}^3 / (\text{t} \times \text{day}) \text{ HNO}_3$.

The liquor (nitroleum) coolers (fig. I-61). The shell of the coolers is made of carbon or stainless steel and the tube is made of aluminum pipes or pipes made of stainless steel 32 x 3 mm in diameter. The aluminum pipes and the pipe grids are made of aluminum with purity of 99.5%. The surface of the liquor coolers made of aluminum pipes is $2 \text{ m}^2 / (\text{t} \times \text{day}) \text{ HNO}_3$.

Washing tower (fig. I-62) is made of stainless steel. In the center, the tower is divided by a partition into two independent sections, the sprinkling stages. The partition has a vent which is covered by a cupola for passage of gases. A ceramic packing is placed at each stage.

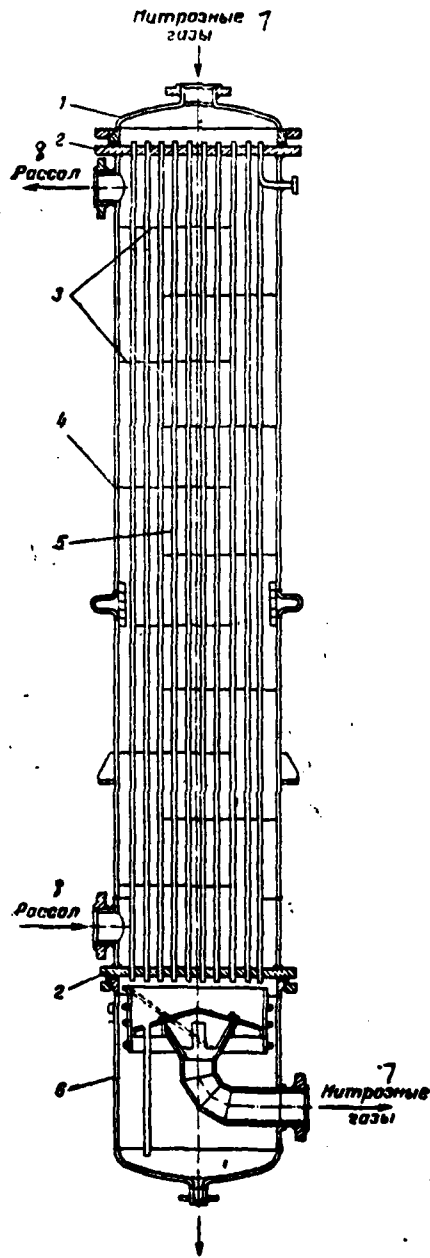


Figure I-65. Condenser of Nitric₂Oxides (Height 6.6, m, F=95 m²)

Key:

1. Upper cover
2. Pipe grids
3. Partitions
4. Housing
5. Stainless steel pipes
6. Separator
7. Nitrous gases

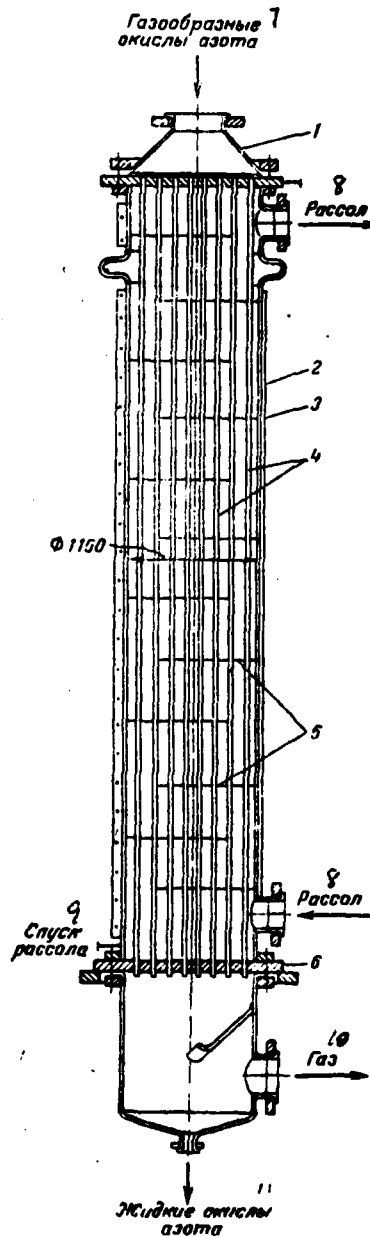


Figure I-66. Condenser of Nitric Oxides (Height, 9 m, F=210 m²)

Key:

1. Cover
2. Shell
3. Housing
4. Aluminum pipes
5. Partitions
6. Pipe grid
7. Gaseous nitric oxides

[continued from previous page]

- | | |
|-----------|--------------------------|
| 8. Liquor | 8. Liquor |
| | 9. Liquor drain |
| | 10. Gas |
| | 11. Liquid nitric oxides |

The first (lower) stage is sprinkled with diluted nitric acid formed in the gas cooler. The second (upper) stage is sprinkled with water. Both stages can have common sprinkling. The gases from the washing column are removed into the atmosphere through the separator. The specific volume of the washing tower equals $0.6 \text{ m}^3 / (\text{day}) \text{ HNO}_3$.

Whitening column (fig. I-63, I-64). In order to separate the dissolved nitric oxides from the acid, columns of packing and plate-cascade type are used.

The column of the packing type is made of aluminum. The column housing is covered with a layer of insulation (30-50 mm). The column can be arbitrarily divided into three parts: upper, fractionating, middle, rectification and lower, cube. The upper and middle parts of the column are a welded pipe that is filled with ceramic or porcelain rings that are placed on grids. In the lower, cube part of the column there is a boiler with two sections of heating aluminum coils. In the upper part of the fractionator that is free of packing, there is a sprayer to feed solutions of concentrated acid containing nitric oxides.

The output of this type of column reaches 50 t/day of whitened acid. The specific heating surface is 0.3 m^2 per 1 t of HNO_3 per day.

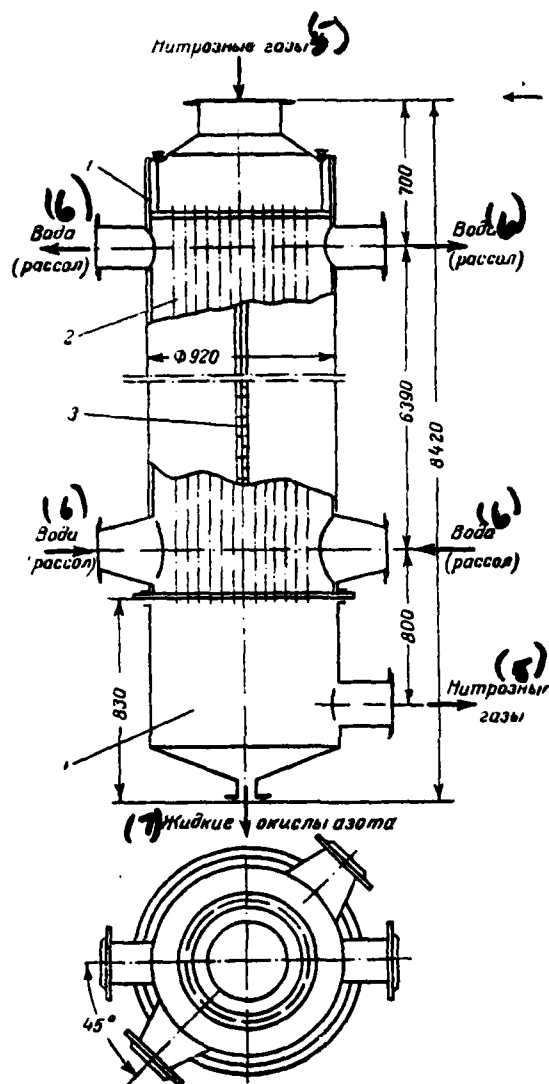
The housing of the column of plate-cascade type is made of aluminum, the shell is made of carbon steel. In contrast to the packing column, the liquid in the plate-cascade column is heated through the housing wall (steam is fed into the heating sleeve). Some columns of this type consist of two seamless pipes (upper and lower), 345 mm in diameter that are connected by flanges.

In the lower pipe of height 2670 mm, there are 7 plates which

Figure I-67. Nitric Acid Condenser

Key:

1. Shell
2. Pipes
3. Joint seam of shell
4. Liquid separator
5. Nitrous gases
6. Water (liquor)
7. Liquid nitric oxides



are equal distance from each other and are built so that the solutions flow over the wall of the pipe which is heated by steam. This is attained as follows: the solution from the upper pipe is fed to the cap, directing the acid into the concentric recess formed by the wall of the pipe and the plate. In the upper pipe, height 2100 mm, cascade partitions are installed in a checkerboard pattern. These are the semiplates over which the solution flows in a thin film. Flowing from the semiplates, the solutions that are to be whitened form a screen through which the hot nitric oxides pass that are lifted upwards.

Certain whitening columns of this type (diameter 350 mm, height 9318 mm) consist of three sheet-steel cylinders (seamless pipes).

The two lower sheet-steel cylinders are equipped with steam sleeves. The heating surface of these columns equals 3.5 m². Whitening columns 450 mm in diameter which are welded from aluminum sheets 14 mm thick are also used.

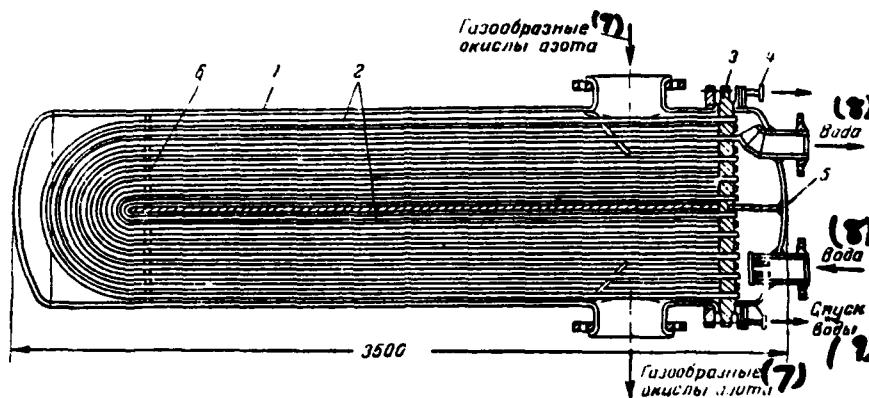


Figure I-68. Reverse Cooler ($F=50 \text{ m}^3$)

Key:

1. Housing
2. Pipes
3. Pipe grid
4. Air pipe
5. Cover
6. Partitions
7. Gaseous nitric oxides
8. Water
9. Water drainage

One of the versions for the design of whitening columns of the plate-cascade type is presented in fig. I-64. The column is made of special stainless steel and the steam sleeves are made of carbon steel.

Nitric oxide condensers (fig. I-65-I-67) of the shell-and-tube type, vertical, (less often inclined) are installed after high-speed coolers. The pipes 25 x 2 and 32 x 4 mm in diameter and pipe grids are made of stainless steel or of aluminum with purity of 99.5%. The tube is enclosed in a sectional shell made of carbon steel. Nitrous gases enter the pipes, while a 40-42% solution of calcium nitrate (cooling liquor) enters the intertube space.

The upper cover of the apparatus has a connecting pipe to feed in gaseous nitric oxides. The lower part of the condenser is designed to separate and remove the liquid nitric oxides, as well as to remove the gaseous nitric oxides with inert gases.

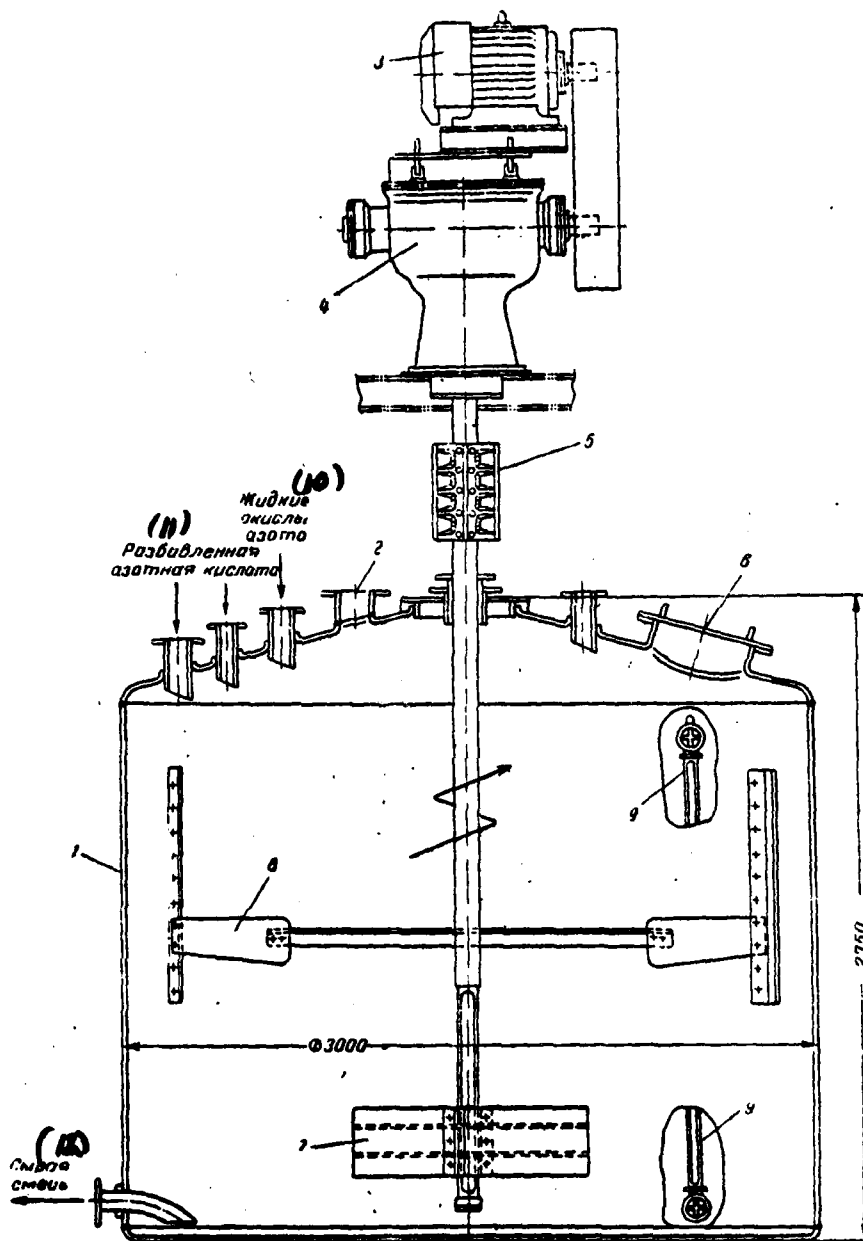


Figure I-69. Mixer of Raw Mixture

- | | | |
|------|---|--------------------------|
| Key: | 1. Housing | 10. Liquid nitric oxides |
| | 2. Connecting pipe for suctioning off gases | 11. Diluted nitric acid |
| | 3. Electric engine | 12. Raw mixture |
| | 4. Reducer | |
| | 5. Connecting piece | |
| | 6. Manhole | |
| | 7. Blade mixer | |
| | 8. Device for mixing | |
| | 9. Level indicator | |

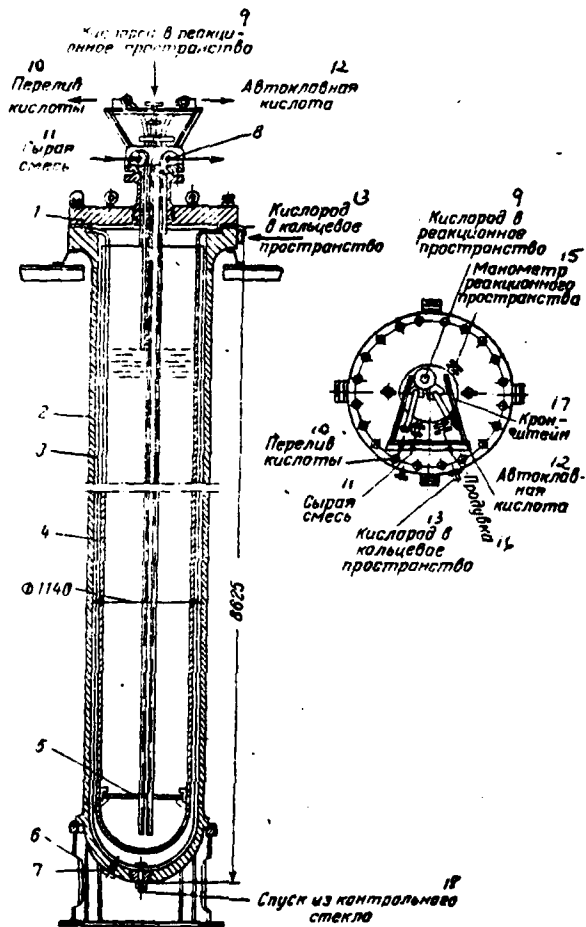


Figure I-70. Autoclave of Periodic Action

- Key:
1. Cover
 2. Housing of autoclave
 3. Protective vessel
 4. Reaction vessel
 5. Distributing disk
 6. Support
 7. Control connecting pipe
 8. Line for blow-through
 9. Oxygen into reaction space
 10. Acid overflow
 11. Raw mixture
 12. Autoclave acid
 13. Oxygen to ring space
 - ~~14. Acid to reaction space~~
 15. Manometer of reaction space
 16. Blow-through
 17. Cantilever
 18. Drainage from control vessel

Below are the characteristics of certain nitric oxide condensers:

Diameter, mm	1048	870	920	1150	1250
Height, mm	8300	8300	8420	9069	10,000
Number of pipes	-	-	255	337	385
Length of pipes, mm	-	-	6500	7000	7000
Cooling surface, m ²	165	100	175	210	240

The specific surface of heat exchange of the nitric oxide condensers equals $3.5-4.0 \text{ m}^2 / (\text{T} \times \text{day}) \text{ HNO}_3$.

The coolers of whitened acid are made of aluminum pipes. Coolers of two types are used: submersible (coil) and shell-and-tube. The shell-and-tube coolers consist of individual horizontal elements with U-shaped pipes 32 mm in diameter.

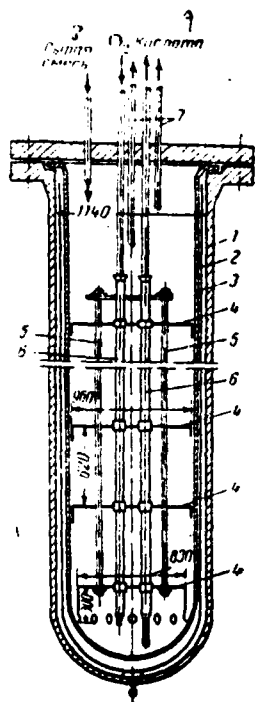
Reverse cooler (fig. I-68) is a horizontal heat exchanger of shell-and-tube type made of aluminum with U-shaped pipes 32 mm in diameter. It most often has a cooling surface of 50 m^2 . It is designed for preliminary cooling by water of gaseous nitric oxides that emerge from the whitening columns of different types.

Mixer (fig. I-69) is a tank 3000 mm in diameter and 2750 mm high with a cover. It is equipped with a vertical mixer and stationary mixing devices. The apparatus is made of stainless steel, and less often aluminum. The rotation rate of the mixer is 60-70 rpm.

Autoclaves. The production of concentrated nitric acid uses autoclaves of periodic and continuous action. The autoclaves of continuous action differ from the periodic only in the presence of packing and small changes in the piping that is linked to the supply of raw mixture and the removal of autoclave nitric acid. Figure I-70 presents the autoclave of periodic action and fig. I-71 presents the autoclave of continuous action with one of the types of packing of various types.

The main parts of the autoclave of periodic action are:

Figure I-71. Autoclave of Continuous Action



Key:

1. Housing
2. Protective vessel
3. Reaction vessel
4. Sieve-plates
5. Rod
6. Pipe-frames for oxygen and acid pipe
7. Overflow pipes
8. Raw mixture
9. Acid

outer thick-walled cylinder-housing made of carbon steel. The inner diameter of the housing is 1140 mm, the height is 8625 mm and the wall thickness is 36 mm;

R inner protective vessel made of aluminum; if there is a breach in the packing of the reaction vessel, the inner vessel protects the steel cylinder from the action of nitric oxides and acid. The diameter of the vessel is 1100 mm, the height is 8400 mm and the thickness of the bottom wall is 10 mm;

the inner reaction vessel that is made of 99.8% aluminum; the process of acid formation occurs in it. The inner diameter of the vessel is 1026 mm, the height is 8300 mm, the thickness of the wall is 25 mm and the working capacity is 6 m³. The upper part of the reaction vessel is flanged and pressed between the cover and the flange of the steel housing so that the vessel is located in a suspended position inside the housing. The reaction vessel is welded from sheets of aluminum and for the most part has one longitudinal and four transverse (ring) seams;

reinforcing unit-head that is attached to the vent of the steel cover of the autoclave. This design makes it possible to view and replace the inner pipes that are included in the autoclave, without removing its cover;

support design under the autoclave.

The cover of the autoclave is lined from the inside with sheet aluminum. To pack the parts of the autoclave, aluminum pipes that are 25 mm in diameter, flattened and welded among themselves, or other corrosion-resistant packings (for example, fluoroplastic) are used.

Four short and two long pipes enter the reaction vessel of the autoclave. The short pipes are designed to feed the raw mixture into the autoclave, overflow it back into the mixer if the autoclave is overfilled, connection to the manometer indicating the pressure in the reaction vessel, and output of the blow-through gases. Oxygen enters the autoclave on one of the long pipes. It is fed to the distributing plate (board) which has cuts in the form of slits that extend to the edges of the plate (there are also other existing designs of devices for distribution of oxygen). At the same time, the oxygen enters through the connecting pipe in the housing flange to the ring space between the protective steel housing and the reaction aluminum vessel where pressure of 52 atm. is maintained. This makes it possible to equalize the pressure in the inner reaction volume (inside and outside the reaction vessel) and prevent crumpling or rupture of the seams of the reaction vessel (for this purpose, special devices are also often installed on the autoclaves).

The autoclave acid is forced out in the second long tube from the autoclave by the nitrous gases present in it. A connecting pipe is welded in the lower part of the housing to the outlet pipe for control of the integrity of the protective and reaction vessels. All the regulators and control-measuring instruments of the autoclave are on the control panel. It is placed in an isolated room.

The autoclaves of periodic action may be adapted for con-

tinuous action. For this purpose, a packing is installed in them which consists of 9 (and more) sieve-bubbling plates 830 mm in diameter and 8 mm thick with holes 2 mm in diameter and 30 mm spacing. The plates are made of aluminum brand AVO and are attached with the help of four aluminum rods. The plates and the rods form a stack that is freely installed within the reaction vessel of the autoclave. The oxygen and acid pipes pass through the plates.

Concentration of Nitric Acid with the Use of Sulfuric Acid

Standard distillation of diluted nitric acid may increase its concentration to 68.4% HNO₃. This corresponds to a boiling temperature of the solution of 121.9°C. At this temperature, the azeotropic mixture (68.4% HNO₃ and 31.6% water) begins to distill. Under production conditions, one can obtain nitric acid with concentration no higher than 66%.

TABLE I-49. BOILING TEMPERATURE OF AQUEOUS SOLUTIONS OF NITRIC ACID AND COMPOSITION OF LIQUID AND VAPOR⁴¹ AT 760 mm Hg

Температура кипения °C (до 68.4% HNO ₃)	Содержание HNO ₃ , вес. %		Температура кипения °C (выше 68.4% HNO ₃)	Содержание HNO ₃ , вес. %	
	в жидкости	в парах		в жидкости	в парах
106,5	24,2	2,16	85,8	98,0	99,9
112,0	33,0	5,9	90,5	90,2	99,7
118,5	49,8	19,85	98,0	85,2	98,0
121,5	61,0	41,0	112,0	80,0	97,0
121,8	65,21	65,1	118,0	75,8	92,0
121,9 *	68,4	68,4	121,5	70,1	84,0

Key:

1. Boiling temperature, °C (to 68.4% HNO₃)
2. HNO₃ content, weight. %
3. In liquid
4. In vapors
5. Boiling temperature, °C (above 68.4% HNO₃)

*Temperature of formation of an azeotropic mixture.

During distillation of nitric acid of varying concentration at atmospheric pressure, its boiling temperature gradually increases, while the concentration of condensate that is formed from vapors approaches 68.4% HNO₃. In distillation of nitric acid that contains over 68.4% HNO₃, the first fractions of condensate will have greater

TABLE I-50. DATA ON EQUILIBRIUM BETWEEN LIQUID AND VAPOR IN $\text{HNO}_3\text{-H}_2\text{O}$ SYSTEM WITH VACUUM³

Температура °C	Содержание HNO_3 вес. %		Температура °C	Содержание HNO_3 вес. %	
	жидкость	пар		жидкость	пар
При 600 мм рт. ст.			При 450 мм рт. ст.		
97,3	14,8	0,28	89,7	19,8	0,5
102,0	29,8	3,3	92,4	27,1	0,9
103,5	36,1	6,2	100	43,6	10,6
108,2	44,9	18,7	102	52,6	25,5
110,8	55,0	28,9	103,8	59,4	30,8
113,5	64,2	56,7	105,3	64,5	57,7
113,7	67,3	67,0	106	67,2	67,0
113,8	67,5	67,5	106	67,15	67,15
112,8	73,2	81,7	104	74,7	84,4
102,1	83,1	97,2	91,5	85,5	96,6
93,3	88,8	99,0	79,5	91,7	98,3
87,8	90,3	99,2	74,6	94,1	99,0
79,5	96,7	99,8	73,1	96,0	99,4
76,8	98,8	99,8	72,2	97,0	99,3
—	—	—	70,0	98,8	99,2

Key:

1. Temperature, °C
2. HNO_3 content, weight. %
3. Liquid
4. Vapor
5. At 600 mm Hg
6. At 450 mm Hg

acid concentration than the subsequent. In this case, because of the reduction in HNO_3 concentration, its boiling point gradually rises, while the distillable fractions are united by the acid until the equilibrium condition is reached at 121.9°C (68.4% HNO_3 in the liquid and the vapors).

By dehydrating the vapors which are distilled from the diluted solutions of nitric acid, we can obtain acid of the required concentration. Industry makes extensive use of 92-94% sulfuric acid (oil of vitriol) as the water-removing substance. It forms a triple system $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ with diluted nitric acid. The partial pressure of the water vapors above this mixture is low (fig. I-72, I-73).

During distillation of diluted nitric acid in a mixture with H_2SO_4 , the sulfuric acid is diluted with water. Depleted sulfuric acid is obtained in which there is a small quantity of HNO_3 and

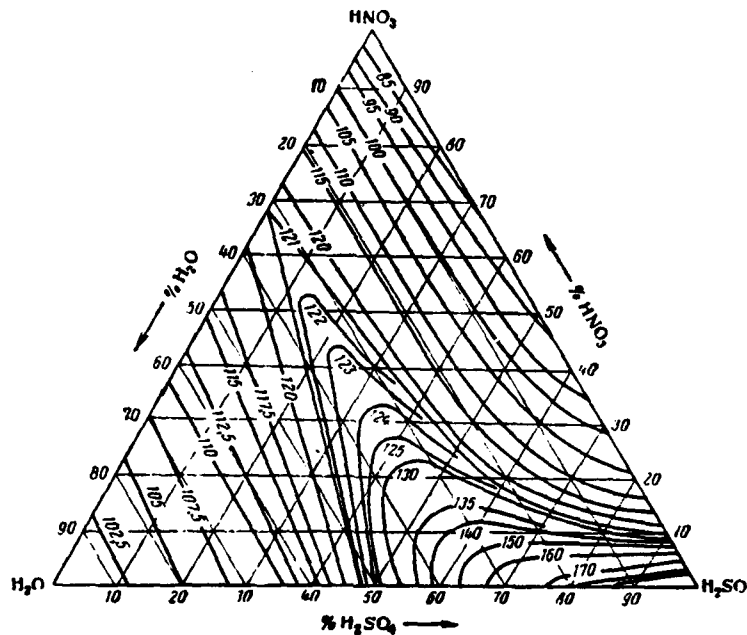


Figure I-72. Boiling Point of Triple Mixtures
 $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$

nitric oxides. The latter form with sulfuric acid nitrososulfuric acid HNSO_4 with concentration to 0.01%. With subsequent concentration by evaporation of the spent sulfuric acid in order to obtain oil of vitriol, the nitrososulfuric acid is broken down.

The process of concentrating nitric acid is done in columns that are made of ferrosilide. The heat necessary for distillation is brought to the column with live steam. The released vapors of nitric acid are condensed with a small quantity of water vapors when cooled in the cooler-condensers. The concentrated nitric acid that is formed here is returned to one of the upper plates of the concentration column for blowing off of the nitric oxides dissolved in the acid. Then the acid is cooled in a water cooler and transferred to the storehouse for finished products.

The uncondensed vapors of nitric acid, nitric oxides, water vapors and inert gases are sent from the cooler-condensers to small absorption towers. Here 40-45% nitric acid is formed. It is sent

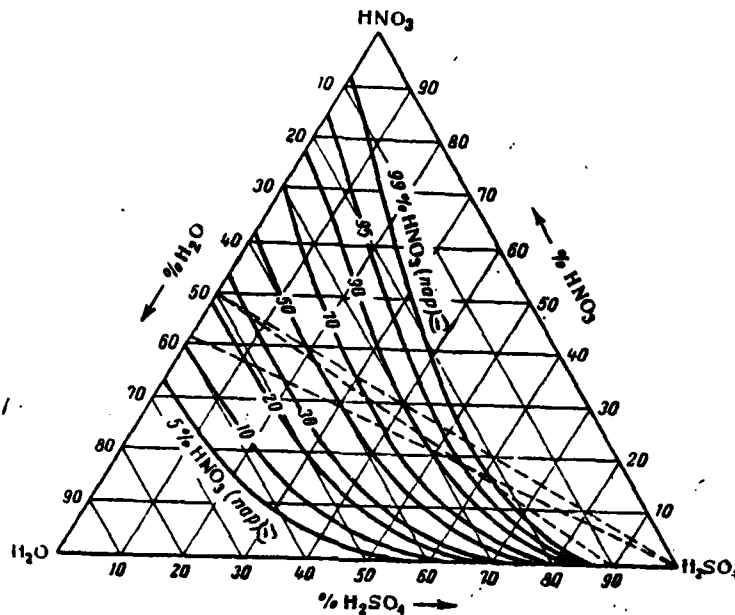


Figure I-73. Equilibrium Concentrations of Nitric Acid in Vapors above Triple Mixtures HNO₃-H₂SO₄-H₂O 1. Vapor

for concentration or is transferred to the production of diluted nitric acid. The gases of the absorption towers are removed to the atmosphere. The spent sulfuric acid after the concentration columns goes for concentration by evaporation (p. 151).^(R107) Studies made in recent years revealed certain new relationships of the main parameters of the process of concentrating nitric acid in the presence of sulfuric acid. This makes it possible to work out a plan for automating this process.^{86,87}

In conducting the process of concentrating nitric acid whose technological plan is presented in fig. I-74, certain work procedures are used which make it possible to intensify distillation of the HNO₃ vapors and increase the output of the concentration column:

in the majority of cases, about half of the diluted nitric acid is preheated to 115-120°C and sent for concentration in the form of hot liquid and steam;

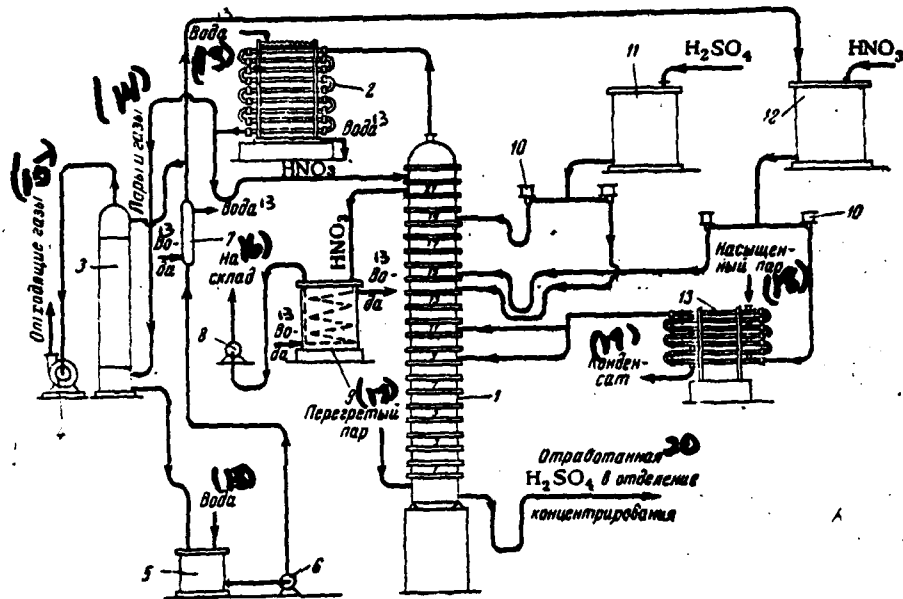


Figure I-74. Plan for Concentrating Diluted Nitric Acid with Help of Sulfuric Acid

Key:

1. Concentration column
2. Cooler-condenser
3. Absorption tower
4. Exhauster
5. Collector
- 6,8. Centrifugal pumps
7. Cooler of circulating diluted acid
9. Cooler of production acid
10. Control light
- 11,12. Pressure tanks
13. Water
14. Vapors and gases
15. Exhaust gases
16. To storehouse
17. Superheated steam
18. Saturated steam
19. Condensate
20. Spent H_2SO_4 to concentration section

92-94% of the sulfuric acid often enters the concentration column also in the preheated state, etc.

The selection of points for input of the nitric and sulfuric acids into the column is determined in the majority of cases by experiment since it depends on the methods of assembling the concentration columns, the number of plates (from 20 to 24), the diameter

of the overflow pipes and other conditions.

Below are the main indicators of the technological regime for concentrating nitric acid:

Concentration of original nitric acid, %	47-58
Content of nitric oxides (NO ₂) in original acid, %, no more	0.15
Vapor pressure (absolute), atm.	
of saturated, diluted nitric acid fed to the evaporator	4-6
of heated, fed to column	15
Vacuum in upper part of column, mm Hg	20-40
Temperature, °C	
of vapors of acid at outlet from column	80-85
at plate (trap)	110-120
of gases after cooler-condenser, no higher	40
of nitric acid after cooler of finished product, no higher	35
of spent sulfuric acid after column	150-170
HNO ₃ concentration in finished product, %	97-98.5
Content of nitric oxides (N ₂ O ₄) in the finished product, % no higher	0.4
Concentration of sulfuric acid, % no less	
original	92
spent	65-68
Content of nitric oxides (in conversion for HNO ₃) in spent sulfuric acid, % no more	0.03

Figure I-75 presents the quantity of sulfuric acid (oil of vitriol) that is required to concentrate the diluted nitric acid, and figure I-76 presents the consumption of vapor for 1 $\frac{5}{2}$ of HNO₃ depending on the concentration of nitric and sulfuric acids.

The consumption coefficients for 1 $\frac{5}{2}$ of concentrated nitric acid:

Diluted nitric acid (in conversion for 100% HNO ₃), $\frac{5}{2}$	1.010-1.015
Sulfuric acid (92% H ₂ SO ₄), $\frac{5}{2}$	
with concentration of 47-49% nitric acid	4.0-4.2
with concentration of 56-58% nitric acid	2.9-3.2
loss	0.01-0.014
Water for cooling, m ³	30-40
Steam, million kcal	
superheated	0.25-0.35
saturated	0.2
Electricity, kW x h	10-15

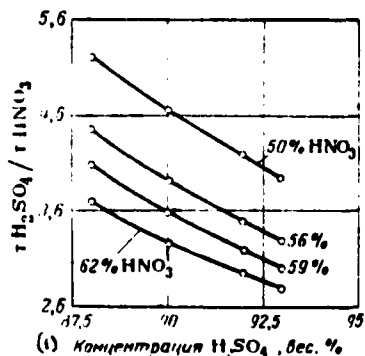


Figure I-75. Quantity of Sulfuric Acid (Oil of Vitriol) Required to Concentrate Diluted Nitric Acid Depending on Its Concentration

Key: 1. Concentration of H₂SO₄, weight. %

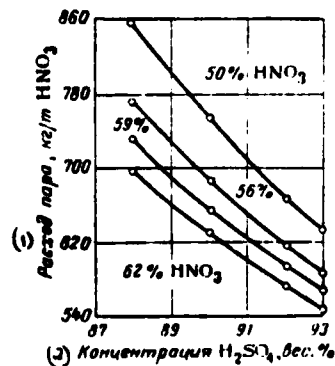


Figure I-76. Dependence of Consumption of Steam for Concentration of Diluted Nitric Acid on Concentration of Sulfuric Acid

Key: 1. Consumption of steam, kg/t
2. Concentration of H₂SO₄, weight. %

Basic Equipment

Concentration column (fig. I-77) of the bubbling type consists of 18-24 cylindrical steel-sheet cylinders, spherical cover and bottom part which is designed to feed live steam and is a small buffer for the spent sulfuric acid. The height of the steel-sheet cylinders is 360 mm (except for the upper and lower which are 760 mm tall). Each steel-sheet cylinder has two overflow connections each.

The column and all of its parts (connections, caps, etc.) are made of ferrosilide. Asbestos cardboard or paronite impregnated with bituminous varnish is used as the packing material in assembling the column. Packing made of fluoroplast or paronite with winding of fluoroplast foil is also used.

Industry uses columns 800-850 and 1000 mm in diameter (thickness of the walls 25 mm). The total height of the column when the 22 steel-sheet cylinders are installed is 9600 mm. In the center of each steel-sheet cylinder there is a hole (vent) 350 mm in diameter for passage of gases and steam. It is covered by a rough bubbling cap 660 mm in diameter with slits in the form of teeth. The vent

with cap guarantees bubbling of the vapors and gases through the layer of liquid on the plate. Bubbling caps are not installed on those two steel-sheet cylinders to which high nitric acid is fed. Sometimes columns are used which have 7-8 seven-ray caps.

The column operates with a vacuum of 20-40 mm wat. col., with the exception of its lower part where live steam is fed to and where slight pressure is maintained.

Before start-up, the column is filled with 92% sulfuric acid and diluted with water. In this case, a considerable quantity of heat is released. Then steam is gradually fed into the column and it is heated for 5-6 h. Only after this is feeding of diluted nitric acid into the column and the corresponding quantity of H_2SO_4 started.

The evaporator is designed to warm up the diluted nitric acid that is sent for concentration. Evaporators of the "pipe in pipe" type are used in the majority of cases. The internal ferrosilide pipes have a diameter of 80/106 mm and length of 2000 mm. The external pipes (steam sleeve) are made of carbon steel.

The evaporator consists of several parallel sections (fig. I-78) of 8 pipes in each. The evaporator sections are interconnected by lower and upper collectors. Steam under pressure of 4-6 atm. enters from above into the steam sleeves that are interconnected by connecting pieces. The total heat-exchange surface of the evaporator which is installed in each concentration column is 11.5-13 m^2 . The specific surface of the evaporator equals 0.2-0.3 $m^2/(2 \times \text{day}) HNO_3$.

Cold nitric acid enters the lower pipes, while the forming steam-liquid mixture at 120°C emerges through the upper collector.

The cooler-condenser of the sprinkling type is designed to condense vapors of nitric acid. It is made of ferrosilide pipes 124/100 mm in diameter and 2000 mm long that are connected into 6 parallel sections with 9 pipes in each. The sections (fig. I-79) are interconnected by input and output collectors. Water is fed to

sprinkle the pipes through the distributing trays which have holes and slits. The acid vapors at 80-90°C are sent to the upper part of the collector. The concentrated nitric acid with the nitric oxides dissolved in it emerge at 30-45°C through the lower collector.

A condenser with surface of 30-40 m² (depending on its output and the temperature of the cooling water) is installed in each column. The specific surface of the cooler-condenser equals 0.85-0.65 m²/($\frac{1}{2}$ x day) HNO₃.

Cooler of concentrated nitric acid (fig. I-80). Coil coolers of the submersible type are usually used. The coils that are made out of aluminum pipes brand AV-2 with diameter of 50/60 mm are placed in a tank (housing) made of carbon steel. The diameter of the tank is 1550 mm and the height is 2035 mm. The water enters the lower part of the tank and flows out upwards. The surface of cooling is 30 m². Nitric acid is cooled from 80 to 40°C.

Concentration of Spent Sulfuric Acid

During concentration by evaporation of diluted solutions of sulfuric acid to a concentration of 70% H₂SO₄, only water evaporation occurs. As the solution concentration rises at a constant temperature, the pressure of the water vapors drops and the pressure of the sulfuric acid vapors above the solution rises.

In the vapor phase above the acid with concentration lower than 98% H₂SO₄, the H₂O:H₂SO₄ ratio is greater than in the solution. By heating the diluted acid, one can increase the concentration of H₂SO₄ if the vapors forming above the solution are simultaneously removed. Only 98.3% sulfuric acid whose boiling point is 338°C has the same composition of vapor and liquid phases, i.e., forms an azeotropic mixture. The boiling points of sulfuric acid are shown in fig. I-81.

The spent sulfuric acid is stabilized in two- and three-chamber bubbling type concentrators (table I-51). In order to concentrate

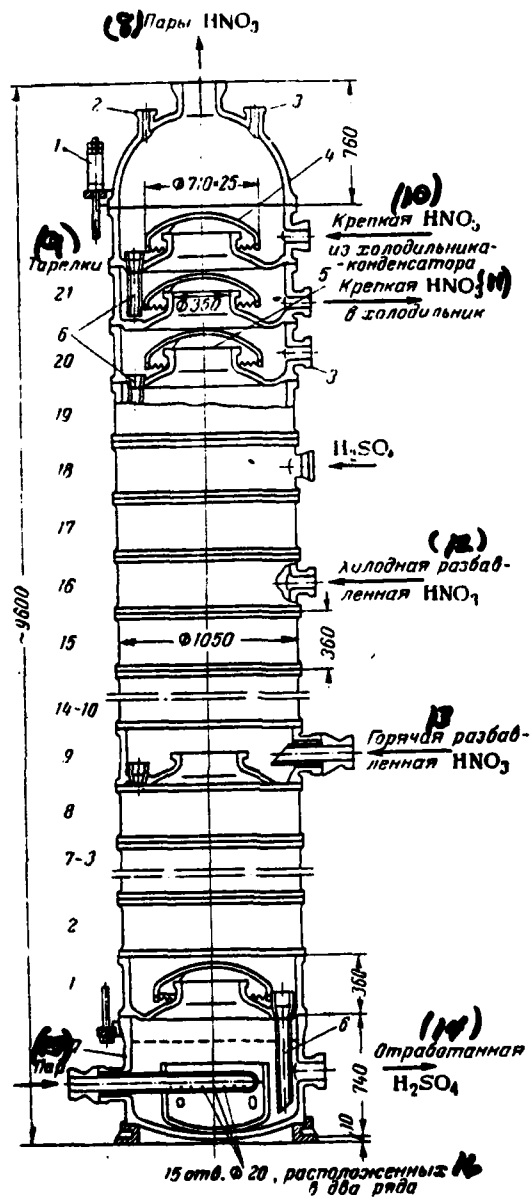


Figure I-77. Concentration Column (One of Variants)

- Key:
1. Vessel with spring
 2. Connecting pipe for manometer
 3. Connecting pipes for thermometers
 4. Bubbling cap
 5. Vent of plate for passage of vapors and gases
 6. Overflow connections
 7. Bottom part of column

[continued from previous page]

8. Vapors
9. Plates
10. Strong HNO_3 from cooler-condenser
11. Strong HNO_3 to cooler
12. Cold diluted HNO_3
13. Hot diluted HNO_3
14. Spent H_2SO_4
15. Steam
16. 15 holes ~~placed~~ ^{placed} in two rows

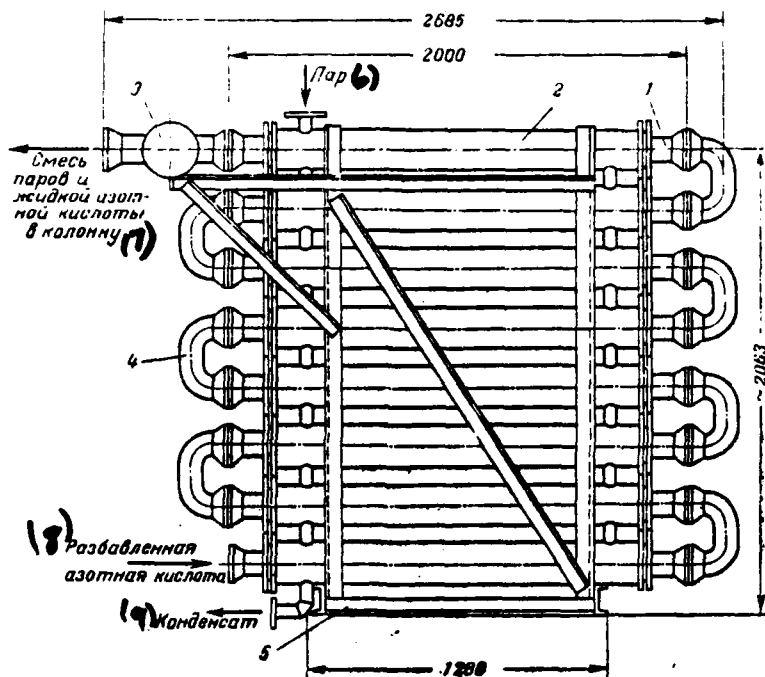


Figure I-78. Section of Evaporator ($F=11.5 \text{ m}^2$)

- Key:
1. Pipe
 2. Steam sleeve
 3. Collector
 4. Elbow
 5. Support
 6. Steam
 7. Mixture of vapors and liquid of nitric acid to column
 8. Diluted nitric acid
 9. Condensate

by evaporation the spent sulfuric acid, furnace gases are used which are formed during the burning of natural gas, mazut or rich gas (see vol. I of Reference Book for the Nitrogen Industry Worker).

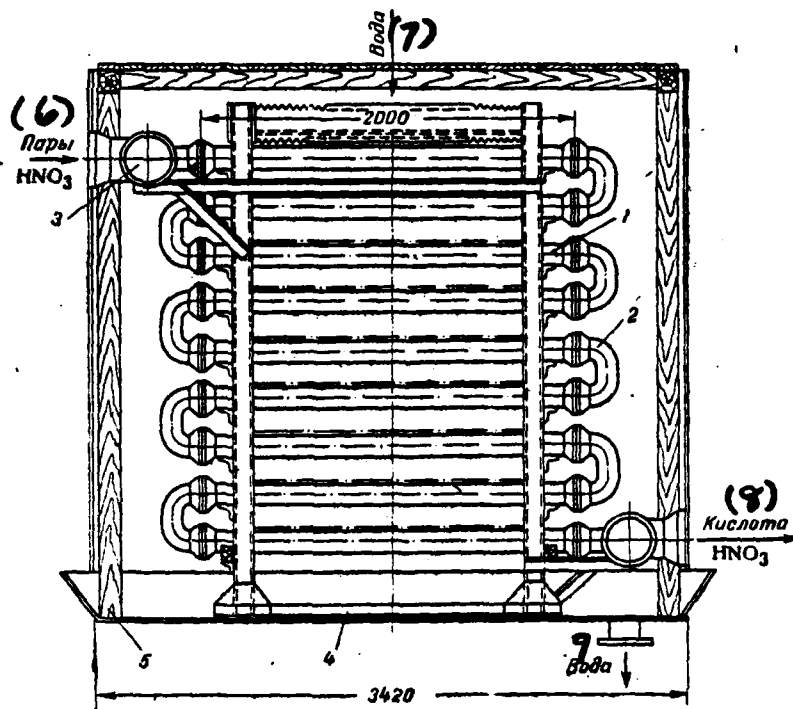


Figure I-79. Section of Cooler-condenser ($F=28 \text{ m}^2$)

Key:

1. Pipe
2. Elbow
3. Ferrosilide collector
4. Support
5. Shell
6. Vapors
7. Water
8. Acid

The fuel gases are fed to the concentrator furnace at pressure of 1500-1600 mm wat. col. The furnace gases from the mixing chamber first enter on the line gas pipes and bubbling pipes to the second condenser chamber in the acid course. Here, by bubbling through the acid, the gases intensively heat it, at the same time being saturated with water vapors. The gases further enter the chamber which is first on the acid course where they are additionally saturated with water vapors, and at a temperature of 155-160°C are sent through the electric filter to the exhaust pipe. The gases that emerge from the concentrator contain 30-40 g/m³ of sulfuric acid, and after purification in the electric filter, they contain up to 0.8 g/m³ H₂SO₄.

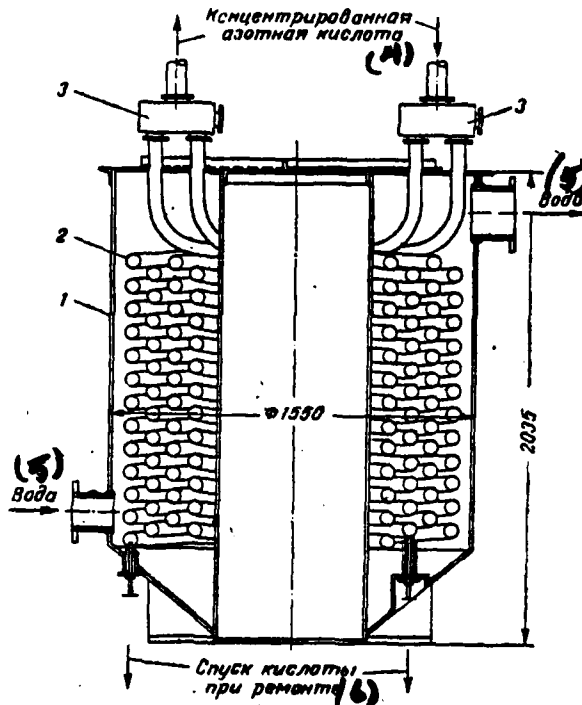


Figure I-80. Cooler of Production Concentrated Nitric Acid

- Key:
1. Housing
 2. Coils
 3. Precast blocks
 4. Concentrated nitric acid
 5. Water
 6. Drainage of acid during repair

TABLE I-51. INDICATORS FOR OPERATION OF THREE-CHAMBER CONCENTRATOR OF SULFURIC ACID*

(1) Распределение горячего топочного газа по камерам, %			(2) Содержание серной кислоты в газе после третьей камеры, г/м ³		
(3) первая	(4) вторая	(5) третья	(6) в виде тумана	(7) в виде паров	(8) всего
100	0	0	40.0	0.05	40.05
57	27	16	9.0	0.1	9.1
32	46	22	4.1	0.2	4.3
16	51	33	4.1	0.3	4.4

*Calculated data of A. G. Amelin

- Key:
1. Distribution of hot furnace gas over chambers, %
 2. Sulfuric acid content in gas after third chamber, g/m³
 3. First 4. Second 5. Third
 6. In form of fog 7. In form of vapors
 8. Total

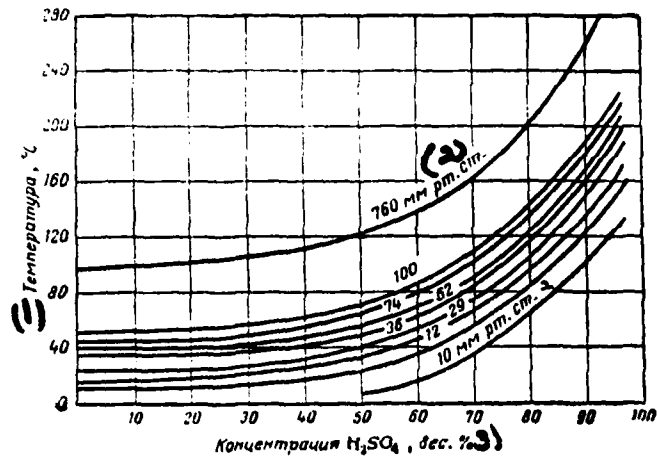


Figure I-81. Boiling Points of Solutions of Sulfuric Acid in Vacuum

Key: 1. Temperature, °C
 2. mm Hg
 3. H₂SO₄ concentration, weight. %

In order to reduce the quantity of fog of sulfuric acid in the gases, sometimes a small absorber with packing sprinkled by the spent sulfuric acid is installed in front of the electric filter. The exhaust gases from the electric filter contain roughly the following quantities of acid admixtures: 0.2 g/m³ of foggy sulfuric acid, 0.45 g/m³ of sulfur dioxide and 0.15 g/m³ of nitric oxides.

Figure I-82 presents the plan for a unit for concentrating spent sulfuric acid.

Below are the basic indicators for the technological regime:

Concentration of spent sulfuric acid, %	65-68
Content of nitric oxides (in conversion for HNO ₃) in spent sulfuric acid, % no more	0.03
Temperature of mazut before sprayer, °C	65-75
Pressure of mazut before sprayer, atm.	11-14
Pressure of air blower, mm wat. col.	1100-1200
Pressure (gage), mm wat. col.	
of air at inlet to furnace	800-1000
of gas at outlet from concentrator	45-50
Temperature of gases, °C	
in furnace	1000-1200

at inlet to first chamber	800-900
at transition from first to second chamber	230-250
at outlet from concentrator	140-160
Sulfuric acid concentration, %, no less	92
Temperature, °C	
at inlet to coolers	220-240
at outlet from coolers	40-50
Content in exhaust gases after electric filter	
of sulfuric acid, g/m ³ , no more	0.6
of oxygen (during operation on gaseous fuel), %	to 0.5

coefficients for 1 $\frac{5}{4}$ of 100% H₂SO₄:

Spent sulfuric acid, τ	1.004-1.005
Steam, million kcal	0.16-0.17
Electricity, kW x h	20.0-25.0
Water for cooling, m ³	9.0-10.0
Rich gas (calorific value 5000 kcal/kg), m ³	97.5
or mazut, kg	50-60
Air, m ³	1400-1500

Below are approximate data on the effect of certain factors on the output of the sulfuric acid concentrator and the temperature of the exhaust gases:

Indicators	Increase in output, %	Increase in temperature (in °C) of gases at outlet from concentrator*
Increase in temperature of furnace gases by 100°C	13	3
Increase in air pressure before furnace by 100 mm wat. col.	5	Almost no effect
Increase in temperature of spent sulfuric acid by 50°C	9	6
Increase in concentration of spent sulfuric acid by 1%	4	3

*In helmet pipe.

With a decrease in the concentration of sulfuric acid by 1%, the output of the concentrator diminishes by 3% and the temperature of the exhaust gases by 4°C.

Basic Equipment

Concentrator (fig. I-83) of the drum type with output of roughly 180 $\frac{5}{4}$ /day has a diameter of 2390 mm and length of 7830 mm.

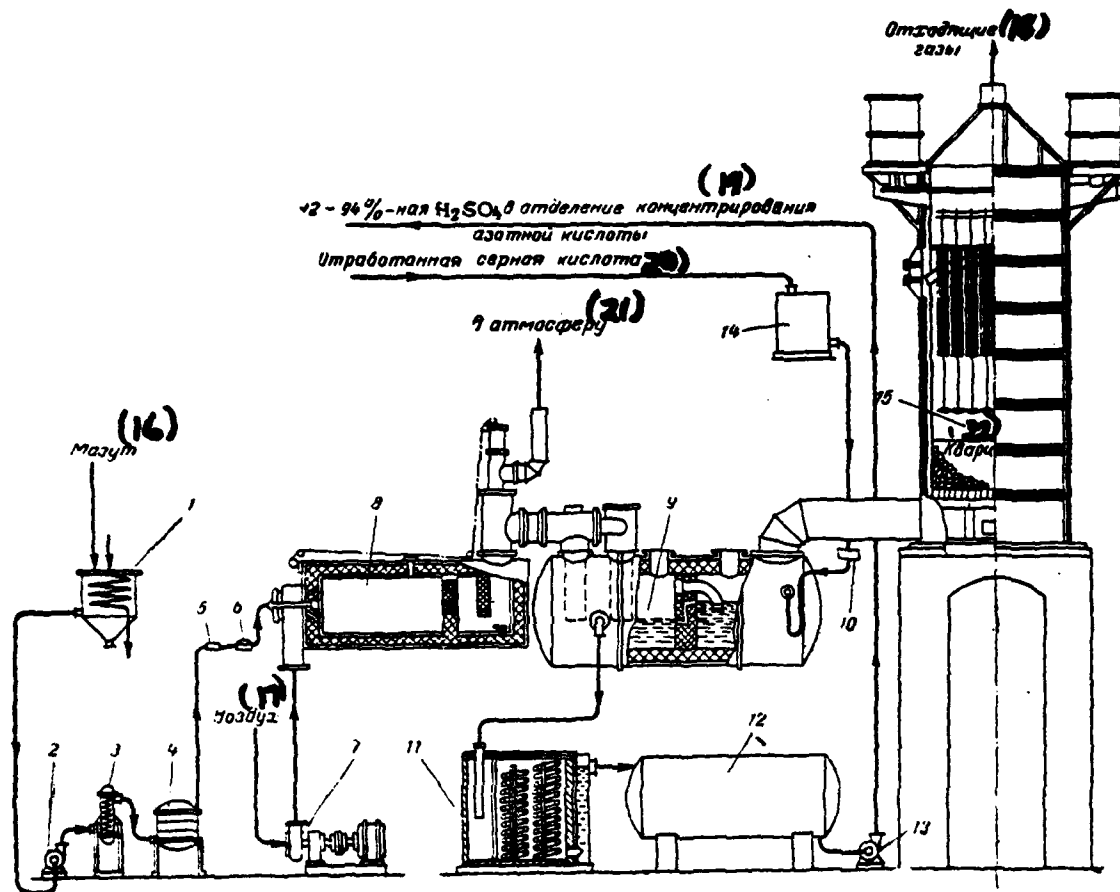


Figure I-82. Plan of Unit for Concentrating Spent Sulfuric Acid

- | | | |
|------|--|---|
| Key: | 1. Pressure vessel for mazut | 12. Acid collector |
| | 2. Pump for mazut | 13. Pump |
| | 3. Preheater | 14. Pressure tank |
| | 4. Filter | 15. Electric filter |
| | 5. Control preheater of mazut | 16. Mazut |
| | 6. Control filter | 17. Air |
| | 7. Air blower | 18. Exhaust gases |
| | 8. Furnace | 19. 92-94% H_2SO_4 in nitric acid concentration section |
| | 9. Concentrator | 20. Spent sulfuric acid |
| | 10. Control box | 21. To atmosphere |
| | 11. Cooler of 92.5%-94% H_2SO_4 (Oil of vitriol) | 22. Quartz |

The concentrator housing is welded from sheet carbon steel and is reliably protected from the effect of acid and vapors by a multilayer lining (asbestos cardboard, sheet lead, then again asbestos cardboard, and finally, two layers of andesite slabs on acid-resistant paste or cement). The concentrator is divided into

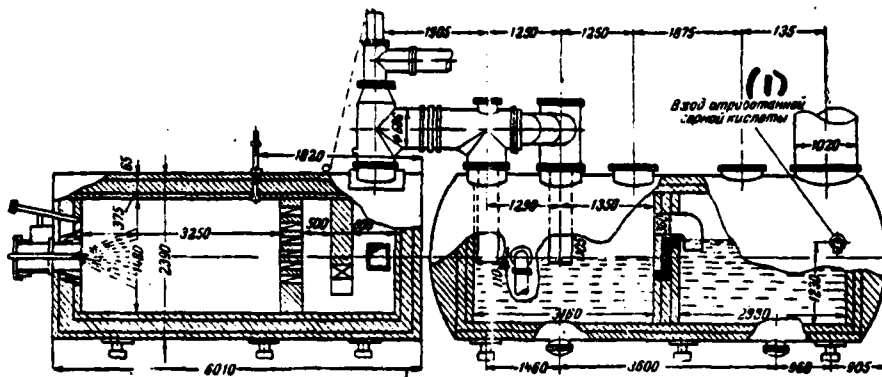


Figure I-83. Two-chamber Concentrator with Furnace (one of variants)

Key: 1. Input of spent sulfuric acid

chambers by a brick partition made of andesite or beschtsaunite that has two openings, for the elbow pig-iron bubbling pipes and for acid overflow from one chamber to another. The bubbling pipes are made of chrome pig iron (25-30% Cr), ferrosilide, and less often from common pig iron.

The upper part of the concentrator has manholes 520 mm in diameter and a connecting pipe to join the bubbling pipes with the gas lines of the furnace gases, and for input of the helmet pipe on which the gases emerge from the concentrator. In the lower part of the concentrator there are two connecting pipes with valves for drainage of the acid and sludge during repair or cleaning of the apparatus. The second chamber on the gas line is equipped with a connecting pipe for input of spent sulfuric acid, and the first with a connecting pipe for output of concentrated acid.

Air blower. The output of the air blower to feed air into the concentrator is 25,000 m³/h, pressure 1200 mm wat. col., rotation rate of the shaft of the air blower 2950 rpm. The consumption of air for 1 T of 100% H₂SO₄ when operating on mazut or fuel gases (temperature in the mixing chamber 800°C) is roughly 1620 m³.

Acid pumps. Pumps whose characteristics are given in table I-52 are used to pump the concentrated sulfuric acid and blend.

TABLE I-52. CHARACTERISTICS OF PUMPS

(1) Тип насоса	(2) Производительность м ³ /ч	(3) Напор жидкости м	(4) Скорость вращения вала об/мин	(5) Необходимая мощность двигателя кВт
15Kh-6L	5,4-14,4	20-12	1,5-1,9	2,8-4,5
2Kh-9L	14,4-32,4	20-13	2,0-2,5	2,8-4,5
2Kh-6L	18,2-34,2	34-20	4,0-5,0	5,5-10,0
3Kh-9L	28,8-54,0	35-27	7,5-9,0	10-18
4Kh-12L	65-108	40-30	12,5-15,5	20-28
5Kh-18L	108-180	35-28	18-20	28-40

- Key:
1. Type of pump
 2. Output, m³/h
 3. Pressure of liquid, m
 4. Rate of shaft rotation, rpm
 5. Necessary power of engine, kW

Cooler of oil of vitriol. The housing of the coil cooler is made of carbon steel and is lined with acid-resistant brick. The pipes of the coils are lead or made of ferrous metals.

Concentration of Nitric Acid Using Magnesium Nitrate Melt

Industry also uses concentrated nitric acid with magnesium nitrate melt⁸⁸⁻⁹¹ as the dehydrating agent.

The equilibrium conditions of the system $\text{HNO}_3\text{-H}_2\text{O-Mg(NO}_3)_2$ make it possible during heating to obtain high concentrations of HNO_3 in the vapor phase. The presence of magnesium nitrate in aqueous solutions of nitric acid drastically alters the composition of the azeotropic mixture of nitric acid and water towards a reduction in HNO_3 concentration. As a consequence, its content in the vapor phase becomes considerably greater^{3,92} than during distillation of the binary system $\text{HNO}_3\text{-H}_2\text{O}$.

The new method of concentrating nitric acid with the help of magnesium nitrate melt is based on these properties of the $\text{HNO}_3\text{-H}_2\text{O-Mg(NO}_3)_2$ system.

The technological and design makeup of the process are reduced to the following. In roughly the middle of the concentration column, heated (or cold) diluted nitric acid is fed. At the same time (several plates higher), 72-74% magnesium nitrate melt $\text{Mg}(\text{NO}_3)_2$ is introduced. The $\text{HNO}_3:\text{Mg}(\text{NO}_3)_2$ ratio is maintained in limits of 1:5-1:7, depending on the concentration of original nitric acid.

The lower part of the concentration column is connected with two shell-and-tube boilers that can be heated by steam with pressure of 13-14 atm. Circulation of the mixture of nitric acid and magnesium nitrate through the boiler makes it possible to supply heat to the column which is needed for occurrence of the processes of distillation in it (in the lower and middle parts of the column) and rectification (in the upper part). A temperature of 160-170°C is maintained in the lower part of the column. Rectification is conducted at 135-140°C.

The vapors of HNO_3 and H_2O that are formed in the column are washed with a fresh solution of magnesium nitrate that additionally arrives at one of the upper column plates. The vapors emerging from the column are condensed at normal temperature in the water cooler with the formation of production acid (98% HNO_3 and higher). A small part of this acid in the form of reflux is sent to the upper plate of the column. Its main quantity is removed to the storehouse.

The spent solution of magnesium nitrate that contains roughly 64-69% $\text{Mg}(\text{NO}_3)_2$ and 0.2-0.3% HNO_3 is continually removed from the cube part of the column for stabilization in the vacuum-evaporator.

The formed liquor-tanned vapors come from the evaporator for condensation in the cooler of the sprinkling type or the barometric condenser. The condensate that is obtained in this case and contains 1-2% HNO_3 is used to feed the absorption column or towers in the production of diluted nitric acid.

All the main apparatus (column, acid preheater, cooler-condensers) are made of ferrosilide. The boilers and evaporator are made of stainless steel. The original raw material for producing mag-

magnesium nitrate melt is burned magnesium or magnesium carbonate which are easily dissolved in 47-56% nitric acid.

TABLE I-53. SOLUBILITY OF MAGNESIUM NITRATE IN WATER³

(1) Температура °C	(2) Плотность насыщенного раствора g/cm ³	(3) Содержание Mg(NO ₃) ₂ g/100 g раствора	(4) Твердая фаза
-5	1.092	12	Лед (5)
-15	1.202	22.7	"
-25	1.268	28.5	"
-31.6	1.302	32.3	Mg(NO ₃) ₂ ·9H ₂ O
-20	—	35.3	То же (a)
-33	—	—	Mg(NO ₃) ₂ ·6H ₂ O
-8	—	37.5	То же (b)
+1	1.365	38.5	"
+15	1.379	40.4	"
50	1.422	45.8	Mg(NO ₃) ₂ ·6H ₂ O
75	1.454	50.3	То же (b)
60	—	66.5	"
55.6	—	67.4	Mg(NO ₃) ₂ ·2H ₂ O
40.5	—	67.5	То же (b)
100	—	71.7	"
130	—	82.0	Mg(NO ₃) ₂
186	—	84.6	То же (b)

Key:

1. Temperature, °C
2. Density of saturated solution, g/cm³
3. Mg(NO₃)₂ content, g/100 g of solution
4. Solid phase
5. Ice
6. The same

TABLE I-54. DENSITY OF AQUEOUS SOLUTIONS OF MAGNESIUM NITRATE⁹³ (in g/cm³)

(1) Температура °C	(2) Концентрация нитрата магния, вес. %								
	58	58	60	62	64	66	68	70	72
90	1.500	1.539	1.565	1.591	1.616	1.642	1.667	1.694	1.718
100	1.495	1.533	1.559	1.584	1.609	1.635	1.660	1.685	1.710
110	1.489	1.528	1.553	1.579	1.605	1.630	1.656	1.681	1.707
130	—	—	1.543	1.568	1.593	1.618	1.644	1.668	1.696
150	—	—	—	—	—	1.608	1.631	1.657	1.682

Key:

1. Temperature, °C
2. Concentration of magnesium nitrate, weight. %

The described method of concentrating the diluted nitric acid has a number of advantages over the method in which sulfuric

acid is used as the water-removing agent.⁹¹ The most important advantages of the new method include lower net cost of processing the diluted nitric acid (roughly by 7-10%) and the lack of harmful admixtures in the exhaust gases.

Tables I-53-I-57 present certain data on aqueous solutions of magnesium nitrate.

TABLE I-55. VISCOSITY OF AQUEOUS SOLUTIONS OF MAGNESIUM NITRATE⁹³ (in centipoise)

Температура °C	Концентрация MgNO ₃ , вес. %							
	60	62	64	66	68	70	72	75
100	13,8	19,0	26,3	36,2	50,0	74,0	115,0	—
110	10,8	14,4	19,7	27,2	37,6	52,0	74,0	—
120	8,7	11,5	15,4	20,8	28,2	38,0	53,0	—
130	7,3	9,4	12,5	16,5	21,7	28,5	39,5	65,0
140	—	—	—	13,4	17,4	22,8	30,0	47,0
150	—	—	—	—	14,1	18,4	24,0	35,0

Key:

1. Temperature, °C
2. MgNO₃ concentration, weight. %

TABLE I-56. VAPOR PRESSURE ABOVE AQUEOUS SOLUTIONS OF MAGNESIUM NITRATE³ (in mm Hg)

(1) Температура °C	(2) Содержание Mg(NO ₃) ₂ %	(3) Давление паров	(1) Температура °C	(2) Содержание Mg(NO ₃) ₂ %	(3) Давление паров
25	41,94	12,45	45	45,05	33,22
35	43,04	21,38	50	41,94	49,95
40	45,05	25,45	50	45,05	42,88

Key:

1. Temperature, °C
2. Mg(NO₃)₂ content, %
3. Vapor pressure

The specific heat capacity *c* of the aqueous solutions of Mg(NO₃)₂ at 18-19°C (*n*—number of moles of dissolved Mg(NO₃)₂ in 1 l of solution) are presented below:

n..... 112.2 53.91 20.49
c, kcal/(kg x deg)... 0.92 0.85 0.758.

TABLE I-57. SOLUBILITY OF MAGNESIUM NITRATE* IN AQUEOUS SOLUTIONS OF NITRIC ACID AT 25°C

(1) Содержание г/100 г насыщенного раствора		(2) Твердая фаза	(1) Содержание г/100 г насыщенного раствора		(2) Твердая фаза
HNO ₃	Mg(NO ₃) ₂		HNO ₃	Mg(NO ₃) ₂	
0.0	42.5	Mg(NO ₃) ₂ ·6H ₂ O То же ⁽³⁾ » » »	41.0	36.7	Mg(NO ₃) ₂ ·2H ₂ O То же
28.1	22.1		58.4	25.6	
45.4	13.2		84.4	9.4	»
40.9	34.3		91.0	4.7	Mg(NO ₃) ₂
39.6	36.0		99.6	6.2	То же

Key:

1. Content g/100 g of saturated solution
 2. Solid phase
 3. The same
- *Boiling point of ~74% Mg(NO₃)₂ melt equals 175°C.

TABLE I-58. FREEZING TEMPERATURE OF BLEND³

(1) Состав смеси, вес. %			(2) Плотность при 26°C г/см ³	(3) Температура замерзания °C
HNO ₃	H ₂ SO ₄	H ₂ O		
87.97	7.38	4.67	1.5176	-48
91.16	6.89	1.95	1.5215	-46
64.60	14.25	21.15	—	(4)Ниже -80
68.40	9.50	22.10	—	-42

Key:

1. Composition of blend, weight. %
2. Density at 26°C, g/cm³
3. Freezing temperature, °C
4. Below

Preparation of Blend

The blend is a mixture of concentrated nitric and sulfuric acids and is prepared according to GOST 1500-57 or according to the specifications agreed upon with the consumer. In order to prepare the blend, the concentrated nitric acid is fed by centrifugal pump from the storage tank into the mixer. Then the necessary quantity of concentrated sulfuric acid is added. The mixture of acids is circulated by a pump in the mixer for roughly 30 min., then the obtained blend is poured into the storage tank.

According to GOST 1500-57, the blend must correspond to the following requirements:

Content, % no less	
HNO ₃	89
H ₂ SO ₄	7.5
Nitric oxides (N ₂ O ₄), % no more	0.3
Calcined residue, %, no more	0.1

Storage and Transporting of Nitric Acid, Sulfuric Acid and Blend

The storehouse of concentrated nitric acid and blend is located on an open platform or under an awning. Railroad tracks must be laid along the storehouse and the platform must be equipped for emptying tank cars. The pumping facilities for pumping the acids are placed in a building or under an awning.

The concentrated sulfuric acid is stored in unlined tanks of varying capacity that are made of carbon steel. Sulfuric acid of lower concentration, as well as the blend are stored in steel tanks lined with ceramic materials. The storehouse of weak nitric acid (up to 60% HNO₃) is made of stainless steel. Concentrated nitric acid is stored in vessels made of aluminum.

Acids are shipped long distances in railroad tank cars with carrying capacity from 12 to 60 t. Diluted nitric acid is sent to the small consumers in glass bottles. Concentrated nitric acid in individual cases is poured into aluminum barrels with capacity of 100-120 kg. It is forbidden to ship concentrated nitric acid in barrels and bottles by railroad.

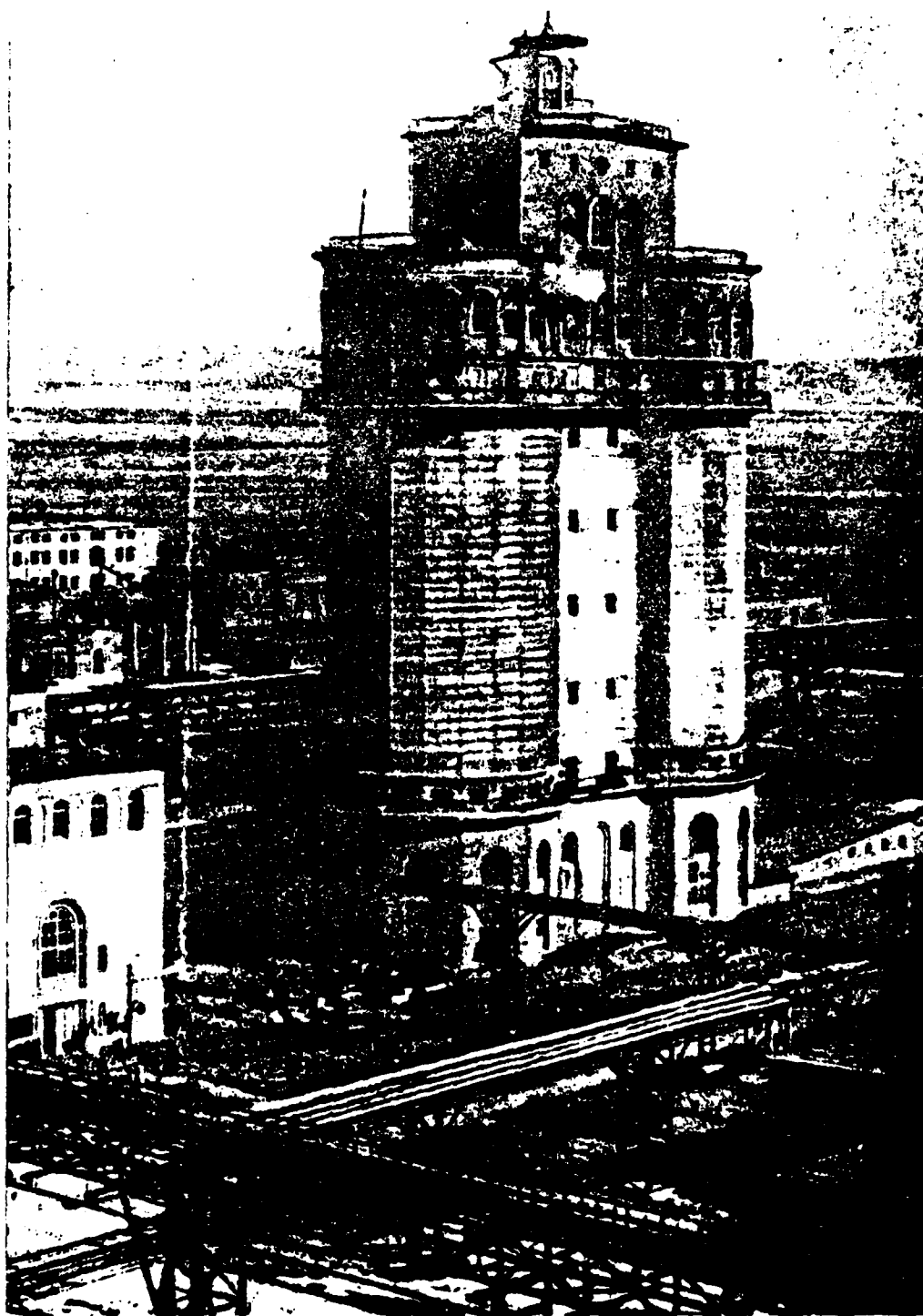
If the tank cars are contaminated, before filling they are cleaned in a separate washing area. The tank cars for diluted nitric acid are made of stainless steel, and those for concentrated nitric acid are made of aluminum. Those for the blend and oil of vitriol (concentrated sulfuric acid) are made of carbon steel.

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II. Production of Nitrogen Fertilizers

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General Information

Because of the increasing needs of mankind for food products and the acute need to increase the fertility of soils, the world production of mineral fertilizers is developing at relatively high rates that significantly exceed the average rates of growth of other industrial products.

The rates of development of the mineral fertilizer industry are especially significant in the USSR (2-fold higher than in the capitalist and developing countries). In 1958, the Soviet Union produced 12 million T of mineral fertilizers (in conventional units), 31.3 million T in 1965 (average annual increase of 14.7%), 35.8 million T in 1966, and 43.4 million T in 1968. In the next 5 years, the USSR plans to increase the output of mineral fertilizers to 48 million T. The highest rates of increase are planned for 1969 and 1970 during which our country should start up new shops and plants with total output of about 13 million T of fertilizers per year (average annual increase in 1966-1970, 15.8%).

The dynamics for the production of mineral fertilizers in the capitalist and developing countries is illustrated by the following figures (in million T):

Nutrients	1958-1959	1965-1966	Average annual increase %
Nitrogen (N)	7.92	14.87	9.4
Phosphorus (P ₂ O ₅)	7.78	12.13*	6.5
Potassium (K ₂ O)	5.61	9.31*	7.5
Total	21.31	36.31	7.9
*Estimate (approximate data)			

It is apparent from these data that the rates of growth in output of nitrogen fertilizers is higher than potassium, and especially phosphorus fertilizers. In recent decades, the percentage of nitrogen fertilizers in the modern structure of the world production of mineral fertilizers has drastically risen. Thus, in 1965-1966, the ratio of nutrients (N:P₂O₅:K₂O) in the mineral fertilizers produced in the capitalist and developing countries was respectively

1:0.8:0.63. Judging from the predictions for 1970-1975 and subsequent years, the percentage of nitrogen fertilizers in the world production of mineral fertilizers will increase even more.

The structure of production of nitrogen fertilizers in the USSR is presented in volume I of the Reference Book for the Nitrogen Industry Worker (p. 9).

Below is the structure for world production of nitrogen fertilizers for 1959-1965 (in %):

Fertilizers	Years					
	1959-1960	1960-1961	1961-1962	1962-1963	1963-1964	1964-1965
Ammonium nitrate	28	28	28	29	29	29
Ammonium sulfate	26	26	23	21	19	18
Carbamide	6	8	8	9	10	11
Potassium nitrate	5	4	4	4	3	3
Sodium nitrate	3	2	3	2	2	2
Calcium cyanamide	3	3	2	2	2	2
Other nitrogen fertilizers						
solid	11	12	13	14	15	15
liquid	18	19	19	19	20	20

*Including ammonium sulfate-nitrate and lime-ammonium nitrate.

One can draw the conclusion from here that ammonium nitrate (including lime-ammonium nitrate) continues to remain the main nitrogen fertilizer. The percentage of ammonium nitrate is especially considerable in the total volume of production of nitrogen fertilizers in the Soviet Union, and its leading role will be maintained in the next 10 years.

The percentage of ammonium sulfate in the world production of nitrogen fertilizers is noticeably dropping. The USSR only produces ammonium sulfate as a side product from coking coals and the synthesis of caprolactam.

There is a steady increase in the production of carbamide. The scales of its production have risen most significantly in the

USSR, United States and Japan. For example, in the last two countries, the volume of carbamide production in 1960 was respectively 666,000 and 660,000 t , and in 1966 increased to 1,615 and 1,504 million t . In the Soviet Union, the production of carbamide during this period rose 29-fold. Its percentage as concentrated fertilizer will increase in future years in the balance of nitrogen fertilizers, but at slower rates. One should note the general trend towards a transition to producing more concentrated fertilizers which is characteristic both for the nitrogen industry of the USSR and as a whole for the domestic industry of mineral fertilizers. The nitrogen concentration in nitrogen fertilizers produced in the USSR in 1965 was 33%.

Liquid fertilizers occupy second place in the world production of nitrogen fertilizers. The United States makes extensive use of liquid fertilizers. This country in 1964 used 56% of the production of fixed nitrogen in the form of liquid fertilizers (liquid ammonia and ammoniates). The production of ammoniates in the United States primarily used ammonium nitrate and carbamide. Ammonia water is used on insignificant scales as a nitrogen fertilizer.

The consumption of liquid nitrogen fertilizers in the United States is characterized by the following data (in thousand t of nitrogen):

(1) Годы	(2) Жидкий аммиак (82% N)	(3) Аммониады (30-50% N)	(4) Аммиачная вода (20-25% N)	(5) Всего
1959-1960	507,0	144,0	88,0	739,0
1960-1961	616,0	255,0	77,0	948,0
1961-1962	707,2	343,4	99,2	1141,5
1962-1963	884,2	438,4	102,2	1424,8
1966-1967	1803,5	786,6	156,7	2726,8

Key:

1. Years
2. Liquid ammonia (82% N)
3. Ammoniates (30-50% N)
4. Ammonia water (20-25% N)
5. Total

The United States also manufactures liquid complex fertilizers, triple with percentage ratio of $N:P_2O_5:K_2O$ equal, for example, to 8:16:8; 10:10:10; 5:10:10, and double, containing N and P_2O_5 in ratios of 8:24; 12:36; 10:15 etc. However, the quantity of nitrogen that is used in the form of liquid complex fertilizers is very small in the balance of U.S. nitrogen fertilizers. For example, in 1966-1967, only 7% of the complex fertilizers were used in the liquid form.

Liquid fertilizers, both nitrogen and complex, are produced in other countries in very small quantities. The large percentage of liquid fertilizers in the world production of nitrogen fertilizers is therefore due to the large-scale production of them in the United States. By the end of the current five-year plan, the Soviet Union plans a noticeable rise in the consumption of liquid ammonia as a fertilizer, except for ammonia water.

In contrast to the United States, the West European countries (FRG, England, France, Italy) produce triple and double solid complex fertilizers in large quantities. In 1964-1965, 30.5% of the nitrogen fertilizers in these countries were produced in the form of complex fertilizers. The United States and Japan also manufacture ammonia phosphates as complex fertilizers (ammophos, diamphos, etc.) which contain over 60% nutrients (N and P_2O_3). The United States used 32.9% fixed nitrogen total in the form of complex (complex and mixed) fertilizers in 1966-67.

Japan has begun production on an industrial scale of slowly assimilated carbamide-formaldehyde fertilizers and ammophoska which includes carbamide-formaldehyde complexes.

The Soviet Union plans in the near future to primarily develop the production of concentrated complex and mixed fertilizers. Consequently, a more significant part of the production of fixed nitrogen will be used in the form of complex fertilizers. Part of the one-sided (single) fertilizers, including the nitrogen, is currently used to produce fertilizer mixtures. It is planned in the future

to introduce at a number of plants new methods for producing complex-mixed and mixed fertilizers and to set up production of single and complex fertilizers for dry fertilizer mixing. In this case, all the nitrogen fertilizers will be produced in noncaking forms.

1. Ammonium Nitrate

Physical-Chemical Properties of Ammonium Nitrate

Ammonium nitrate NH_4NO_3 in the pure form is a white crystal substance (molar weight 80.043) which contains 60% oxygen, 5% hydrogen and 35% nitrogen in ammonia and nitrate forms. The technical product has a white color with yellowish hue and contains no less than 34.2% nitrogen.

The main physical and chemical properties of ammonium nitrate are presented below:

Density, g/cm^3	1.69-1.725	Heat	
Bulk density, g/cm^3 of freely poured granules (1% moisture content, 20°C; particles 1-2 mm) with dense packing of particles	0.8262	of melting, kcal/kg	16.2
Temperature, °C melting	169.6-170.4	of formation from simple substances (at 18°C and 1 atm.), kcal/mole	87.2
decomposition	over 190	Coefficient of heat con- ductivity (at 0-100°C), kcal/(m x h x deg)	0.205

The specific heat capacity of the ammonium nitrate \bar{c} (in kcal/(kg x deg)) depending on the temperature, changes as follows:

t, °C	-100	0	10	20-28	100	82-124
\bar{c}	0.306	0.397	0.396	0.422	0.428	0.426

The angles α of rest of ammonium nitrate with varying relative humidity E of the air and temperature 10-30°C have the following values:

E, % α°	At 10°C			At 20°C				At 30°C			
		50	60	70	40	50	60	70	30	40	50
	36	36	38.5	36	36.5	37	45	34	35	37	37

Ammonium nitrate can be crystallized in five different modifications (I, II, III, IV, V) as well as in the metastable form with area of transition¹ in the temperature interval 44-57°C. Polymorphous transformations of crystals (transition of one crystal modification into another) are accompanied by a change in the density and organic chemistry of the crystals and the release of a different quantity of heat (tables II-1, II-2).

Crystals of ammonium nitrate of rhombic shape which are stable at temperatures from -16.9 to +32.3°C do not cake and are the best form of nitrate when it is used as a fertilizer. At a temperature above 32.3°C, the ammonium nitrate crystals increase in volume.

TABLE II-1. CRYSTAL MODIFICATIONS OF AMMONIUM NITRATE²⁻⁴

Modifications	Temperature of stability of crystal modifications, °C	Density of crystals ρ g/cm ³
Cubic (I)	169.6-125.2	-
Tetragonal (II)	125.2-84.2	1.69(84.2°C)
Rhombic or monoclinal (III)	84.2-32.3	1.66(32.3°C)
Rhombic bipyramidal (IV)	from +32.3 to -16.9	1.725?
Tetragonal (V)	below -16.9	1.725 } ρ _{ср}

TABLE II-2. HEATS OF CONVERSIONS OF MODIFICATIONS OF AMMONIUM NITRATE²⁻⁴

1 Преобразование	2 Температура °C	3 Теплота преобразования ккал/г
Расплавленная соль ⇌ I . . .	169.6	16.75
I ⇌ II	125.2	12.24
II ⇌ III	84.2	4.17
III ⇌ IV	32.3	4.99
IV ⇌ V	-16.9	1.6

Key:

1. Conversions
2. Temperature, °C
3. Heat of conversion, cal/g
4. Melted salt

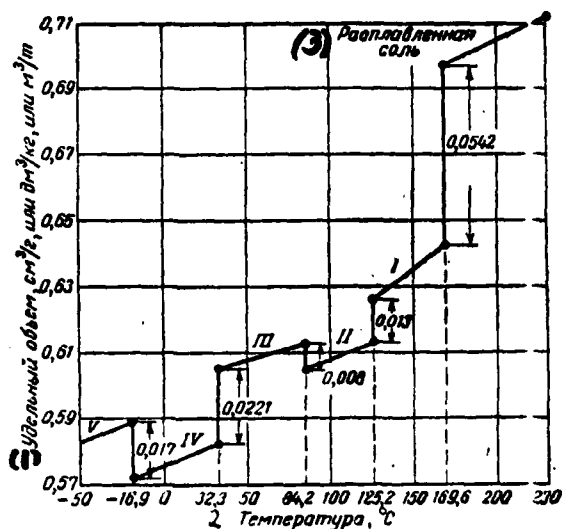


Figure II-1. Dependence of Specific Volume of Crystals of Ammonium Nitrate on Temperature

Key:

- I. Cubic modification (regular)
- II. Tetragonal
- III. Rhombic or monoclinial
- IV. Rhombic bipyramidal
- V. Tetragonal
1. Specific volume cm^3/g or in^3/kg , or m^3/t
2. Temperature, °C
3. Melted salt

The dependence of the specific volume of crystal modifications of ammonium nitrate on the temperature is presented in fig. II-1.

Ammonium nitrate is a strong oxidizer of a number of inorganic and organic compounds. It reacts intensively with certain substances that are in a molten state (for example, with sodium nitrite melt) all the way to explosion.

If gaseous ammonia is passed over solid ammonium nitrate, then a very mobile liquid is rapidly formed, ammoniate (compounds of the type $2\text{NH}_4\text{NO}_3 \times 2\text{NH}_3$ or $\text{NH}_4\text{NO}_3 \times 3\text{NH}_3$).

Ammonium nitrate dissolves well in water (table II-3), in ethyl and methyl alcohols, pyridine, acetone and liquid ammonia.

TABLE II-3. SOLUBILITY OF AMMONIUM NITRATE IN WATER⁴

(1) Температура °C	(2) Растворимость NH ₄ NO ₃		(1) Температура °C	(2) Растворимость NH ₄ NO ₃	
	(3) кг/кг воды	(4) г/100 г раствора		(3) кг/кг воды	(4) г/100 г раствора
0	1,198	54,49	90	7,718	88,53
5	1,343	57,31	95	8,748	89,74
10	1,497	59,96	100	9,942	90,86
15	1,676	62,63	105	11,470	91,98
20	1,872	62,18	110	13,300	93,01
25	2,085	67,59	115	15,700	94,01
30	2,333	70,00	120	18,880	94,97
32,5	2,443	70,98	125	23,390	95,90
35	2,557	71,88	125,6	24,450	96,07
40	2,802	73,70	130	28,400	96,61
45	3,077	75,48	135	33,130	97,07
50	3,388	77,21	140	40,500	97,59
55	3,727	78,84	145	52,180	98,11
60	4,107	80,42	150	64,380	98,47
65	4,536	81,94	155	94,230	98,95
70	5,006	83,35	160	148,300	99,33
75	5,555	84,74	165	356,100	99,72
80	6,183	86,08	169,6	∞	100,00
85	6,898	87,34			

Key:

1. Temperature, °C
2. Solubility of NH₄NO₃
3. kg/kg of water
4. g/100 g of solution

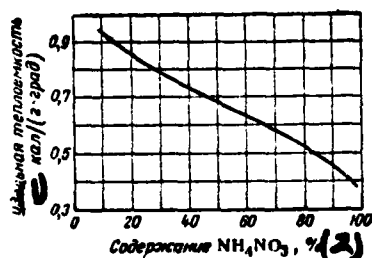


Figure II-2. Heat Capacity of Aqueous Solutions of Ammonium Nitrate at 25°C

Key:

1. Specific heat capacity cal/(g x deg)
2. Content of NH₄NO₃, %

Ammonium nitrate is dissolved in water with absorption of a large quantity of heat, therefore with an increase in temperature, the solubility of NH₄NO₃ considerably rises. When ammonium nitrate is dissolved in an equal volume of water, the temperature of the solution diminishes roughly by 25°C, for example from 15°C to -10°C.

With increased humidity and temperature of the air, the volume of ammonium nitrate increases roughly 1.5-fold.

Great efforts are required to crush completely dry particles

TABLE II-4. DENSITY OF AQUEOUS SOLUTIONS OF AMMONIUM NITRATE OF VARYING CONCENTRATION

(2) See page 17

(3) See Appendix 5, H₂NO₃, sec. 5.

Temp. °C	Concentration of NH ₄ NO ₃ , weight %									
	10	20	30	40	50	60	70	80	90	100
10	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
15	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
20	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
25	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
30	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
35	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
40	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
45	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
50	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
55	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
60	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
65	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
70	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
75	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
80	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
85	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
90	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
95	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075
100	1.030	1.035	1.040	1.045	1.050	1.055	1.060	1.065	1.070	1.075

Key:
 1. Density g/cm³
 2. Temperature, °C
 3. Concentration of NH₄NO₃, weight %

[table continued on next page]

Table with multiple columns of numerical data, likely representing a ledger or account book. The table is oriented vertically on the page and contains several rows of numbers.

TABLE II-6. BOILING POINT OF AQUEOUS SOLUTIONS OF AMMONIUM NITRATE⁵

(1) Концентрация вес. %	(2) Давление, мм рт. ст.	(3) Температура кипения °C	(4) Концентрация вес. %	(5) Давление, мм рт. ст.	(6) Температура кипения °C	(7) Концентрация вес. %	(8) Давление, мм рт. ст.	(9) Температура кипения °C
58.0	168.8	74.5	84.7	463.2	120.8	96.9	648.0	189.8
	366.8	93.2		763.2	137.8		756.6	196.0
	461.8	99.2		176.0	95.6		164.0	143.5
	766.8	112.8						
62.6	161.0	74.0	91.92	575.8	146.5	97.3	292.0	167.0
	250.8	84.5		148.0	98.0		470.0	186.2
	750.8	115.9		200.0	108.0		572.0	193.5
	70.0	144.4		74.0	94.99		470.0	140.6
256.4		88.0	570.0	148.1		457.2	187.6	
356.4		97.0	156.0	118.0		587.2	198.2	
756.4		120.2						240.6
75.6	151.0	77.6	96.9	340.6	145.2	98.57	186.0	172.5
	251.0	92.3		540.6	163.0		249.6	191.5
	351.0	101.7		740.6	176.0		309.6	199.5
	451.0	109.0		176.6	139.8		649.6	219.0
84.7	180.0	90.8	96.9	240.0	151.5	98.57	749.6	226.0
	263.2	104.2		421.0	173.5			

Key:

1. Concentration, weight. %
2. Pressure, mm Hg
3. Boiling point, °C

TABLE II-7. PRESSURE OF WATER VAPORS ABOVE SOLUTIONS OF AMMONIUM NITRATE²

(1) Температура °C	(2) Давление мм рт. ст.	(3) Концентрация g/100 g воды	(4) Температура °C	(5) Давление мм рт. ст.	(6) Концентрация g/100 g воды
10	6.45	147	70	84.9	498
15	8.55	165.5	80	115.4	580
20	11.25	187	84.2	130.3	614
25	14.7	212.5	90	143.0	716
30	19.0	242.5	95	156.5	803
40	29.2	293	100	169.4	890
50	42.95	352	105	183.4	978
60	61.1	421	—	—	—

Key:

1. Temperature, °C
2. Pressure, mm Hg
3. Concentration g/100 g of water

saturated nitrate solution, then it will dry up. The pressure of the water vapors in the air in rare cases is equal to their pressure above the saturated nitrate solution. In this case, an equilibrium state occurs the nitrate does not absorb or give off moisture.

TABLE II-8. SURFACE TENSION σ OF SATURATED AQUEOUS SOLUTIONS OF AMMONIUM NITRATE⁶ (in dyne/cm)

t, °C	σ	t, °C	σ	t, °C	σ	t, °C	σ
-10	85.2	40	87.8	80	88.0	140	86.0
0	86.0	50	88.0	90	87.8	150	86.5
10	86.9	60	88.0	100	87.5	160	85.2
20	87.4	70	88.0	120	86.8		
30	87.6			130	85.5		

Hygroscopicity of ammonium nitrate (or other hygroscopic salts) is characterized by so-called hygroscopic point, the ratio of pressure of the saturated water vapor above the solution of the given substance to the pressure of water vapor that saturates the air at the given temperature (i.e., the relative air humidity at which the substance does not lose water and does not absorb it from the air). The pressure of the water vapors that saturate the air changes very strongly depending on the temperature.

The hygroscopic points of ammonium nitrate (in %) have the following values:

Hygroscopic point, %	75.3	69.8	66.9	62.7	59.4	52.5	48.4
Temperature, °C	10	15	20	25	30	40	50

It follows from these data that a moist and warm climate is very unfavorable for storing ammonium nitrate.

The only factor which can be regulated in order to reduce the rate of vapor absorption is the size of the salt surface.⁸ The larger the salt particles, the smaller its surface. However, the presence of large particles creates conditions for the penetration of air into the mass of the salt, and consequently, a larger surface participates in the process of moisture absorption. It can be considerably reduced if the particles of ammonium nitrate are covered by hydrophobic film.^{8,9}

For several years the Soviet Union has been covering ammonium nitrate with paraffin mazut in order to reduce the rate of absorption of moisture from the air. The results of this treatment of the

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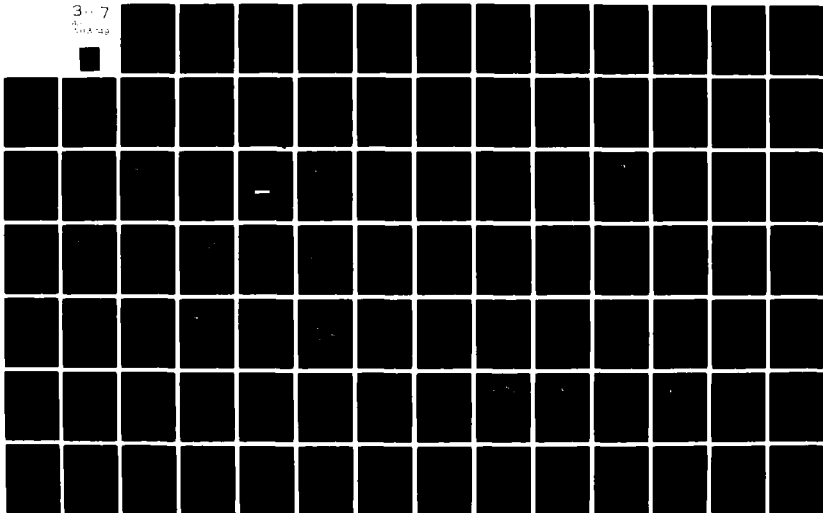
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product have been quite satisfactory¹⁰, since the rate of moisture absorption from the air was drastically reduced, but this procedure was not safe and it had to be abandoned.

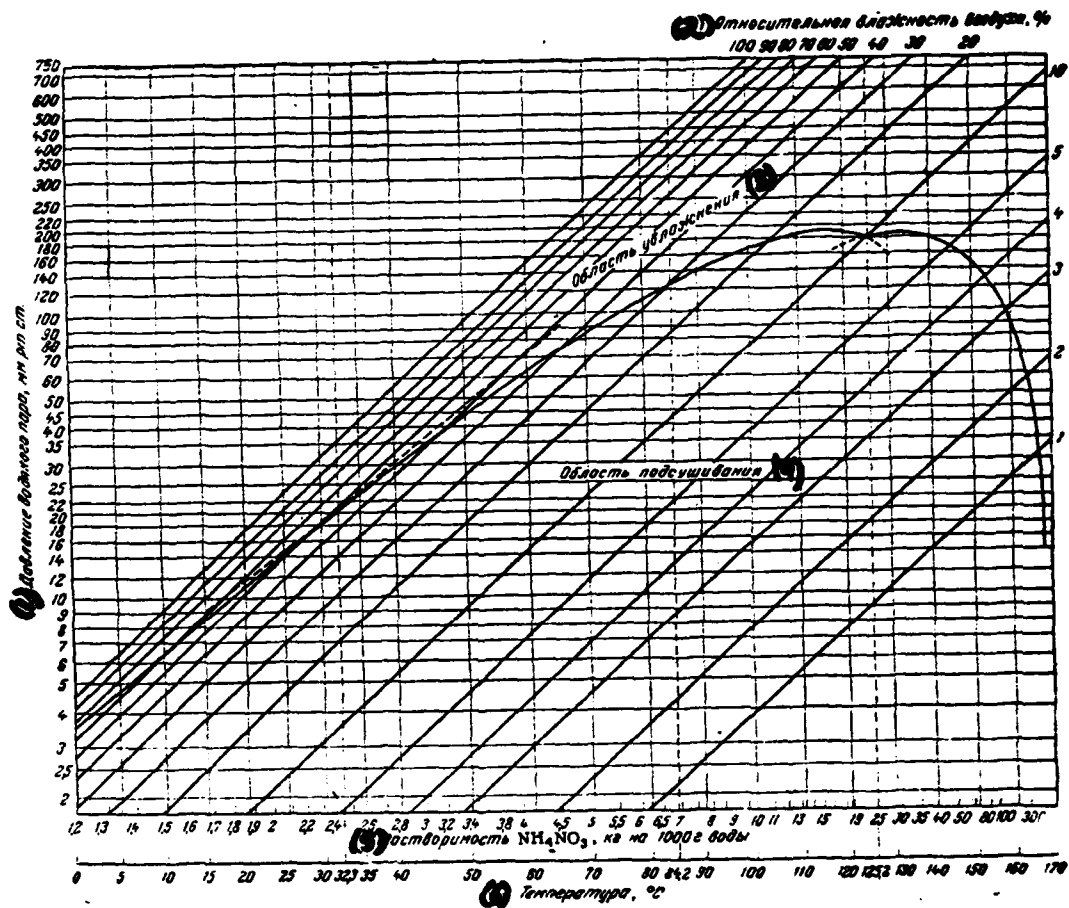


Figure II-3. Nomogram to Determine the Equilibrium Pressures of Water Vapor above Saturated Solutions of Ammonium Nitrate Depending on the Temperature and Air Humidity

Key:

1. Pressure of water vapor, mm Hg
2. Relative air humidity, %
3. Region of wetting
4. Region of drying
5. Solubility of NH_4NO_3 , kg per 1000 g of water
6. Temperature, °C

Figure II-3 presents a nomogram to determine the equilibrium pressures of water vapor above the saturated solutions of ammonium nitrate with different temperatures and air humidity.² The nomogram

shows equilibrium relative air humidity, whose temperature equals the temperature of ammonium nitrate. In addition, regions are isolated of drying and wetting of the solid ammonium nitrate.

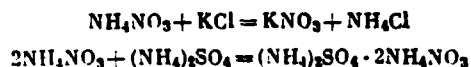
By knowing the hygroscopic point of ammonium nitrate (or correspondingly the pressure of the vapors above its saturated solutions), one can, by starting from the average meteorological data on temperature and pressure of the air vapors, determine the degree of absorption of moisture or drying of the salt at any time of the year and in different climate regions.

The rate of absorption by ammonium nitrate of moisture from the air with an increase in its temperature is drastically increased. Thus, at 40°C, the rate of moisture absorption from the air is 2.1-fold greater than at 23°C.

It has been established that mixing of ammonium nitrate with superphosphate, precipitate, potassium chloride, ammonium chloride, ammonium sulfate and other substances makes it possible to improve the friability of the finished products to a greater or lesser degree. However, the hygroscopicity of these mixtures remains high.¹¹ The hygroscopic points of the mixtures of ammonium nitrate with certain salts (at 30°C) are given below:

Mixture of salts (molar ratios)	Hygroscopic point, %
NH_4NO_3	59.4
$\text{NH}_4\text{NO}_3 + (\text{NH}_4)_2\text{SO}_4$	62.3
$\text{NH}_4\text{NO}_3 + \text{KNO}_3$	59.9
$\text{NH}_4\text{NO}_3 + \text{NH}_4\text{H}_2\text{PO}_4$	58.0
$\text{NH}_4\text{NO}_3 + \text{NH}_4\text{Cl}$	51.4
$\text{NH}_4\text{NO}_3 + \text{NaNO}_3$	46.3
$\text{NH}_4\text{NO}_3 + \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{NH}_4\text{Cl} + \text{NaNO}_3$. .	42.2
$\text{NH}_4\text{NO}_3 + \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. .	28.2
$\text{NH}_4\text{NO}_3 + \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	23.5
$\text{NH}_4\text{NO}_3 + \text{CO}(\text{NH}_2)_2$	18.1

Somewhat better results are reached in mixing or alloying ammonium nitrate with salts that chemically interact with it, for example:



Granulation of ammonium nitrate also results in a decrease in the rate of moisture absorption by the salt from the air. The granulated ammonium nitrate has a smaller surface than the fine crystalline product, and therefore absorbs the moisture from the air at a slower rate. The hygroscopicity of the ammonium nitrate is one of the reasons for its caking.

Caking

Ammonium nitrate cakes strongly and loses friability during storage, and under certain conditions is even converted into a monolithic mass that is difficult to pulverize. A lot of labor has to be expended to crush 1 t of this nitrate before it is added to the soil.

The addition of certain inorganic additives to ammonium nitrate makes it possible only to reduce its caking, but does not make it possible to obtain fertilizer that meets the requirements of agriculture for friability.

In order to obtain ammonium nitrate which would maintain for a long time 100% friability, a new technological plan has been worked out. It stipulates procedures that make it possible to prevent caking of the finished product for no less than 6 months of storage under different climate conditions.

The caking of ammonium nitrate is due to many reasons^{7-10,12,14-21,23} of which the chief are:

- increased moisture content in the finished product;
- heterogeneity and mechanical weakness of the particles;
- change in the crystal modifications of the salt;
- hygroscopicity.

The particles of ammonium nitrate of any shape that were obtained according to the previously active production plans contained 0.8-1% moisture in the form of mother liquor (saturated). The NH_4NO_3 content in this solution corresponds to the solubility of salt at the temperatures of loading it into the container. When the nitrate cools, the mother liquor passes into the supersaturated state, and if there is a further drop in temperature, salt crystals 0.2-0.3 mm in size precipitate out of the supersaturated solution. These new crystals link the previously unbound salt particles, as a consequence of which the nitrate is converted into a caked mass.

The number of crystals released from the mother liquor as the salt temperature changes can be judged from the data presented in figure II-4. For example, with cooling of the salt that when put into the container has 1% moisture, from 70 to 10°C, about 40 kg of new crystals precipitate out for every ton of finished product.

It follows from here that the lower the moisture content of the product and the lower its temperature when packed into the container, the lower the caking of the salt will be with other conditions equal.

Ammonium nitrate is manufactured in the form of round particles (granules), less often in the form of flakes, as well as in the form of small crystals. Nitrate particles of any shape are generally nonuniform. Granules have the most regular shape, however, even among them there is occasionally a large number of particles of unequal shape, especially hollow granules that are distinguished by low mechanical strength. These granules are crushed already under slight pressure.

When granulated nitrate that is packed in containers is stored in stacks 2.5 m high each, the salt is exposed to great pressure under its own weight. As a result of this, the nitrate particles are crushed. They contain an increased quantity of moisture and form dust. It compacts the nitrate mass and increases its caking.

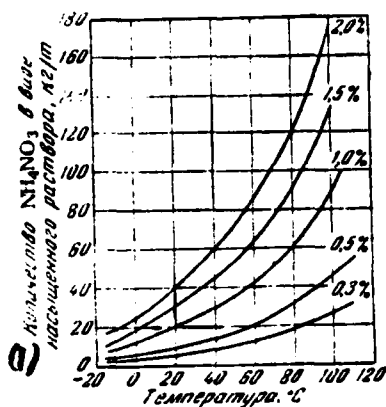


Figure II-4. Quantity of NH_4NO_3 Contained in Form of Saturated Solution in Finished Product with Varying Temperature and Moisture Content from 0.3 to 2%.

- Key:
1. Quantity of NH_4NO_3 in form of saturated solution, kg/100g
 2. Temperature, °C

Practice has demonstrated that the presence of hollow particles in the granulated ammonium nitrate and their destruction rapidly accelerate the caking process. In this case, "inoculation" of the mass of fairly strong particles with fragments of crystals seems to occur. It has been established that the hollow granules are exposed to recrystallization to the greatest degree.

Mutual transitions of crystalline modifications of ammonium nitrate under the influence of temperature changes should be considered one of the important reasons for its caking. As noted (p. 174) the modification transformations of the crystals are accompanied by changes in their structure, density and other properties of the ammonium nitrate which influence the friability of the product.

One of the five crystal modifications of ammonium nitrate that exists at a temperature below 32.3°C, as indicated above, is essentially noncaking.

At the previously active productions of ammonium nitrate, the salt was loaded into a container at a temperature not below 50°C in the summer. The salt temperature was only lower in the winter and with cooling of the product in apparatus with a fluidized bed (see (p. 228)). Under these temperature conditions, the modification

transformations of the nitrate crystals are inevitable with an increase in the caking. The force of the compressed caked granulated ammonium nitrate that is loaded into the container at temperatures above 32°C rises strongly. This can mainly be explained by the modification transformations that occur when salt that has a high temperature and increased humidity is loaded into the container.

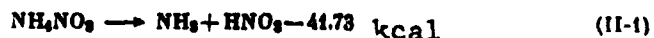
The hygroscopicity that is inherent to ammonium nitrate severely promotes its caking. With a change in the pressure of the water vapors in the air depending on the geographical zone, season and even day, the ammonium nitrate is wetted or dries up since the container (paper sacks) is air-permeable. The caking is influenced especially strongly by the absorption by the salt of the moisture in the air. The saturated solution that is formed in the upper layer of the nitrate gradually penetrates into the space between the granules, then through the pores and capillaries passes into the mass of the salt. With a further drop in temperature of the surrounding medium, processes begin to occur which increase the caking of the ammonium nitrate (see above).

In order to reduce the effect of hygroscopicity of the nitrate on its caking, the most effective measure is packing the product in a hermetically sealed container, for example, in polyethylene bags.

Other methods are also used to reduced caking,²² in particular, the addition to the nitrate of such additives as products of nitric acid breakdown of dolomites (DLM additive)¹⁹ or apatite or phosphorite powder (RAP, REM additives)^{12,23}.

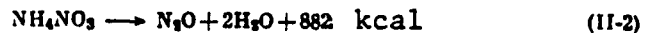
Thermal Breakdown

During lengthy heating, solid ammonium nitrate initially melts, and at 110-150°C begins to dissociate:



The rate of this reaction at atmospheric pressure is low.

Ammonium nitrate breaks down with further heating:

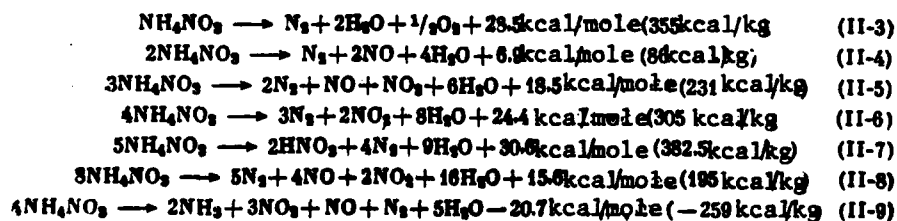


According to the data of some researchers, this reaction begins at 170-190°C, and according to others, at 210°C.

It is thought that thermal breakdown of ammonium nitrate occurs successively in the following stages:²⁴ hydrolysis (dissociation) of the salt, thermal breakdown of the nitric acid that is formed in hydrolysis, interaction of the oxides of nitrogen and ammonia obtained in the first two stages.

With intensive heating of the ammonium nitrate to 220-240°C, its breakdown in individual cases can cause a flash of the melted salt mass. The presence of moisture in the ammonium nitrate has a very strong effect on the composition of gases formed during its thermal breakdown. Thus, when dry nitrate is heated to 220°C, the gas phase contains 71.2% N₂O, 2.5% O₂ and 26.3% of other components. When moist nitrate is heated to 220°C, the gas phase has 45% N₂O, 13% NO, 10% NH₃, 6.12% O₂ and 28-35% N₂.

The breakdown of ammonium nitrate can also occur according to the following reactions²⁴:



The breakdown of ammonium nitrate is considerably intensified when it is heated in the presence of nitric, hydrochloric and sulfuric acids, certain organic substances (for example, oil, paraffin) and many metals in powder state (zinc, copper, etc.). Ammonium nitrate in the form of a melt does not react with iron, tin or aluminum. In the presence of substances that increase the sensitivity of ammonium nitrate, the temperature of its breakdown

drops, in particular in the presence of oil and chlorides in NH_4NO_3 solutions that can be concentrated by evaporation.

The tendency of ammonium nitrate to break down under the influence of high temperatures is significantly reduced in the presence of calcium and magnesium nitrates, limestone dust, tricalcium phosphate and especially carbamide.

Thermal breakdown of ammonium nitrate with an increase in pressure (to a certain limit) can be intensified. Under pressure of about 6 atm and corresponding temperature^{24a}, the entire mass of melted nitrate is rapidly broken down. In order to prevent (or suppress) breakdown of nitrate at high temperatures, regardless of the presence or absence in the salt of the substances listed above, it is most effective to maintain an alkaline medium when concentrating NH_4NO_3 solutions by evaporation.

Ammonium nitrate is not very sensitive to jolts, impacts, friction and sparks, and only explodes under the influence of a strong detonator, during thermal breakdown in a closed, limited volume or during heating of densely caked nitrate. The process of breakdown can end with an explosion as a consequence of secondary reactions in the gas phase.²⁵

When nitrate interacts with certain reducers (copper, sulfides, pyrite etc.), ammonium nitrite is formed. In its presence the possibility of nitrate explosion drastically rises. With an increase in the particle size of ammonium nitrate, its sensitivity to explosion is very reduced.

Losses of ammonium nitrate during its thermal breakdown are comparatively low. For example, when a melt is produced that contains 98.5-99% NH_4NO_3 , in an industrial evaporator under high temperature conditions, the following losses of nitrate because of its thermal breakdown are observed:

Temperature, °C	230	215	200
Losses, %	0.5	0.25	0.15

Taking into consideration that under certain conditions, ammonium nitrate can explode, strict observance of the established safety rules is required during its production, storage and transporting.

The inflammability of ammonium nitrate is a consequence of the release from it at moderately high temperatures of oxygen. It increases the intensity of the flame. Certain easily oxidized metal powders (for example, zinc) when they come into contact with moist ammonium nitrate can ignite it. Organic or other oxidizing substances that are impregnated with ammonium nitrate or are in contact with it rapidly burn when ignited.

The mixtures that contain superphosphate, ammonium nitrate and organic products can ignite spontaneously as a consequence of the occurrence of oxidizing reactions in this case. They begin even at normal temperatures. A temperature of about 290°C is required to ignite pure ammonium nitrate.

Paper bags or barrels in which there is ammonium nitrate can spontaneously ignite even under the influence of solar rays. It is categorically forbidden to store these bags and barrels; they should be burned.

When the container with ammonium nitrate catches fire, nitric oxides and vapors of nitric acid are released. There are known cases²⁵ of spontaneous ignition of the bags with ammonium nitrate in railroad cars when they are not sufficiently cleaned of coal dust or residues of pyrite. These fires develop most often when uncooled ammonium nitrate (70-90°C) is loaded into the cars in paper sacs.

Spontaneous breakdown and inflammation of the ammonium nitrate are autocatalytic processes. Only water puts out the fires. The production of ammonium nitrate is fire- and explosion-dangerous.

Quality of Ammonium Nitrate

GOST 2-65 stipulates that two brands of ammonium nitrate be produced: brand A, crystalline and flaky nitrate (for industry), and brand B, granulated nitrate (for agriculture and industry).

Table II-9 presents the basic requirements for the quality of ammonium nitrate.

TABLE II-9. REQUIREMENTS FOR QUALITY OF AMMONIUM NITRATE (GOST 2-65)

Indicators	Brands	
	A	B
Content of nitrate and ammonia nitrogen in dry substance, % no less		
in conversion for NH_4NO_3	99.5	97.7
in conversion for nitrogen	34.8	34.2
Content of additives in dry substance, %, no less		
phosphates in conversion for P_2O_5	Missing	0.5
or calcium and magnesium nitrates in conversion for CaO	Missing	0.3
Moisture content, %, no more	0.5	0.4
Substances insoluble in water, % no more	0.5	Not defined
Substances that can be oxidized by potassium permanganate	Sample withstands testing by standard technique	The same
Reaction of solution	Neutral	Neutral or slightly alkaline (not more than 0.05% NH_3) or slightly acid (not more than 0.02% HNO_3)
Friability, % no less	Not determined	100
Granulometric composition, %		
granules size 1-3 mm, no less	-	90
granules smaller than 1mm, no more	-	6
Temperature at packing, °C no higher	-	30

Ammonium nitrate of brand B which is designed for use in industry can contain 0.5-1.2% phosphates (in conversion for P_2O_5), 0.3-0.6% calcium and magnesium nitrates (in conversion for CaO) and

no more than 0.2% of substances that are insoluble in 10% nitric acid.

The plants that manufacture ammonium nitrate with phosphorus-containing additives are permitted to produce brand B products with content of no less than 96% NH_4NO_3 , and no less than 33.6% nitrogen.

The friability of nitrate brand B is guaranteed by the manufacturing plant for 6 months when the product is transported and stored under the appropriate conditions.

Determination of friability. The control check of the friability of ammonium nitrate is performed by single throwing of five bags with the product flat from a height of 1 m, and subsequent sifting on sieves 1100 x 700 mm in size with height of the side 120 mm. The sieves are made of steel wire grids (stainless steel) with square cells with inside dimension of 5 mm (GOST 3826-47). The bag contents are screened on the sieve in two procedures. Before each screening operation, the sieve is filled to side height of no more than 60 mm. It is permitted to have a residue on the sieve of individual pieces that are easily crushed by hand.

The control check of friability of ammonium nitrate is performed at the manufacturing plant at the end of the 6-month storage period. This check does not free the manufacturer of responsibility for claims against the quality of the nitrate made by the consumers.

Different rapid methods are currently being developed for determining the caking of nitrate that are planned for introduction into industrial practice.

Determination of granulometric composition. In order to determine the granulometric composition of ammonium nitrate, it is screened on a special instrument that is installed on a wooden panel 550 x 360 mm in size. The sieves are tightly attached to the moving platform with a clamp. They are actuated with the help of a worm or belt gear from an electric motor.

The moving platform is placed on three support eccentrics that together with it are actuated by a guide eccentric. The sieves must make 150 ± 3 rockings in 1 min. The movement of the platform must be smooth, without jerks.

The granulometric composition is determined as follows: 250 g of granulated nitrate that is weighed with accuracy of ± 0.5 g is screened for 2 min. on stamped sieves with cells 3 and 1 mm in size (GOST 214-57). It is allowed to screen by hand with the same intensity for 2 min. The residues on the sieves with cells 3 and 1 mm in size and the particles which pass through the sieve with cells 1 mm in size are weighed separately.

The percentage content of individual fractions of granules is computed according to the formula:

$$x = \frac{g \times 100}{250}$$

where g is the weight of the fraction, g.

Production of Ammonium Nitrate

The basic raw material for the production of ammonium nitrate is: gaseous ammonia (moisture content no more than 1%; admixtures of oil, catalyst dust, etc. are not permitted) and diluted nitric acid (47-49% and 56-58%; the presence of over 0.2% nitric oxides).

The production of ammonium nitrate also uses ammonia-containing gases, wastes from the synthesis of ammonia or carbamide (p. *R216* and following). A sample composition of these gases is given in table II-10.

When low-caking and water-resistant ammonium nitrate (p. *R159* and following) is produced, the preparation of the additives requires: dolomite (32-33% CaO, 43-44% CO₂, 16-19% MgO, no more than 2.5% SiO₂, no more than 0.5% Al₂O₃ and no more than 0.7% Fe₂O₃ with saturation density of 2 T/m³); apatite concentrate (GOST 3277-54); phosphorite powder (TU 1494-49, bulk density 1.68-1.7 T/m³);

sulfate (GOST 6981-54); sulfuric acid 92-94% (GOST 2184-65); aliphatic acids and mixtures of them with paraffin (table II-11).

The enterprises that manufacture ammonium nitrate by the new technological plan (p.152*) use a talcum-magnesia mixture supplied according to temporary specifications in order to dust the granules.

TABLE II-10. COMPOSITION OF AMMONIA-CONTAINING GASES (In %)

1 Компоненты	2 Танковые газы	3 Продувочные газы	4 Газы дистилляции плава карбамида
NH ₃	57-60	7-8	54-56
H ₂	25-27	55-60	—
N ₂	8-9	28-20	—
CH ₄	9-3,5	10-11	—
Ar	1-0,5	2-1	—
CO ₂	—	—	33-35
H ₂ O	—	—	13-9

Key:

1. Components
2. Tank gases
3. Blow-through gases
4. Gases of distillation of carbamide melt

TABLE II-11. CHARACTERISTICS OF ALIPHATIC ACIDS AND THEIR MIXTURES WITH PARAFFIN

Indicators	Aliphatic acids	Mixtures of paraffin and aliphatic acids (1:1)
Consistency at 20°C	Solid	Solid
Color	Dingy yellow	
Ether number, mg KOH	9	72
Nonsaponifiable compounds, %	4	-
Temperature, °C		
of melting	50	56
of solidification	47	46
of flash (according to Brenken)	213	195
Conventional viscosity, °CV	1.73 (at 100°C)	1.23 (at 90°C)
Water content, %	0.045	0.043
Mechanical admixtures, % no more	0.046	-
Moisture	Missing	

The process of ammonium nitrate production consists of the following basic stages:

- 1) production of solutions of nitrate by neutralizing the

*This refers to the Russian pg 195

nitric acid by gaseous ammonia or ammonia-containing gases;

- 2) concentration by evaporation of solutions of ammonium nitrate until a melt is obtained;
- 3) crystallization of salt from the melt in the form of granules of spherical shape, small crystals or flakes;
- 4) cooling or drying of the salt;
- 5) packing of the finished product in a container.

In the production of low-caking or water-resistant ammonium nitrate there also are stages of producing additives. Certain plants also screen the salt and dust it.

Production of Solutions of Ammonium Nitrate

When the normal operating regime is observed, the reaction



occurs without the formation of by-products.

The thermal effect of this reaction depends on the concentration and temperature of the nitric acid (fig. II-5) and the temperature of the gaseous ammonia or ammonia-containing gases^{2,26,27}. The thermal effect of the process of neutralization is reduced by the amount of heat of dilution of nitric acid by water and dissolving of ammonium nitrate. Thus, the influx of heat during neutralization is determined by the quantity of heat introduced by the original components (nitric acid and ammonia) and released during the interaction of these reagents. The heat of the neutralization process is removed by the formed solution of ammonium nitrate, is lost into the surrounding atmosphere, and is consumed for the evaporation of water from the solution. With the appropriate apparatus design of this stage of the process, the heat of the neutralization reaction may be sufficient to evaporate almost all the water introduced with the nitric acid.

Figure II-6 shows the dependence of the concentration of obtained solutions of ammonium nitrate on the use of heat released in the process of neutralization and on the concentration of

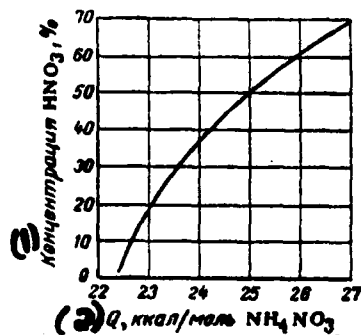


Figure II-5. Dependence of Quantity of Heat Q Released during Formation of NH_4NO_3 on the Concentration of Original Nitric Acid (at 1 atm. and 18°C)

Key: 1. HNO_3 concentration, %
2. Q , kcal/mole NH_4NO_3

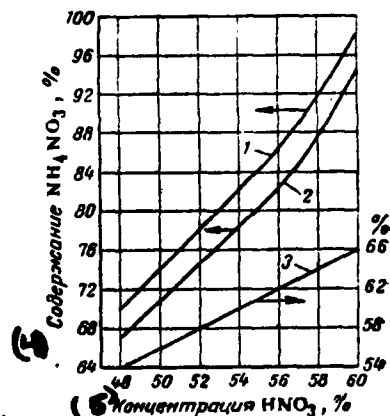


Figure II-6. Dependence of Concentration of Solutions NH_4NO_3 Obtained during Neutralization of HNO_3 by Ammonia on the Concentration of Original Nitric Acid (temperature of ammonia 60°C. loss of heat into surrounding medium 11,000 kcal/T, pressure 1 atm.);

Key: 1. with use of reaction heat. temperature of HNO_3 70°C
2. The same, temperature of HNO_3 30°C
3. without the use of reaction heat
4. Content of NH_4NO_3 , %
5. Concentration of HNO_3 , %

of the employed nitric acid²⁸. Nitric acid whose concentration does not exceed 60% HNO_3 is usually used to obtain solutions of ammonium nitrate. The use of more concentrated acid would result in a considerable increase in the temperature in the neutralizers, and consequently, a noticeable breakdown of nitric acid.

Only the reaction heat of neutralization is currently used²⁹ for partial concentration by evaporation of the solutions of ammonium nitrate. Part of the liquor vapor is used for evaporation of liquid ammonia or warming the gaseous ammonia and nitric acid sent to the neutralization apparatus (concentration of the solution of ammonium nitrate in preheating of the acid by the liquor vapor to 55-60°C is increased by 1.5-2%). Concentration by evaporation

of liquid and preheating of gaseous ammonia used in the production of nitric acid previously required 200-250 kg of live steam per 1 t of production acid.

Industrial units for production of solutions of ammonium nitrate with the use of the neutralization reaction heat are divided into four types:

- 1) units that operate at atmospheric pressure (gage pressure of liquor steam is 0.25-0.3 atm.);
- 2) units that operate with the use of a vacuum-evaporator;
- 3) units that operate under increased pressure;
- 4) combined units that operate under pressure in the zone of neutralization of the original components and with rarefaction in the zone of separation of liquor steam from the solution (melt) of ammonium nitrate.

Domestic industry produces solutions of ammonium nitrate with the use of reaction heat in systems of neutralization that operate under atmospheric pressure, and in systems with self-evaporation of the solution during rarefaction in a vacuum-evaporator. The most popular is the first system of neutralization. It is simple in technological operation and design and is distinguished by stability of the operating pattern.

Neutralization with a vacuum-evaporator is only used in individual cases if it is necessary to refine the blow-through, tank and other ammonia-containing gases. It is cumbersome and inconvenient to service. The systems of neutralization under pressure of 3.5-6 atm are used abroad. They require a fairly high consumption of electricity to compress the consumed ammonia, comparatively complicated regulation of the nitric acid feed under pressure, etc. This plan was used many years ago in the Soviet Union, but was abandoned because of the listed shortcomings.

The USSR does not use combined units, but similar domestic plans have been developed.³⁰

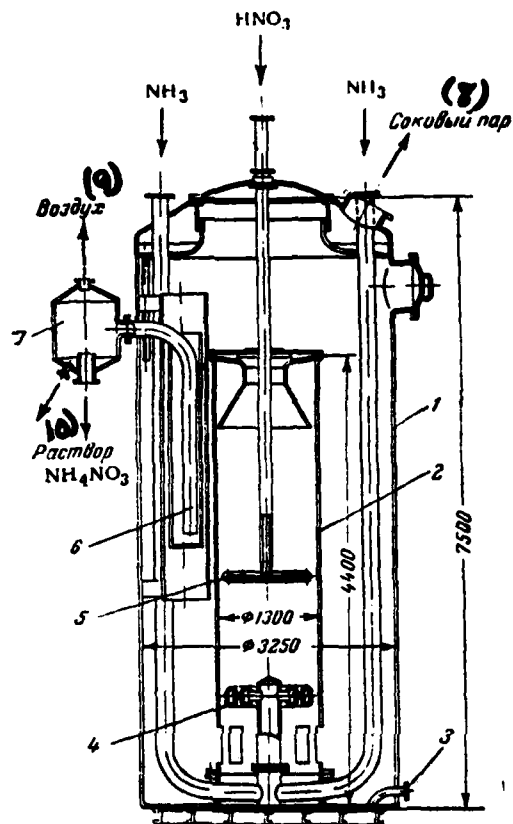


Figure II-7. Neutralization Apparatus ITN with Natural Circulation of Solution

Key:

1. Cylindrical tank
2. Inner cylinder (vessel)
3. Connecting pipe for discharge of solution (during repair or inspection of apparatus)
4. Device for supplying ammonia
5. Device for supplying nitric acid
6. Hydraulic gate
7. Separator
8. Liquor steam
9. Air
10. Solution

Industry uses neutralizer apparatus employing the reaction heat and operating at atmospheric pressure with natural circulation of the solutions.³¹ Nitric acid and ammonia interact in these units in the liquid phase under a certain hydrostatic pressure of the liquid

column. This prevents boiling up of the solutions and formation of a foggy ammonium nitrate. A number of changes were made in the original design of the neutralization units in the course of many years. Now the units with natural circulation of the solutions* differ little from each other.

The ITN units now used guarantee the minimum time for interaction of the nitric acid and ammonia and the production of solutions of ammonium nitrate with assigned temperatures.

The neutralization units that operate under atmospheric pressure consist of ITN units and auxiliary units, final neutralizers-mixers, collectors and others.

The ITN unit is shown in fig. II-7.

The characteristics of the frequently employed ITN units are:

Diameter, m	3.25	2.4
Height, m	10.15*	7.63**
Diameter of inner vessel, m	1.3	1.0
Output, T/day NH_4NO_3	650-700	450

*with final neutralizer

**without final neutralizer

The inner cylinder 2 (vessel) is the neutralization part of the apparatus in which a reaction occurs between the nitric acid and the ammonia. Liquor steam is additionally released in the ring space between the outer and inner cylinders (circulation-evaporation part of the apparatus) from the solution. Intensive circulation of the liquid between the neutralization and the circulation-evaporation parts of the ITN apparatus is created because of the difference in the densities of the solutions in both parts of the unit.

Nitric acid and ammonia are fed to the neutralization part of the ITN countercurrent on pipelines on whose ends there are distribution devices 5 and 4. This makes it possible to create in the ITN

*We will further call all the units that use neutralization heat, ITN units.

unit a large contact surface between the liquid and the gas. The neutralization process occurs at 110-135°C, depending on the concentration of the employed nitric acid and its temperature, as well as on the temperature of the gaseous ammonia. The solution of ammonium nitrate that is formed in vessel 2 flows into the ring space. The absolute pressure above the evaporation mirror of the solutions reaches 1.2-1.3 atm. Consequently, the liquor steam can be used as the heating steam.

It is expedient to conduct the neutralization process in a slightly acid medium since in this case the losses of ammonia, nitric acid and nitrate with the liquor steam are lower than in the slightly alkaline medium. As follows from tables II-12 and II-13. when there is a surplus of nitric acid, the pressure of the HNO₃ vapors above the solutions of ammonium nitrate is lower than the pressure of the ammonia vapors above the NH₄NO₃ solutions.

TABLE II-12. PARTIAL PRESSURE OF STEAM OF NITRIC ACID AND WATER^{2,32} ABOVE NH₄NO₃-HNO₃-H₂O SYSTEM

(1) Концентрация NH ₄ NO ₃ , вес. %	(2) Температура °C	(3) Парциальное давление мм рт. ст.		(1) Концентрация NH ₄ NO ₃ , вес. %	(2) Температура °C	(3) Парциальное давление мм рт. ст.	
		H ₂ O	HNO ₃			H ₂ O	HNO ₃
(4) При концентрации HNO ₃ 0,5%				(5) При концентрации HNO ₃ 1%			
86,2	142,9	764,3	2,5	83,8	136,0	756,5	3,7
				91,3	157,5	739,3	8,5
87,5	132,5	564,7	2,1	96,2	194,5	733,3	24,0
87,7	135,5	544,5	3,2	96,7	195	721,6	43,4
95,5	182,5	542,5	14,8	85,5	139,9	563,6	3,8
91,6	145,8	542,1	5,7	95,0	117,5	541,6	15,8
97,0	179,0	358,4	6,6	96,6	186,0	524,8	30,2
95,7	169,3	348,5	8,8	95,5	173,2	506,2	47,5
92,4	138,5	346,4	1,4	95,0	161,0	341,5	12,5

Key:

1. Concentration of NH₄NO₂, weight. %
2. Temperature, °C
3. Partial pressure, mm Hg
4. With HNO₃ concentration of 0.5%
5. With HNO₃ concentration of 1%

Calculations show² that, for example, with a change in the solution of ammonium nitrate of the content of ammonia from 0.1 to 0.5 g/l, the losses of NH₃ with the liquor steam increase from 2 to 10 kg per 1 t of finished product. If the HNO₃ content in the

TABLE II-13. PARTIAL PRESSURE OF STEAM OF AMMONIA AND WATER ABOVE SYSTEM^{2,32} $\text{NH}_4\text{NO}_3\text{-NH}_3\text{-H}_2\text{O}$

Концентрация, вес. %		(2) Температура °C	(3) Парциальное давление мм рт. ст.		Концентрация, вес. %		(2) Температура °C	(3) Парциальное давление мм рт. ст.	
NH_4NO_3	NH_3		H_2O	NH_3	NH_4NO_3	NH_3		H_2O	NH_3
59.3	9.28	60	39.6	707.9	91.7	0.32	120	281.6	488.6
	7.63		98.9	510.1		0.50		341.1	271.1
	5.63		63.7	394.9		0.23		310.7	154.5
65.9	3.59	80	101.0	205.0	95.4	0.64	130	155.8	592.0
	3.74		146.0	604.5		0.37		288.3	341.3
	3.06		117.6	482.9		0.20		212.9	234.9
	1.06		104.3	347.2		0.18		277.1	172.5
78.2	0.79	70	158.9	137.1	96.3	0.40	150	142.9	624.5
	5.64		50.1	701.0		0.26		171.5	445.3
	4.42		46.2	553.8		0.13		226.9	239.9
85.6	3.06	90	72.1	379.9	97.3	0.48	150	98.0	664.9
	1.79		73.4	228.6		0.45		143.2	606.2
	2.49		48.4	705.2		0.35		116.0	485.0
	1.60		85.7	463.3		0.40		120.4	641.2
86.2	0.75	100	168.3	181.7	97.4	0.27	160	164.8	446.8
	1.82		201.6	547.1		0.31		65.0	695.2
						0.25		98.4	511.8
						0.16		123.2	337.0

- Key:
1. Concentration, weight. %
 2. Temperature, °C
 3. Partial pressure, mm Hg

nitrate solution changes, for example, from 0.2 to 1 g/l, the losses of nitric acid with the liquor steam rise only from 0.4 to 1 kg per 1 t of product. However, at individual plants, the process of neutralization is still conducted in a slightly alkaline medium, since corrosion of the welded seams of the pipelines and equipment significantly increases in a slightly acid medium.

Figure II-8 shows the solubility of ammonia in the solutions of ammonium nitrate.

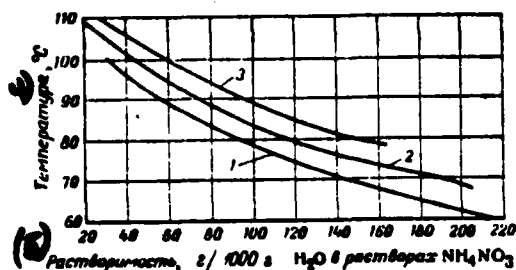


Figure II-8. Solubility of Ammonia in Solutions of Ammonium Nitrate

- Key:
1. in 50% solution of NH_4NO_3
 2. in 60% solution
 3. in 70% solution
 4. Temperature, °C
 5. Solubility, g/1000 g H_2O in NH_4NO_3 solutions

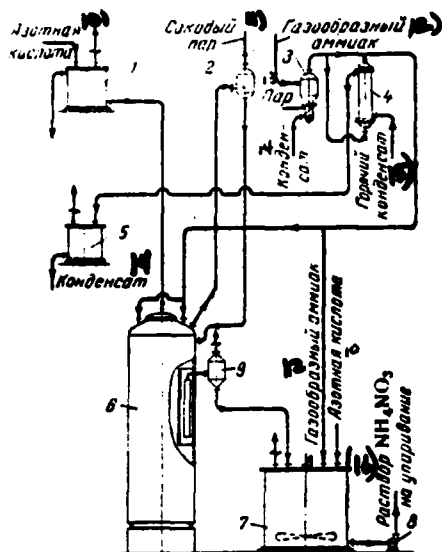


Figure II-9. Plan for the Process of Neutralization at Atmospheric Pressure

Key:

1. Pressure tank for nitric acid
2. Trap of liquor steam
3. Evaporator
4. Preheater
5. Condensate collector
6. Neutralizer
7. Final neutralizer
8. Centrifugal pump
9. Separator
10. Nitric acid
11. Liquor steam
12. Gaseous ammonia
13. Steam
14. Condensate
15. Hot condensate
16. Solution of NH_4NO_3 to concentration by evaporation

The nitric acid used to obtain solutions of ammonium nitrate must be preliminarily blown through with air in order to remove the nitric oxides dissolved in it (permissible content of nitric oxides in the acid is no more than 0.2%).

If the nitric acid is not sufficiently freed of nitric oxides, they form ammonium nitrite with the ammonia. It is broken down in the reaction zone into water and elementary nitrogen. Ammonia losses as a result of this reaction can be considerable, roughly 0.5kg of nitrogen per 1 % of nitrate.

The condensate of liquor steam from the neutralization section is often used to sprinkle the absorption columns in the production of nitric acid. In certain cases, the condensate is purified from admixtures of ammonia and ammonium nitrate on ionites ^{32a}.

The plan for the neutralization unit that operates at atmospheric pressure is shown in fig. II-9.

Nitric acid (sometimes with inorganic additives that reduce the caking of nitrate, p. 157*) goes through the pressure tank 1 that is equipped with an overflow. Gravity flow occurs under constant

*This refers to Russian page

pressure in the ITN unit 6 (in a number of cases, nitric acid is preheated by liquor steam to 55-60°C before being fed into the ITN unit). At the same time, gaseous ammonia is fed here. It preliminarily passes through evaporator 3 a spray of gaseous ammonia and is preheated in unit 4 by steam condensate. The preheaters of ammonia and nitric acid are units of the shell-and-tube type whose characteristics are presented below:

	Ammonia preheater	Acid pre-heater
Diameter of housing, mm	476	600
Diameter of housing, mm	3000 (pipes)	3224 (total)
Length, mm	3504	-
Height, mm	~29	35
Heat exchange surface, m ²	25 x 3	25 x 2
Diameter of pipes, mm	Carbon steel	Steel Kh18N9T
Material		

The ammonium nitrate that is formed in the neutralizer enters the final neutralizer where ammonia or nitric acid is added to create the assigned pH of the medium. The solutions of ammonium nitrate are sent from the final neutralizers for concentration by evaporation. The final neutralizers are also buffer vessels that guarantee continuous operation of the evaporation station in the case of short stoppages of the neutralizers.

The final neutralizer (fig. II-10) is a cylindrical vessel made of stainless steel that is equipped with a blade mixer that rotates at a velocity of 30 rpm. It operates at atmospheric pressure and temperatures of 80-120°C.

Neutralization units with vacuum-evaporator. Production of ammonium nitrate solutions from ammonia-containing gases (tank, blow-through gases or gases of distillation from the carbamide shop) uses a scrubber type neutralizer, vacuum-evaporator and corresponding auxiliary equipment.

Joint processing of the ammonia-containing gases and gaseous ammonia is not efficient, since large losses of the reagents with the liquor steam are possible and since methane, hydrogen and other admixtures are present in the ammonia-containing gases. By bubbling

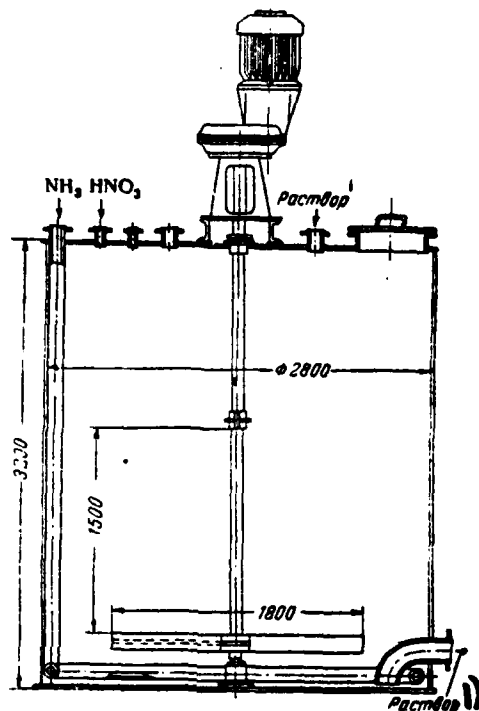


Figure II-10. Final Neutralizer

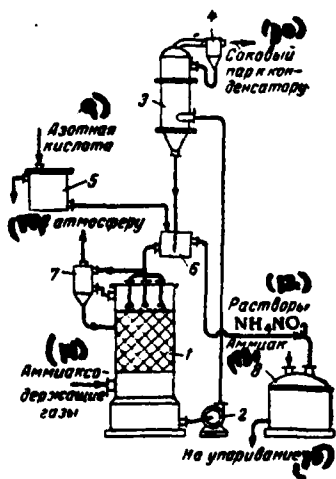
Key:

1. Solution

Figure II-11. One of the Versions of the Plan for the Process of Neutralization with a Vacuum-Evaporator

Key:

1. scrubber-neutralizer
2. pump
3. vacuum-evaporator
4. trap
5. pressure tank
6. hydraulic gate
7. separator
8. collector
9. nitric acid
10. liquor steam to condenser
11. to atmosphere
12. solutions
13. ammonia
14. ammonia-containing gases
15. to concentration by evaporation



ammonium nitrate through the hot solution, these admixtures can

carry away the ammonia, the steam of nitric acid and the ammonium nitrate. In addition, with joint processing of these gases, the possibility of using the liquor steam is excluded because of the presence in it of a fairly large quantity of gaseous admixtures.

One of the versions for the process of reprocessing ammonia-containing gases into ammonium nitrate is shown in fig. II-11. The gases enter the lower part of the scrubber-neutralizer. A solution of NH_4NO_3 which contains a surplus of nitric acid is fed to its upper part.

The circulating solution of nitrate is mixed with the acid in the hydraulic gate of the mixer.

The scrubber type neutralizer for reprocessing the ammonia-containing gases is a cylindrical apparatus 2.4 m in diameter and 5.15 m high. The scrubber has sieve plates which are sprinkled by a mixture of acid and circulating solution. In the top of the scrubber there is an unsprinkled layer of metal or ceramic rings (50 x 50 x 5 mm) which is the settling tank. The velocity of the gas in the free section is 0.4 m/s.

The temperature in the scrubber-neutralizer is maintained at roughly 90°C, i.e., 15-20°C below the boiling point of the formed solution of nitrate. For this purpose, a solution is fed to sprinkle the scrubber which is preliminarily cooled in a vacuum-evaporator. The spent gases come from the scrubber to the sieve washer (sprinkled by condensate and nitric acid) where they are freed of the unreacted ammonia and sprays of the nitrate solution which are carried away from the scrubber. They are then sent for burning or are removed into the atmosphere. A 20-30% solution of ammonium nitrate is obtained in the washer.

According to another version, the solution of ammonium nitrate is sent from the scrubber-neutralizer to the collector from which it is pumped into the vacuum-evaporator or is sucked into it. Rarefaction in the vacuum-evaporator is created by means of condensation

of the liquor steam (washed in the sieve washer) in the barometric condenser and maintained by the vacuum-pump that removes the uncondensed gases into the atmosphere. In the vacuum-evaporator that operates with rarefaction of ~ 600 mm Hg, the solution is concentrated by evaporation roughly to a concentration of 65% NH_4NO_3 and flows into the hydraulic gate-mixer. From here, a large part of the circulating solution, mixed with nitric acid, is returned to the neutralizer. The remaining solution is sent to the final neutralizer where it is mixed with the solution of ammonium nitrate that is obtained in the ITN apparatus. These solutions are processed into a commercial-grade product according to the standard plan (see below).

Below are the indicators for the normal technological operating regime at the stage of production of solutions of ammonium nitrate (with the use of 47-49% nitric acid):

Temperature at inlet to ITN apparatus, °C	
of ammonia	60-80
of nitric acid	not above 50
Temperature of solutions at outlet, °C	
from ITN apparatus	125
from vacuum-evaporator	70-80
from scrubber-neutralizers	90-100
Pressure of gaseous ammonia at inlet to neutralization section, atm.	2.5-3.8
Pressure of ammonia-containing gases at inlet to scrubber-neutralizer, atm.	1.2-3
Pressure of liquor steam at outlet from ITN apparatus, atm.	1.2-1.3
Rarefaction in vacuum-evaporator, mm Hg	560-600
NH_4NO_3 concentration in solution, %, at outlet:	
from ITN apparatus	64-65
from vacuum-evaporator	63-65
from exhaust gas washer	20-30
Content of nitric oxides (in conversion for N_2O_4) in nitric acid, %, no more	0.2
Content of HNO_3 in solutions of ammonium nitrate, g/l, at outlet	
from ITN apparatus	to 1.0
from scrubber-neutralizer	to 10.0
Content of NH_3 in solutions of ammonium nitrate after final neutralizers, g/l	0.1-0.2
Content in liquor steam (until its washing), g/l	
of ammonia	to 0.3
of ammonium nitrate	to 1.5

Concentration by Evaporation of Solutions of Ammonium Nitrate

Depending on the method of crystallization of the product, the design of the evaporation apparatus and the purpose of the finished product, solutions of ammonium nitrate are concentrated by evaporation until the state of a melt of varying concentration. Thus, with crystallization in the granulation towers, the solutions are concentrated by evaporation in final concentration units to a concentration of 99.7-99.9% NH_4NO_3 , and in the evaporation units of old design, to 98.4-98.6% NH_4NO_3 . When crystallized on cooling drum-rollers, the solutions are concentrated by evaporation to a concentration of 97-98% NH_4NO_3 ("cold regime") or to 94-96% NH_4NO_3 ("hot regime"). If the melt is crystallized in dish type units, the solutions are concentrated by evaporation to a concentration of 94-95% NH_4NO_3 .

With an increase in the concentration of solutions of ammonium nitrate during their concentration by evaporation, the temperature of the solution (melt) increases and the losses of NH_4NO_3 with the liquor steam rise. Evaporation units are therefore used which operate with rarefaction of 550-600 mm Hg. This makes it possible to concentrate by evaporation the solutions at reduced boiling points. This promotes a drop in the losses of the product at this stage of its production.

A vacuum is created in the evaporation units as a result of condensation of the liquor steam in the barometric condensers that are sprinkled with circulating water. The uncondensed vapors and air are sucked out of them by rotary vacuum pumps.

Figure II-12 shows the boiling points of solutions of ammonium nitrate at atmospheric pressure and rarefaction. One can determine from this graph that temperature to which the solution has to be heated with the given vacuum in order to obtain a melt with the assigned concentration³³ of NH_4NO_3 .

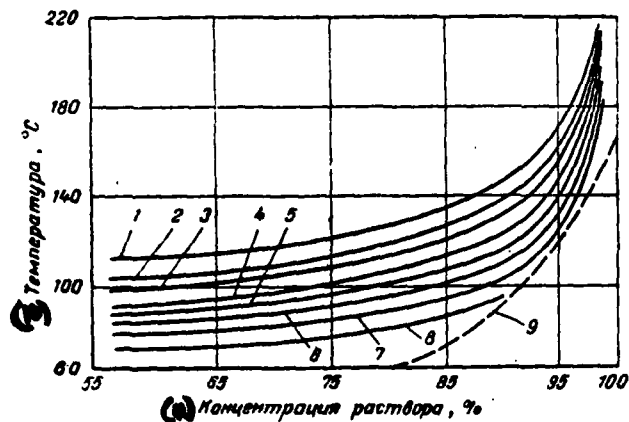


Figure II-2. Boiling Points of Solutions of Ammonium Nitrate at Atmospheric Pressure and Rarefaction

Key:

1. atmospheric pressure
2. rarefaction of 200 mm Hg
3. the same 300 mm Hg
4. the same 400 mm Hg
5. the same 450 mm Hg
6. the same 500 mm Hg
7. the same 550 mm Hg
8. the same 600 mm Hg
9. curve of crystallization of saturated solutions
10. temperature, °C.
11. solution concentration, %

Concentration by evaporation of ammonium nitrate often makes use of a two-stage system of evaporation, less often a three-stage plan in which a certain saving of live heating steam³⁴ is reached. Two-stage concentration by evaporation is done with the calculation that in the first stage of evaporation, the solution concentration is increased roughly to 84% NH_4NO_3 , and in the second stage, to 98.4-98.6% or (when a melt is obtained in the final concentration units) to 99.5-99.7% NH_4NO_3 . The first stage in order to concentrate the nitrate solution by evaporation uses liquor steam from the neutralizers and partially from the evaporation units of the second stage. In order to concentrate the solutions by evaporation in the second stage to the state of a melt, live saturated steam is fed to the evaporation units with pressure of 9 or 13 atm.

If in the production of ammonium nitrate solutions, 54-56% nitric acid is used, for example, their concentration after the

neutralizers reaches 84% NH_4NO_3 . In this case, concentration of the solutions by evaporation to the state of a melt is done in one stage.

Evaporators. The production of ammonium nitrate makes extensive use of evaporators which are shell-and-tube heat exchangers with especially designed separators. The distinguishing feature of these units is concentration of the solutions by evaporation in a fine film (layer) that is moving at a rate of 15-25 m/s and more along the inner surface of the pipes that are heated by the steam. The advantages of the film evaporators include small losses of useful difference in the temperatures because of hydrostatic depression.

The operating principle of the film unit that operates with rarefaction of 600 mm Hg is reduced to the following. At start up, heating steam is first fed into the interpipe space of the boiler, then the solution is collected at 1/4 height of the pipes. Immediately at the inlet to the pipe, the solution starts to boil with the release of a large quantity of steam bubbles. Rising upwards, they take with them the solution that is "creeping" over the walls of the boiler pipes. The steam-liquid emulsion that is formed in this case is discharged at a high rate from the upper part of the pipes into the separator, and hitting the surface of the bent blades here, it acquires a rotating, eddy-like movement. As a result, rapid separation of the liquor steam from the evaporated solution occurs.

An advantage of the film evaporators is also the high coefficient of heat transfer that is due to the small thickness of the layer of solution and the high velocity of its movement ("creeping"), and the single passage of the solution on the boiler pipes. As a result, the ammonium nitrate that is sensitive to increased temperatures is not exposed to breakdown in the process of concentration of its solutions by evaporation.

Solutions of ammonium nitrate of low viscosity are concentrated by evaporation to a concentration of 84% NH_4NO_3 in vertical, less often horizontal evaporators. More viscous solutions--in horizontal

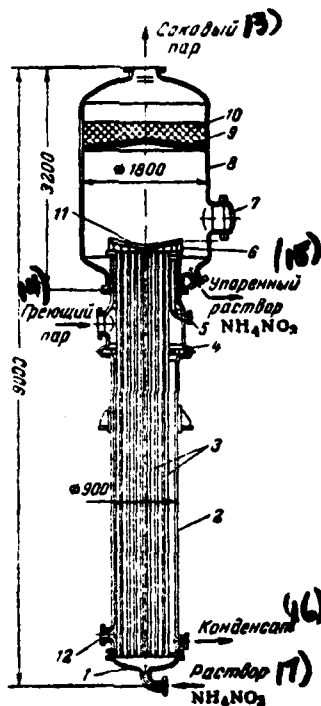


Figure II-13. Evaporator AS-3 of Film Type

Key:

1. Cover
2. Shell-and-tube heat exchanger
3. Boiler pipes
4. Compensator
5. Air pipe
6. Guide blades
7. Manhole
8. Separator
9. Grid
10. Baffle layer of rings
11. Cover of separator
12. Connecting pipe for lower blow-through
13. Liquor steam
14. Heating steam
15. Evaporated solution
16. Condensate
17. Solution

AS units or in vertical film units.

The horizontal evaporators of the second stage are gradually being replaced by vertical that occupy a smaller space. This makes it possible to put so-called final-evaporators (p.162*) in the active shops.

The second stage evaporators are located above the granulation towers. These units consist of 2-4 two-way sections that are installed above each other and connected by connecting pipes. The solution enters the unit from below and passes sequentially through all the sections of the unit upwards. The formed steam-liquid emulsion passes from the upper section into the separator (tangential input of the emulsion is frequent). Here the liquor steam is separated from the melt.

The vertical film evaporator of type AS-3 (fig. II-13) is used most often to evaporate solutions of ammonium nitrate to a concentration of 82-84% NH_4NO_3 . In this case, the liquor vapors from the

*This refers to the Russian page.

ITN unit are used as the heating steam. The evaporator is a vertical shell-and-tube heat exchanger made of stainless steel with a separator that adjoins the upper part of the tube. The tube consists of 900 pipes 32 x 2.5 mm in diameter and 6000 mm long. The heating surface is roughly 500 m². In order to evaporate a 67% solution to 84% concentration of NH₄NO₃, 18-20 m² of heat exchange surface is required for 1 t/h of nitrate.

The steam-liquid emulsion that is formed in the tube emerges into the separator through a central separator which consists of a horizontal cover with guide blades attached along its edges. The drops of liquid that are carried off by the liquor steam are separated by the baffle which is located in the upper part of the separator (grid with metal, less often with ceramic rings).

AS-3 units are also used with heat exchange surface of 400 m² (diameter of the shell 1300 mm, length 6700 mm; tube consists of 590 pipes 38 x 2 mm in diameter and 6000 mm long). Type AS-3 units have been used in recent years to evaporate solutions of ammonium nitrate to the condition of a melt.

The horizontal evaporator AS-2 (fig. II-14) is designed to evaporate solutions to a concentration of 82-84% NH₄NO₃ by liquor steam that is fed into the interpipe space from the ITN unit. It is a unit with two-way tube for the solution without a floating head. Pipes in a quantity of 180 have a diameter of 32 x 2.5 mm and length of 4000 mm. They are rolled into tube grids. The unit, except for the flanges, is completely made of stainless steel and is designed for working pressure of 1.1-1.2 atm. Units are also installed with diameter of the housing 820 mm, length 6200 mm and heating surface 120 m².

The horizontal AS evaporators for evaporation of solutions from a concentration of 82-84% to 98.4-98.6% NH₄NO₃ consist of one or several sections with heat exchange surface of 60 or 120 m² (fig. II-15).

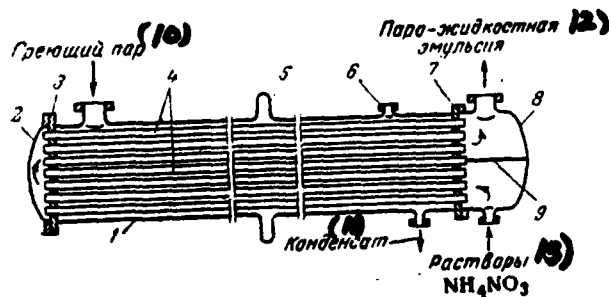


Figure II-14. Horizontal Evaporator AS-2

Key:

1. Housing
2. Rear cover
- 3,7. Pipe grids
4. Pipes
5. Lens compensator
6. Air pipe
8. Front cover
9. Partition
10. Heating steam
11. Condensate
12. Steam-liquid emulsion
13. Solutions

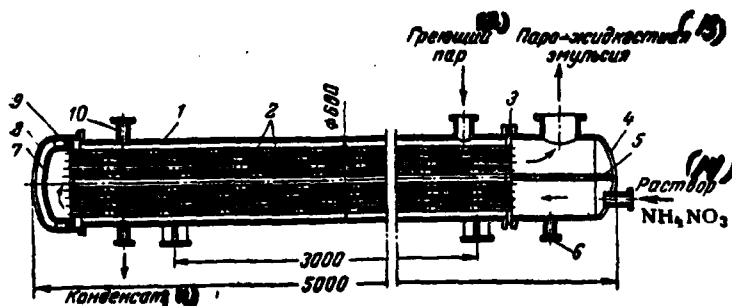
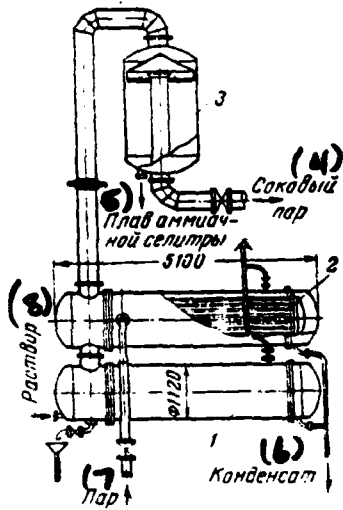


Figure II-15. Section of AS Evaporator

Key:

1. Housing
2. Pipes
- 3,9. Pipe grids
4. Front cover (distributor head)
5. Partition
6. Connecting pipe for solution discharge
7. Cover of floating head
8. Rear cover
10. Air pipe
11. Condensate
12. Heating steam
13. Steam-liquid emulsion
14. Solution

Figure II-16. Evaporation Two-Section AS Unit of Second Stage



Key:

1. First section
2. Second section
3. Separator
4. Liquor steam
5. Melt of ammonium nitrate
6. Condensate
7. Steam
8. Solution

The shell-and-tube unit is two-way for the solution. The tube with heating surface of 120 m^2 consists of 360 pipes 32 mm in diameter. Production of 1 t/h of NH_4NO_3 requires 12.5 m^2 of heating surface.

Figure II-16 shows the evaporation unit of second stage which consists of two sections. Fresh steam is fed parallel to each section. The condensate is removed downwards through the condensation trap (not shown in the figure) and is sent to the expander, from which part of the condensate enters the ammonia preheater of the neutralization section. The steam formed in the expander is also used in the first stage evaporators to evaporate solutions of ammonium nitrate to a concentration of 84% NH_4NO_3 .

In order to obtain 99.5-99.7% melt of ammonium nitrate, vertical shell-and-tube units are used with "falling" film of solution and countercurrent blowing through with hot air (175°C). The heat carrier (steam at pressure of 13 atm.) is fed into the interpipe space. Hot air blows through the pipes from top to bottom and additionally evaporates the melt that is sliding along the inner surface of the pipes, and then is removed into the atmosphere.

The condensers that are used in the production of ammonium nitrate are divided into condensers of mixing and surface condensers.

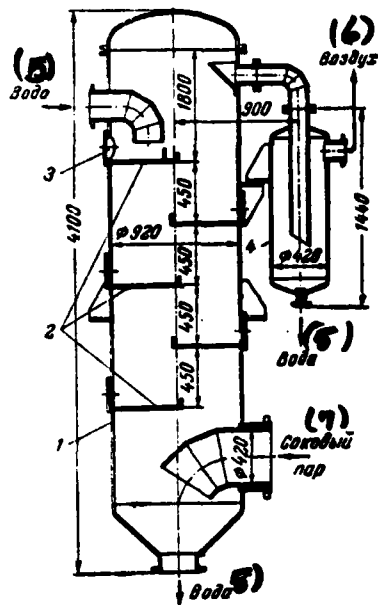


Figure II-17. Barometric Condenser

Key:

1. Housing
2. Floors for water flow
3. Manhole
4. Trap
5. Water
6. Air
7. Liquor steam

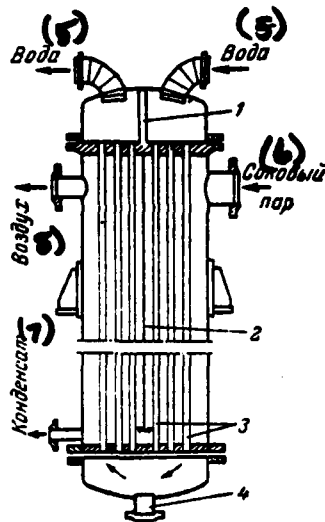


Figure II-18. Surface Condenser

Key:

- 1, 2. Partitions
3. Pipes
4. Connecting pipe for water drainage
5. Water
6. Liquor steam
7. Condensate
8. Air

In the mixing condensers (barometric condensers), the liquor steam is cooled and condensed as a result of mixing with the cooling (industrial) water (fig. II-17). In the surface condensers, the liquor steam and the cooling water are separated by pipe walls (fig. II-18).

The new productions of ammonium nitrate only use surface condensers that are vertical shell-and-tube heat exchangers made of stainless steel. In order to improve the heat exchange conditions, the surface condensers are made two-way (for water). The diameter of the condenser housing is 300 mm, height 4430 mm, diameter of the pipes 25 x 2 mm, total heat exchange surface 125 m².

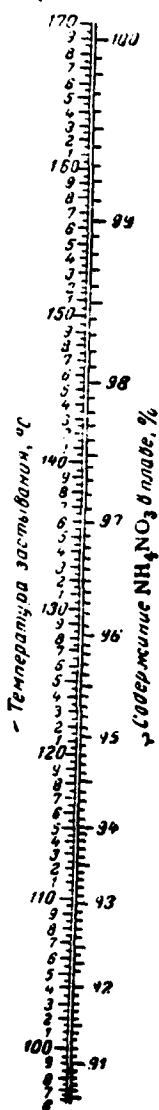


Figure II-19. Nomogram to Determine NH_4NO_3 Concentration in Melt from Temperature of its Solidification

Key:

1. Temperature of solidification, °C
2. NH_4NO_3 content in melt, %

The liquor steam enters the pipes of the surface condensers and the cooling water enters the inter-pipe space. When there are mechanical admixtures in the cooling water (insufficient cleanliness of the water), it is fed into pipes, while the liquor steam is fed into the interpipe space.

Surface condensers require a higher consumption of water than mixing condensers, and their cost is somewhat higher. However, the surface condensers have an important advantage over the mixing condensers: the condensate of liquor steam formed in them can be used for production needs.

When there is a vacuum in the evaporators on the order of 520-550 mm Hg, the losses of ammonium nitrate as a consequence of its removal by the liquor steam is 0.12-0.13% of the total product output. The losses of ammonium nitrate because of its thermal breakdown during evaporation do not exceed 0.03% of the output.

For an approximate evaluation of the NH_4NO_3 content in the melt after the second stage of evaporation, one can use a nomogram (fig. II-19) that is based on the dependence of the solidification point of the melt on the NH_4NO_3 concentration. With an increase in the moisture content in the melt, its solidification point drops.

The indicators for the production regime of the evaporation stage for solutions are presented below:

Temperature, °C	
of liquor steam sent for heating the evaporator of the first stage	105-100
of the steam sent to heat the evaporator of the second stage	170-175
of the water fed to the condensers	25-32; 15-20 (summer) (winter)
Pressure of the heating steam in the evaporators, atm.	
of first stage	1.15-1.2
of second stage	9-13
additional evaporator with falling film	13
Rarefaction in evaporators, mm Hg.	
of first stage	580-600
of second stage	550
NH ₄ NO ₃ concentration at outlet from units, %	
of first stage heated by liquor steam	77-80
of first stage heated by liquor steam with addition of fresh steam	85-86
of second stage	98.4-98.6
of additional evaporator with falling film	99.7-99.9
Temperature of air and melt at outlet from additional evaporator with "falling film", °C	175

Crystallization of Ammonium Nitrate Melt

Depending on the methods of crystallization of the ammonium nitrate melt, a product is obtained in the form of small, partially crushed crystals (dimensions to 0.5 mm), in the shape of dense flakes (plates about 1 mm thick and cross dimension of 3-6 mm), and in the form of spherical granules (diameter primarily 2 mm).

When salt is obtained from an ammonium nitrate melt, a considerable quantity of heat is released because of cooling of the melt, crystallization and recrystallization of the salt. With an increase in the NH₄NO₃ concentration, the quantity of heat that is released during crystallization of the salt from the solutions (melts) is considerably reduced:⁴

Concentration of NH ₄ NO ₃ , weight. %	Quantity of heat, kcal/kg of salt	NH ₄ NO ₃ concentration weight. %	Quantity of heat, kcal/kg of salt
51	57.6	88	36.6
60	55.6	98.4	27.1
64	46.6		

The crystallization temperature of the aqueous solutions of ammonium nitrate are shown in fig. II-20.

Crystallization of nitrate from its melts is done in a unit with complete use of the heat of the process (dish type crystallizers, worm feeders), with partial use of heat (cooling roller drums), and without the use of the heat (granulation towers).

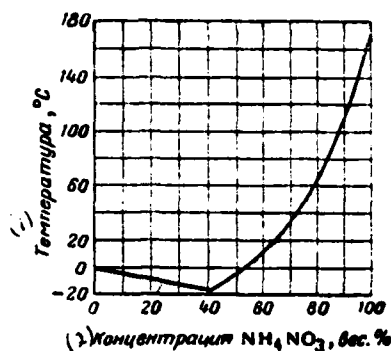


Figure II-20. Crystallization Temperatures of Aqueous Solutions of Ammonium Nitrate

Key:

1. Temperature, °C
2. NH_4NO_3 concentration, weight. %

The dish type crystallizers and the worm-crystallizers are used comparatively rarely in industry because of their cumbersomeness and low output. But these crystallizers have certain merits. Thus, because of the use of the heat released during salt crystallization, one can obtain from the melts with reduced NH_4NO_3 concentration (94-96%) nitrate with moisture content of 0.1-0.2%. The salt is cooled in the dish and worm crystallizers by simple methods to a temperature below 32.3°C. As a consequence, the finished product can maintain its friability for a long time.

The dish type crystallizer is a dish 4.2 m in diameter and 1 m high. The unit is equipped with a planetary mixer and ring pipeline with outlets directed into the dish. A fan feeds air into the ring pipeline. According to the standard plan, the dish crystallizer operates in batches with output of ~ 50 t/day.

The cooling roller drums are continuous units with high output.

The crystallizer drum (fig. II-21) is made of forged pig iron

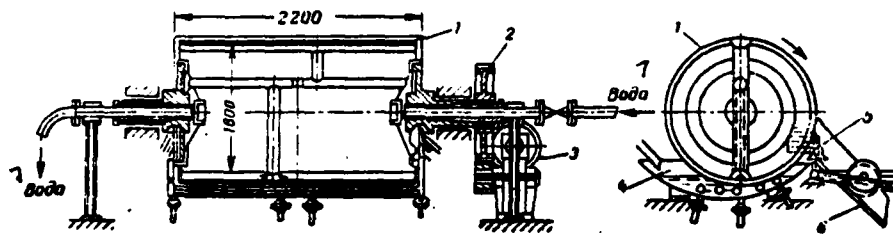


Figure II-21. Drum Crystallizer to Produce Flaked Ammonium Nitrate

Key:

1. Rotating drum
2. Drive gear
3. Reducer
4. Pan
5. Knife
6. Discharge spout
7. Water

addition of 1.5% nickel. The drum diameter is 1.8 m, the length is 2.2 m (sometimes the drums have other dimensions). Within the drum that rotates at a speed of 4-8 rpm, there is a fixed drum of smaller diameter. The drum is actuated by an electric motor through a reducer and gear drive. Flowing cooling water enters the ring space between both drums. It emerges through the hollow shaft and the chambers which are present in the upper half of the inner drum.

Under the drum there is a pan made of stainless steel. The ammonium nitrate melt constantly enters it. The pan is installed so that the drum is submerged into it by no less than 100 mm. In order to maintain the melt temperature in limits of 140-150°C, the pan is heated with the help of steam coils. When the drum rotates, a crust of salt is formed on its surface. This crust is 0.8-1.5 mm thick and is cut by a knife which is attached parallel to the forming drum. In this case, the crust is broken down into agglomerated particles of salt that have the shape of flakes.

The output of the cooling roller depends very strongly on the concentration of melt, intensity of removal of crystallization heat, and the number of drum rotations. The average output of the roller with 5 rpm is from 120 to 150 t/day.

The percentage of ungranulated ammonium nitrate that is obtained in the dish, worm and drum crystallizers is slight as compared to its total output. However, the need for producing a certain quantity of finely-crystallized and flaked product for a number of consumers dictated the updating of the old type of crystallizers. For example, a combination of dish crystallizers with worm-final crystallizers has been developed and successfully realized. This made it possible to obtain finely crystallized nitrate by the continuous method, and roughly double the output of the dish crystallizers.

The plan for producing finely-crystallized ammonium nitrate on cooling rollers in combination with a worm-final crystallizer is also of practical importance. According to this plan (fig. II-22), the melt that contains 95-96% NH_4NO_3 is fed into the roller pan. It rotates at a speed of 16-20 rpm. A pulp-like mass of ammonium nitrate is cut off the surface of the roller. It is sent to the worm feeder for final crystallization. The front part of this worm feeder is equipped with a sleeve in which hot condensate is fed from the evaporators. In the rear part of the worm feeder, there is a large quantity of air ducts for cooling the moving salt mass. The shaft blades along the length of the worm-final crystallizers are installed at unequal angles and have different design.

This plan produces a fine bulk product with moisture content no more than 0.15%. The output of this unit is 15% higher than that of the rollers operating on a standard regime.

Flaked nitrate is only obtained on cooling rollers (fig. II-23). In this case, a product is obtained from the melt with moisture content of 2% and temperature of 70-80°C. The nitrate flakes are dried on the rollers, losing roughly 0.5-0.7% moisture. If 94-95% melt is fed to the rollers at 137-139°C and increased rotations of the roller, a product is successfully produced which is close to a finely crystallized one. In this case, the rollers operate on a "hot regime." The temperature of the cooling water at the outlet

from the roller must be no lower than 70-75°C.

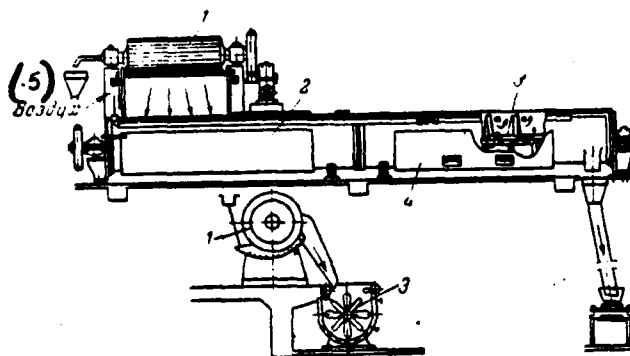


Figure II-22. Cooled Drum with Worm-Final Crystallizer

Key:

1. Cooled drum
2. Steam sleeve
3. Worm-final crystallizer
4. Water sleeve
5. Air

The cooling rollers are intensified almost always by increasing the number of their rotations, and not by increasing the depth of submersion of the roller into the pan with the melt, otherwise the quality of the finished salt is drastically impaired. Before packaging, the flaked nitrate is dried, and sometimes even cooled. The additives which improve the properties of ammonium nitrate are less effective for flaked salt than for the granulated product. A major shortcoming of the cooling rollers is the heterogeneity of the granulometric composition of the forming salt. This prevents its uniform entrance into the soil with the help of fertilizer spreaders.

The cooling rollers have consequently been replaced at almost all the plants that manufacture ammonium nitrate for agriculture by hollow granulation towers. The granulation tower is a cylindrically shape structure, 12 m in diameter and 39 m high, or ~~12~~ 16 m in diameter and 40.5 m high.

Granulation towers have been made in recent years from monolithic reinforced concrete (wall thickness 400 mm). The tower is lined on the inside with acid-resistant brick, laid on diabase mortar. The lower part of the tower is the bottom made in the shape of three truncated cones, between which ring gaps (slits) are formed to suck air into the tower and to clean the cones of excess nitrate. There are also operating towers with cones made of carbon steel. Electric vibrators are installed on their outer surface (see below).

The concentrated ammonium nitrate melt is sent from the units of the second (or third) stage of evaporation to the pressure tank. A small quantity of gaseous ammonia is fed here ($0.05 \text{ kg/t NH}_4\text{NO}_3$) for neutralization of the acid melt. The melt goes from here into the granulator (fig. II-24) which has a sprayer, a basket of conical shape whose lateral surface has several thousand different size holes. The granulator is made of stainless steel and rotates at a rate of 400-450 rpm. The flat ceiling of the tower through which the granulator shaft passes is often protected from corrosion by sheet stainless steel.

Three-four axial-type fans with output of $100,000 \text{ m}^3/\text{h}$ each are installed on the ceiling covering of the tower in the extension pipes. The fans create a draft on the order of 40-60 mm wat. col. to suck out the air from the towers. The air enters the tower through 28 windows that are arranged below on the entire perimeter of the cylindrical part of the tower (as mentioned, the air enters the tower also through gaps in the cones). A quantity of $200,000\text{-}300,000 \text{ m}^3/\text{h}$ of air is fed to each granulation tower. At the outlet from the tower, it contains finely-dispersed particles of nitrate (roughly 0.8 g per 1 m^3 of air).

The drops of melt that fly out of the holes of the granulator, when dropped from a height are washed by a stream of cold air and solidify, forming granules. In this case, they are slightly dried. Depending on the quantity and temperature of the air fed into the tower, and on its melt load, the granules that emerge from the tower have a temperature of $70\text{-}90^\circ\text{C}$, and enter the unit for cooling in the

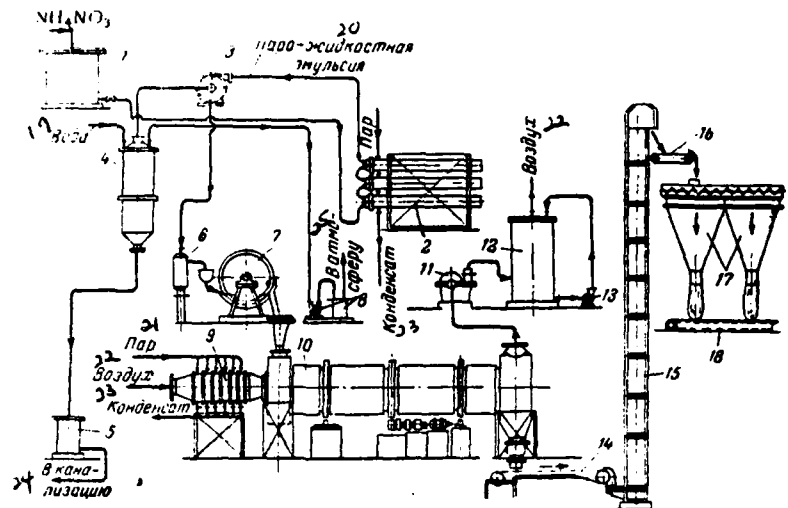


Figure II-23. Plan for Producing Flaked Ammonium Nitrate

Key:

- | | |
|-------------------------|---------------------------|
| 1. Pressure tank | 12. Washing scrubber |
| 2. Evaporator | 13. Pump |
| 3. Separator | 14. Belt conveyer |
| 4. Barometric condenser | 15. Elevator |
| 5. Barometric container | 16. Magnetic separator |
| 6. Hydraulic valve | 17. Bin |
| 7. Cooling roller | 18. Conveyor |
| 8. Vacuum pump | 19. Water |
| 9. Heating element | 20. Steam-liquid emulsion |
| 10. Drying drum | 21. Steam |
| 11. Fan | 22. Air |
| | 23. Condensate |
| | 24. To sewage system |
| | 25. To atmosphere |

fluidized bed to 50-60°C, from which they are sent to the packing division.

The major shortcomings of the granulation towers include: the possibility of using their volume only by roughly 50%, high temperature of the granules after the tower (before cooling),³⁵ as well as the high capital outlays for the construction of the towers, their cumbersomeness, etc. These shortcomings are partially due to the imperfection of the centrifugal granulators that are used to spray the nitrate melt.

When these granulators are operating, the main load for

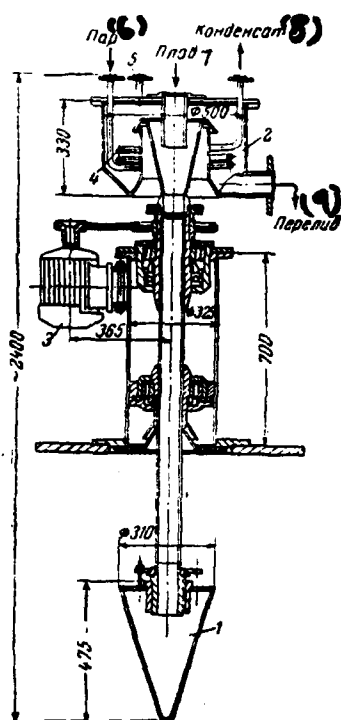


Figure II-24. Centrifugal Type Granulator

Key:

1. Sprayer of melt consisting of three bands of holes (lower--diameter of holes 1 mm, middle--diameter of holes 1.2 mm and upper--diameter of holes 1.4 mm)
2. Vessel for melt overflow
3. Electric motor
4. Coils for preheating melt
5. Air pipe
6. Steam
7. Melt
8. Condensate
9. Overflow

nitrate is on a relatively small ring space that is a distance of 4-6 m from the axis of the granulation tower, and its central and side vessels are practically not operating^{35, 36,13}.

As a consequence of the different angular velocity, even when the best centrifugal granulators are used, drops of melt of unequal dimensions are thrown into the tower. Their cooling and formation requires

varying times and varying tower height.

New designs are currently being tested for the granulation devices (static granulators) that make it possible to obtain a large quantity of granules per unit of volume of the tower and to reduce their temperature.

The granulometric composition of the ammonium nitrate that is obtained when centrifugal granulators are used, is roughly as follows:

Granule dimensions mm	Number %	Granule dimensions mm	Number %
3-7	1.3	1-2	42
2.5-3	5.3	1-1.5	20
2-2.5	30	0.6 and less	Remaining

The higher the concentration of the melt and the more intensive the cooling of its drops, the fewer pores and cracks are formed in

the granules and the higher their strength becomes. This is explained by the fact that under the given conditions, the maximum number of individual crystals is "packed" into each granule. There is almost no migration of the mother liquor¹⁷ between these crystals.

TABLE II-14. TEMPERATURE OF GRANULES, TEMPERATURE³⁶ AND HUMIDITY OF AIR AT HEIGHT OF GRANULATION TOWER

1 Точки отбора проб		2 Температура, °C		3 Относительная влажность воздуха %
4 расстояние от гранулятора м	5 расстояние от оси башни м	6 соли	7 воздуха в башне	
10	7	37,5	34,5	48,5
	3	102,0	44,5	32,5
	0	45,0	41,5	42,5
	5	100,0	45,5	40,0
	7	41,0	35,5	38,0
15	7	40,0	36,0	54,0
	5	100,0	39,0	48,5
	1	71,0	40,5	48,0
	0	46,5	41,5	40,0
	3	90,0	39,5	45,5
20	5	99,0	38,0	41,5
	7	31,0	30,0	51,0
	5	78,0	39,0	42,5
	3	82,5	34,5	42,5
	0	38,5	35,0	51,5
	3	80,0	31,0	—
	5	83,5	36,0	41,5
7	49,0	35,0	47,0	

Key:

1. Points of sample taking
2. Temperature, °C
3. Relative air humidity, %
4. Distance from granulator, m
5. Distance from tower axis, m
6. Salt
7. Air in tower

Normal formation and cooling of the granules that are obtained from the melt that contains 98.4-98.6% NH_4NO_3 requires towers of height³⁶ 26-28 m. Only granules of size to 1 mm are successfully completely formed and hardened at a distance of roughly 10 m from the granulator. The granules of larger dimensions, although they are formed at a distance of 20 m from the granulator, have a high temperature (75-80°C).

Table II-14 presents data on the temperature of the granules, temperature and humidity of the air according to the tower height when 200,000 m³/h of air is fed to it.

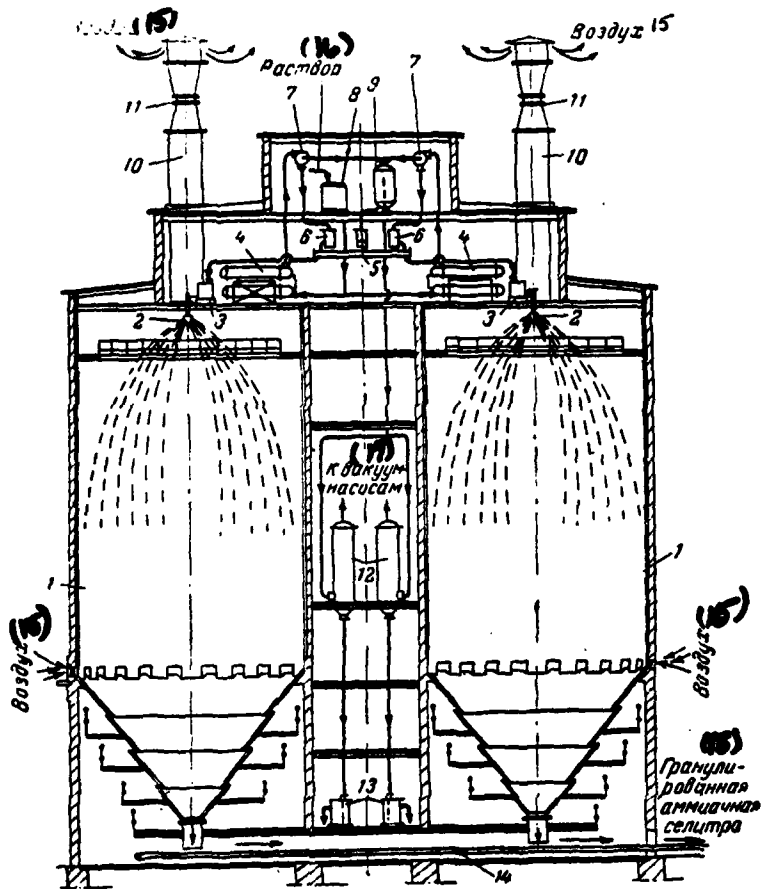


Figure II-25. Plan for Arrangement of Granulation Towers and Evaporator Station

Key:

1. Granulation towers
2. Sprayers of melt
3. Tanks for melt
4. Evaporators
5. Trough for melt
6. Hydraulic valve
- 7, 9. Separators
8. Pressure tank
10. Extension pipes
11. Axial fans
12. Barometric condensers
13. Barometric containers
14. Conveyer
15. Air
16. Solution
17. To vacuum-pumps
18. Granulated ammonium nitrate

With an increase in the quantity of air that is fed to the granulator tower, the temperature is somewhat diminished in its lower part, however in this case, the losses of nitrate that is carried away by the air from the tower significantly rise. For example, according to the average data of studies on granulation towers, the losses of nitrate with the spent air when 150,000 m³/h of air are fed to the tower are 1.19 kg/⌘, and with 200,000 m³/h-- no less than 1.43 kg/⌘ NH₄NO₃.

With an increase in the temperature of the granules, the nitrate adheres in the lower part of the tower. Consequently, the conical part of the towers has been made of steel and vibration devices have started to be used. In this case, a special metal frame is installed in the lower part of the tower which is not connected to its housing. A steel cone is mounted on this frame. The cone consists of four bands, each of which is attached to the frame by suspension arms. The three upper bands of the cone have 24 vibrators: 10 on the upper, 8 on the middle and 6 on the lower.

The vibrators^{37a} are actuated with the help of transmission devices by an electric motor that is periodically turned on, and the cone begins to shake. In this case, the nitrate adhering to the cone is separated from it, rolls downwards towards the discharge hoppers, and further is transported with the entire mass of nitrate to the packing section. On the sections of greatest attachment of the nitrate to the cone, a metal rod is placed on its inner surface. It beats the nitrate when the vibrators are turned on.

The use of vibration cones in the granulation towers has eliminated many shortcomings that are inherent to the fixed cones: the idle time of the towers for cleaning is drastically reduced, there is no need for heavy physical work within the tower when cleaning the cones, and the outlays of labor in operating the towers are considerably reduced.

The combination of vibration cones with cooling of the nitrate in the fluidized bed made it possible to increase the output of the

granulation towers. Thus, the output of towers 40.5 m high and 16 m in diameter reaches 700 t/day and more. No less than two towers were previously installed: one operated while the other was in reserve in case of cleaning or repair.

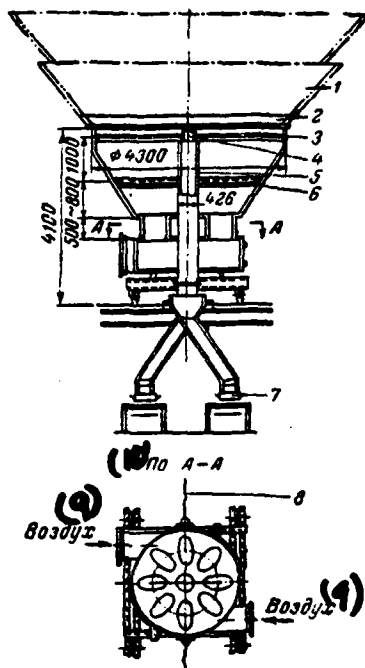


Figure II-26. One of the Versions of Unit Design for Cooling Granulated Ammonium Nitrate in the Fluidized Bed

Key:

1. Tower cone
2. Rubber hood
3. Grid carrying fluidized bed
4. Telescopic device
5. Pipe for removal of cooled granules
6. Grid for air distribution
7. Belt conveyer
8. Cable for moving unit with help of winch
9. Air
10. At A-A

Figure II-25 shows the plan for arrangement of the granulation towers and evaporator station for evaporating solutions of ammonium nitrate to the state of a melt.

Cylindrical, rectangular and other types of towers 9-13 m in diameter and height 60 m and more⁴⁸ are used abroad for granulating ammonium nitrate. These granulation towers are made of aluminum or reinforced concrete, lined with thin aluminum foil. The nitrate melt is often sprayed from a number of stationary-attached heating pipes with holes of definite sizes. This makes it possible to obtain granules of an assigned granulometric composition. A highly concentrated melt that contains no more than 0.4% moisture is generally granulated in the modern foreign ammonium nitrate plants.

Cooling of Ammonium Nitrate

The effect of inorganic additives on the physical properties of ammonium nitrate significantly depends on the temperature at which the salt is loaded into the packaging. When ammonium nitrate is loaded which contains 0.45% additives of nitrates of magnesium and calcium, at a temperature of 70-75°C, the friability of the salt is significantly deteriorated already after 45-day storage in a warehouse. Similar cases were observed when the ammonium nitrate was stored which contained additives of products of nitric acid breakdown of apatite concentrate.

Before a method was worked out for cooling the ammonium nitrate in the fluidized bed (see below), the nitrate was (and now in rare cases) cooled by air in rotating drums 2.8 m in diameter and 14 m long. The air was precooled in a scrubber, sprinkled with fresh water, from which it was injected by fan into the drum where the nitrate was cooled roughly to 50-60°C. The high cost of the unit, the significant consumption of air, abrasion of the salt with the formation of up to 20% fine particles and their piling up in the pipelines dictated the limited use of the rotating drums for cooling ammonium nitrate.

Cooling of granulated ammonium nitrate in the fluidized (pseudo-liquefied) bed^{37-39,115} has been introduced in recent year. Very intensive cooling of the granules occurs in the units with fluidized bed. For example, granules 2 mm in size which have a temperature of 80°C, falling into the fluidized bed whose temperature equals 45°C, are cooled to this temperature in 15-20 s.³⁸

In order to form the fluidized bed of granules, it is sufficient for the linear velocity of the stream of liquefying agent (air) to be on the order of 0.9-1.2 m/s. This is attained by using standard fans.

Hydraulic resistance of the fluidized bed of granules 100 mm high does not exceed 40-50 mm wat. col. The total resistance of the

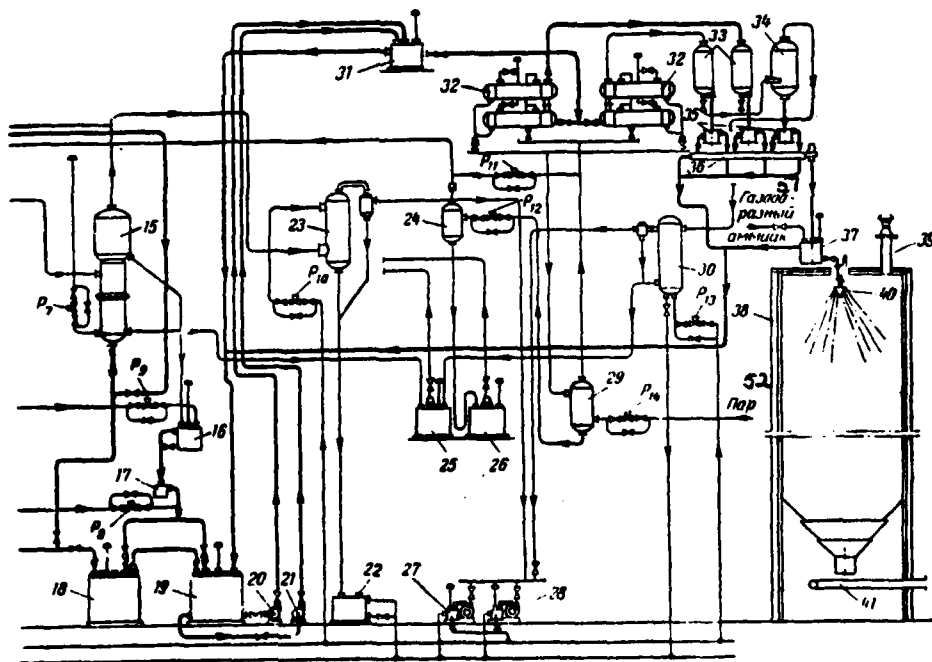
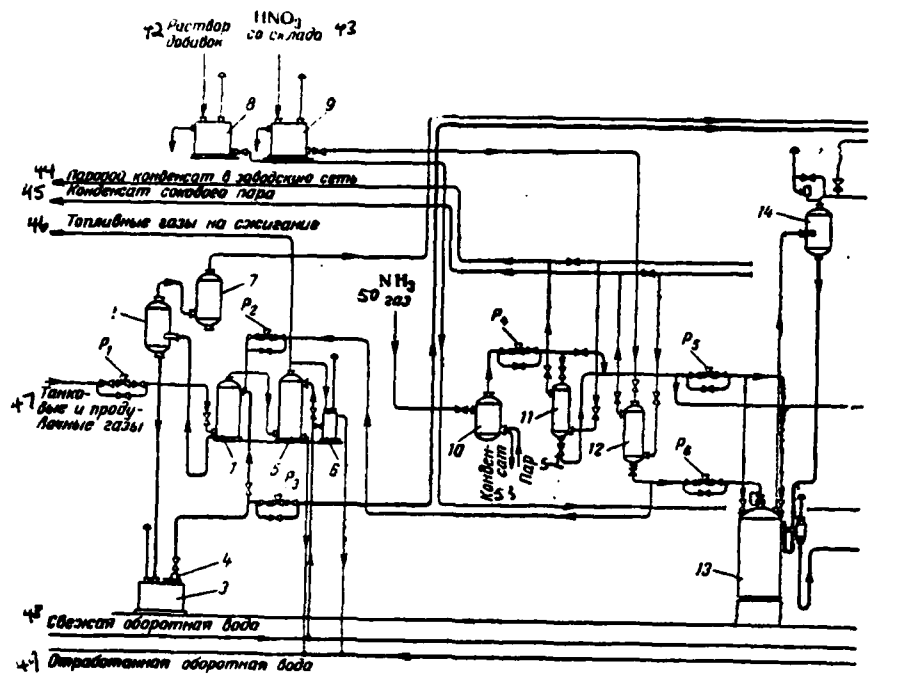


Figure II-27. Production Plan for Ammonium Nitrate and Automatic Regulation of the Process

[Key on next page]

- 1. Scrubber-neutralizer
- 2. Vacuum-evaporator
- 3,6,35. Hydraulic valves
- 4,20,21. Pumps
- 5. Washer
- 7. Trap
- 8,9,31. Pressure tanks
- 10. Separator of liquid ammonia
- 11. Heater of gaseous ammonia
- 12. Preheater of nitric acid
- 13. ITN unit
- 14. Trap-separator
- 15. Evaporator of first stage
- 16. Hydraulic valve-final neutralizer
- 17. Slit flowmeter
- 18,19. Collectors of solution of ammonium nitrate
- 22. Barometric container
- 23. Barometric condenser
- 24. Condensate expander
- 25,26. Condensate collectors
- 27,28. Vacuum pumps
- 29. Steam humidifier
- 30. Surface condenser
- 32. Vacuum-evaporator units of second stage
- 33,34. Separators
- 36. Trough
- 37. Buffer tank for melt of ammonium nitrate
- 38. Granulation tower
- 39. Axial fan
- 40. Sprayer of melt
- 41. Conveyer
- Key: 42. Solution of additives
- 43. HNO₃ to warehouse
- 44. Steam condensate to plant network
- 45. Condensate of liquor steam
- 46. Fuel gases to combustion
- 47. Tank and blow-through gases
- 48. Fresh circulating water
- 49. Spent circulating water
- 50. NH₃ gas
- 51. Gaseous ammonia
- 52. Steam 53. Condensate

Designations of the automatic regulator:

- P₁. Regulator of pressure of ammonia-containing gases ("to itself")
- P₂. Regulator of supply of nitric acid according to acidity of solutions at outlet from scrubber 1
- P₃. Regulator of supply of solutions for evaporation according to level of liquid in tank-hydraulic valve
- P₄. Regulator of pressure of gaseous ammonia ("after itself")
- P₅. Regulator stabilizing the supply of ammonia to the ITN unit
- P₆. Regulator of supply of nitric acid according to acidity of solutions at outlet from ITN unit
- P₇. Regulator of blowing-through of evaporator according to temperature of outgoing solution
- P₈. Regulator of supply of solution of DLM additive according to quantity of solution of ammonium nitrate

- P₉. Regulator of supply of ammonia according to alkalinity of solutions at outlet from final neutralizer
- P₁₀. Regulator of supply of fresh water according to temperature of condensate at outlet from collector 25
- P₁₁. Regulator of supply of fresh steam according to pressure in collector of liquor steam
- P₁₂. Regulator of output of condensate according to level of liquid in steam humidifier
- P₁₃. Regulator of supply of fresh water according to temperature of condensate at outlet from unit 30
- P₁₄. Regulator of pressure of fresh steam ("after itself")

layer of cooling granules of ammonium nitrate and the grid above which the fluidized bed is located is 70-110 mm wat. col. Therefore, for the formation of a fluidized bed it is sufficient to install a fan which creates pressure³⁸ in limits of 150-200 mm wat. col.

The granulated ammonium nitrate in the fluidized bed is cooled in units that are located within or outside of the granulation tower. One of the designs of the portable unit for cooling granules that was developed as applied to the active production of ammonium nitrate is a rectangular box (made of carbon steel), 1400 mm wide and 7000 mm long. It is placed directly under the last cone of the granulation tower. The box holds a grid with section of 9.8 m² made of stainless steel with holes 2.5-3 mm in diameter and spacing of the holes 10-12 mm. The free (passage) section of all the holes is 5-10% of the grid area. The grid can be installed at different angles towards releasing the cooled granules. For better distribution of the air, it is fed under the grid through five cones that are equipped with gate valves.

In order to prevent large pieces of nitrate from falling into the fluidized bed (sometimes they fall off the walls of the towers), a grid is placed above the loading neck of the cooling apparatus. This grid has holes 10-15 mm in size. The cooled granules "flow out" of the unit directly to the belt conveyer that feeds the nitrate into the bin of the packing division.

In the summer, this unit cools granules to 25°C when it is loaded for nitrate in a quantity of 24 t/h and rate of air supply

1-1.3 m/s. In this case, the flying away of salt dust is 0.5-0.7 kg per 1 t of finished product. The spent air from the cooling unit is directed into the granulation tower.

In order to cool the granules in the fluidized bed, a device is also used which is located in the lower part of the cone of the granulation tower. The characteristics of the design and the operating conditions of this device are presented below:

Diameter, mm		Useful area of grid, m^2	15
of cooling grid	4520	Spacing between holes,	
of overflow pipe	1100	mm	10-11
of grid holes	2.5	Velocity of air, m/s	2-3
Height of fluidized bed, mm	100	Quantity of air, m^3/h	60,000

In this device, the nitrate granules in the summer are cooled to 25-35°C. Their temperature at the outlet from the unit does not exceed 50°C. Cases of piling up of the holes of the grid are very rare. The air is suctioned from the granulation tower by axial fans.

Figure II-26 presents one of the designs of the unit for cooling granulated ammonium nitrate³⁸ in a fluidized bed. This unit is installed under the granulation tower (instead of its lower cone) and is cone 1 in which grid 3 is placed. It carries the fluidized bed (diameter of the holes 3 mm, spacing between them 11-12 mm).

The tower cone is connected to the unit with the help of a tightly secured rubber apron 2. In the center of the unit there is a telescopic device 4 which makes it possible to regulate the necessary height of the fluidized bed. This device is installed in the upper cone of pipe 5 which is designed to remove the cooled granules from the fluidized bed. For more uniform distribution of the air that is directed under grid 3 with the fluidized bed of granules, the unit has a second grid 6 with holes. There is a man-hole in the lower part of the cone for examination or cleaning the unit.

The hot granules roll from the cone of the granulation tower to the peripheral sections of the fluidized bed and are moved in

radial direction towards the center of the unit. The cooled granules are continually removed on pipe 5 to belt conveyer 8 which feeds the product into the bin of the packing section. The air from the unit with fluidized bed directly enters the granulation tower. When the tower is being cleaned of excess salt, the described unit is rolled to the side by cable 8 and a small winch.

The following basic operating indicators are adopted in designing such one-stage cooling units for new ammonium nitrate shops:

Load on the grid (output), $\tau / (\text{m}^2 \times \text{h})$	2
Height of layer of granules on grid, mm	50-100
Consumption of air for cooling granules that have temperature of 80°C (summer), m^3 / τ of product	2000
Linear velocity of air in fluidized bed (counting on the complete section of the tower), m/s	1
Losses of nitrate because of wear and tear, kg / τ	to 1.5

The new drafts for the production of ammonium nitrate for reduction of the granule temperature provide for two-stage cooling of them in the fluidized bed (in the lower part of the granulation tower). In a tower of diameter 12 m, the first cooling stage occupies an area of diameter 7.5 m, and is separated from the second stage by a ring metal edge. Air is fed under the grid of the first stage by a fan. The stream of granules at temperature of 120°C enters the fluidized bed of the first stage, is cooled here to 50-52°C, and passes to the second stage of cooling through two diametrically opposed edge openings. The salt in the second stage is cooled by the cross movement of the streams of granules and air which is conditioned for temperature and humidity. Part of the air is pre-cooled by the evaporating ammonia.

The production flowsheet for granulated ammonium nitrate (without separation of its final treatment) with the basic devices and instruments for automatic regulation and control of the process is shown in fig. II-27.

Drying of Ammonium Nitrate

The process of drying ammonium nitrate is done by direct contact of an air stream and the salt in rotating drums with different number of revolutions. Since ammonium nitrate is hygroscopic, its drying occurs slowly and with insufficient completeness.

Ammonium nitrate, like many other hygroscopic salts which have high solubility in water, contains superficial, capillary and adsorption-linked moisture. When ammonium nitrate is dried, it is the most difficult to remove the capillary and adsorption-linked moisture. It must be shifted from inside the salt particles to the surface by capillary forces and the difference in pressures of the water vapors above the saturated solution of salt and in the air used as the drying agent.

The dimensions and shape of the salt particles have a large effect on the rate of drying by heated air. With an increase in the dimension of the particles, the drying of the salt is impaired. Therefore, fine-crystalline ammonium nitrate, because of the large surface of its particles, gives off moisture considerably faster than flaked, and especially granulated nitrate. The granules almost always have a "partially fused" surface which prevents evaporation of the moisture and its movement from inside the granules.

Consequently, granulated ammonium nitrate is generally not dried, and in the melt that is sent for crystallization, an attempt is made to leave no more than 0.3% moisture. Finely-crystallized and flaked ammonium nitrate that are obtained from a melt with relatively high water content have to be dried. In this case, the superficial moisture is mainly removed from the flaked nitrate (initial moisture content of salt 1.5-2.5%, final 0.8-1%).

Industry uses the following methods of drying ammonium nitrate: drying by air heated to 115-120°C ("hot drying"); drying by air heated to 105-110°C, with subsequent cooling of the salt by unheated air; drying with cooled air with simultaneous cooling of the salt

("cold" drying).

In "cold" drying of ammonium nitrate, the processes of drying and cooling of the salt are combined. This makes it possible to obtain a product with somewhat improved physical properties. However, the method of "cold" drying has not become popular, since it has significant shortcomings (low output of the drying drums, high consumption of air, need to cool it with liquid ammonia, etc.).

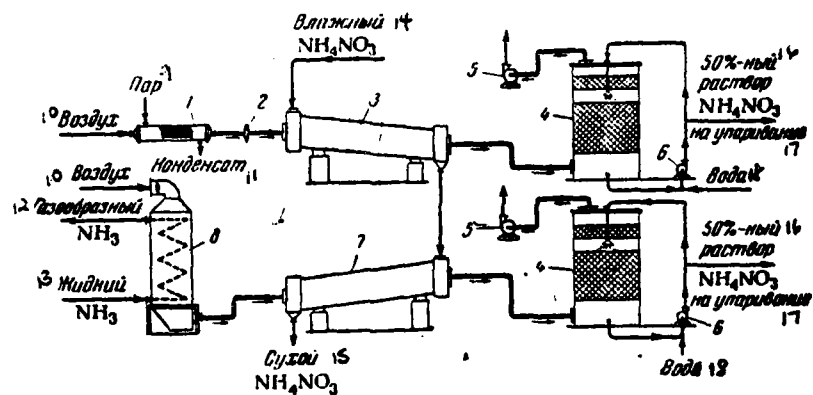


Figure II-28. Plan of "Hot" and "Cold" Drying and Cooling of Ammonium Nitrate

- Key:
- | | |
|----------------------|--------------------|
| 1. Air preheater | 13. Liquid |
| 2. Axial fan | 14. Moist |
| 3. Drying drum | 15. Dry |
| 4. Scrubbers | 16. 50% solution |
| 5. Centrifugal fans | 17. To evaporation |
| 6. Circulating pumps | 18. Water |
| 7. Cooling drum | |
| 8. Air cooler | |
| Key: 9. Steam | |
| 10. Air | |
| 11. Condensate | |
| 12. Gaseous | |

In order for moisture to be removed sufficiently rapidly from the salt, the air must have low relative velocity. In "hot" drying, this is attained by heating the air to 115-120°C. With "cold" drying, the relative air humidity is reduced by partial freezing of the moisture out of it.

Both "hot" and "cold" drying of ammonium nitrate are done in horizontal rotating drums that in the majority of cases have a diameter of 1.7 m, length of 11 m, and are installed with incline towards the movement of the salt particles. Within the drum, over its whole length, there are rounded blades that are designed to sprinkle the salt while the drum rotates and during its movement towards the outlet from the dryer. In "hot" drying, the air that is fed to the drum is preheated by steam in heating elements or shell-and-tube heat exchanger, and is fed to the drum. The air is drawn through the drum by a fan and moves in a direct stream with the dried salt. Small particles of salt are carried away by the air exiting from the dryer. They are then trapped from it in the scrubber which is sprinkled by a solution of ammonium nitrate. After washing in the scrubber, the air is sent into the atmosphere. As the concentration of sprinkling solution reaches roughly 50% NH_4NO_3 , part of it is removed from the scrubber for evaporation. The remaining solution is diluted with water and is again sent for circulation.

As practice indicated, "hot" drying is not very effective: in this case the moisture content of the flaked nitrate is lowered only by 0.7-1%, and the temperature of the salt after drying is found in limits of 50-60°C. One therefore has to sometimes additionally cool the nitrate in a separate drum.

In "cold" drying, the air circulates in a closed system: drum-scrubber-drum. Wet salt enters the drying drum from the rollers, and air is fed by a fan. The air is precooled to a temperature of -5 - -8°C in the scrubber which is sprinkled by a 40-50% cold solution of ammonium nitrate. The sprinkling solution is cooled to -10°C in the ammonium evaporator.

The air heated in the drying drum is cooled in the scrubber, at the same time cleaned of the salt particles it has carried away. When the NH_4NO_3 content in the solution sprinkling the scrubber reaches 50%, part of the solution is removed for evaporation, and water is added to the remaining solution and its circulation continues.

A significant shortcoming of the processes of "hot" and "cold" drying is crushing of the salt in the drums and the formation of dust which is carried off with the air into the pipelines, piles up on the drum blades, intensifies corrosion of the equipment, etc.

Figure II-28 presents a plan of "hot" drying that is combined with "cold" drying and with cooling of the ammonium nitrate (with single use of the air).

Table II-15 presents the characteristics of the operation of units for drying ammonium nitrate that use "hot" and "cold" regimes.

TABLE II-15. CHARACTERISTICS OF OPERATION OF DRUM DRYERS
(drum diameter 1.6 m, length 11 m)

Indicators	"hot" drying	"cold" drying
Air temperature, °C		
at inlet	120	-6
at outlet	80	25
Relative air humidity, %		
at inlet	20	~100
at outlet	25	40
Temperature of dried salt, °C		
at inlet	70	70
at outlet	60	25-30
Moisture content of dried salt, %		
at inlet	1.5	1.5
at outlet	0.8	0.8
Drum output, t/h	7	3.5-4

Packing, Storage and Shipping of Ammonium Nitrate

Packaging. Ammonium nitrate is packed in paper five- and six-layer bags (GOST 2226-62). The inner layer of paper which touches the salt must be uniformly impregnated with bitumen-motor oil mixture (90% bitumen, 10% motor oil). The weight of the bag with the product must be 45-50 kg (permissible deviations ± 1 kg).

In addition to paper bags with open neck sewn up by machine after their filling with nitrate, paper flap bags are used. In one corner they have a hole that is covered from the inside by a paper flap.

The bags that can be used for packing the nitrate have insufficient moisture-impermeability and mechanical strength. As a result, the caking of the nitrate increases and its losses during shipping rise.

According to GOST 2-65, it is permitted to pack ammonium nitrate in polyethylene bags whose neck must be sealed by machine. The polyethylene is distinguished by high chemical stability. It is stable with changes in temperature in limits from -60 to +70°C, elastic and gas impermeable. As indicated by tests of polyethylene bags with nitrate, as well as the practice of their extensive use abroad, these bags are completely hermetically sealed. This excludes the possibility of air moisture penetrating the salt which drastically reduces the quality of the finished product.

Packing. Ammonium nitrate is fed into the section for packing by belt conveyers that are placed in inclined tunnels. The nitrate is discharged from the conveyer into a bin, from which it enters the scale units-sewing machine.

This unit often consists of two semiautomatic scales and sewing machine with output of 30-35 t/h.

The nitrate is poured from the bin into a paper bag attached by a special clamp on the neck of the hopper. The bag filled with salt is weighed and sent to the conveyer to the sewing machine. The sewn bag is advanced to the spiral drain pan and is sent directly to the railroad cars or on a central conveyer to the warehouse. Bags with nitrate are distributed to the warehouse by a mobile cart that places the bags in piles.

Three-connection automatic units are often installed in the packing sections. They fill the flap bags and weigh them.

In order to remove from the nitrate metal objects (nuts, bolts, etc.) that accidentally fall into it, electromagnetic separators are installed above the transporters that feed salt to the bins in the packing section.

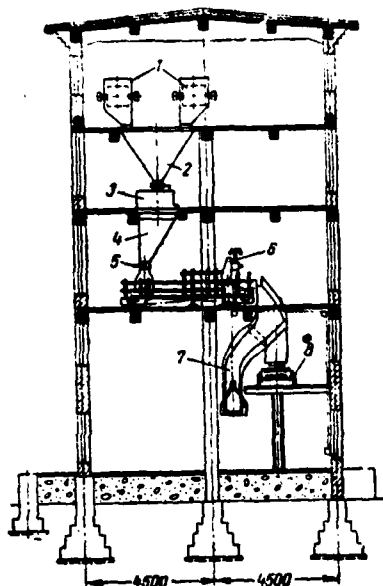


Figure II-29. Plan for Arrangement of Equipment in Ammonium Nitrate Packing Section

Key:

1. Inclined belt conveyers
2. Bin with ammonium nitrate (to automatic scales)
3. Automatic scales
4. Hopper from automatic scales
5. "Clamp" for bags
6. Sewing machine
7. Spiral descent of bags from sewing machine
8. Belt conveyer to warehouse

In order to supply empty bags to the packing section from the packaging warehouse, there is a special hoist.

Figure II-29 depicts the plan for arrangement of the equipment in the packaging section.

The warehouses of nitrate have automatic units that combine the operation of automatic loader and piler to load the nitrate into the railroad cars.

Storage and shipping. If there are interruptions in the shipping of nitrate to the enterprises, it is currently permitted to store not more than 1500 t of this product.

The total capacity of each of the base warehouses that must be of the closed type and be outside the enterprise territory, at a great distance from residential and industrial buildings and structures may correspond to 10-day output of the industry, but not exceed 10,000 t of ammonium nitrate.

Storage and shipping of nitrate in a heap are forbidden in the USSR. Nitrate is stored in separate piles no more than 2 m high.

The gaps between the piles is no less than 8 m and there can be up to 60 t of product in each pile.

It is forbidden to store and ship ammonium nitrate in combination with other chemical products. It is forbidden to smoke in nitrate warehouses, install open type lighting fittings, work with fire, or store used paper bags.

It is permitted to ship ammonium nitrate in paper packages by all types of transportation. Before cars and ship holds are filled with nitrate, they should be cleaned of residues of previously shipped products.

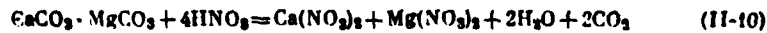
Additives Which Improve the Physical Properties of Ammonium Nitrate

The methods of preparing and using additives that can be obtained from dolomite, apatite and phosphorite dust are similar to each other.¹³ The original raw material is broken down by 45-56% nitric acid. The admixtures that are insoluble in acid are separated from the obtained solution by settling out or with the help of filter presses, and the filtrate (often it is called the extract) is added to solutions of ammonium nitrate that are sent for evaporation, or are added to nitric acid that is entering the neutralizer.

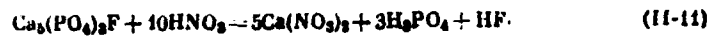
The sludge that is accumulated during the settlement of insoluble admixtures is washed with water and dumped.

During the production of nitric acid extracts, nitric oxides, carbon dioxide, water vapors, nitric acid are always isolated, and in the case of breakdown of phosphorus-containing raw material, a small quantity of hydrogen fluoride. The formed gases and vapors are removed into the atmosphere through the exhaust pipes for the production of weak nitric acid.

The preparation of DLM additives (products of nitric acid breakdown of dolomite) is based on the following basic reaction:



The production of RAP additives (products of nitric acid breakdown of apatite) can be described by the reaction:



During acid breakdown of dolomite and phosphates, heat is released. As a result, the temperature of the solutions in the reactors is increased to 40-50°C. This temperature is sufficient for conducting the process with the required velocity and completeness, and to release gaseous products of the reactions from the solutions.

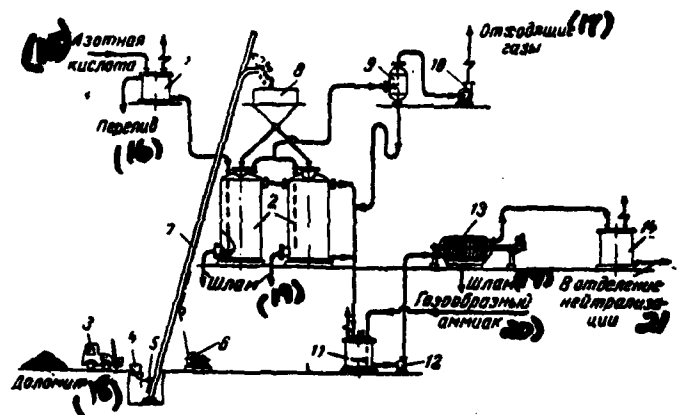


Figure II-30. Plan for a Continuous-Operation Unit to Produce DLM Additive

Key:

1. Pressure tank for nitric acid
2. Reactors
3. Lift truck
4. Bin
5. Scoop
6. Winch
7. Hoist
8. Distribution bin
9. Trap
10. Fan
11. Tank (mixer) for solutions of nitrates of calcium and magnesium
12. Pump
13. Filter press
14. Collector of additive solution
15. Nitric acid
16. Overflow

[continuation of key]

17. Exhaust gases
18. Dolomite
19. Sludge
20. Gaseous ammonia
21. To neutralization section

Additives are also produced which give the ammonium nitrate water-resistance (p. 245).

Figure II-30 presents one of the plans for producing DLM additive.

Nitric acid is poured from pressure tank 1 into reactor 2 (diameter 1.9 m, height 4.3 m) to half of its volume. The dolomite is transported from the warehouse by lift truck 3, poured into bin 4, then into scoop 5 of hoist 7, and with the help of winch 6 is fed to the distribution bin 8.

From here, 1.5 t of dolomite are loaded into the reactor. It is further fed in individual portions of 300-400 kg each. At the same time, nitric acid continually enters reactor 2 with the dolomite. The acid travels on a pipe that is lowered to the bottom of the unit. This makes it possible to create the best contact of the solid and liquid phases. When the reactor is equipped with a circulation pump, a surplus of nitric acid of roughly 100 g/l is maintained in the reaction mixture (solution). When there is no forced circulation of the solution, the surplus HNO_3 is only several grams in 1 l.

The gases and vapors that are removed from the reactor contain up to 0.05 vol.% of nitric oxides.

The acid solutions of nitrates of calcium and magnesium that are formed in the reactors are neutralized in tank 11 (diameter 2.2 m, height 2.1 m) by gaseous ammonia to a content in the solution of 0.2-0.3 g/l NH_3 . The solution is further filtered, and depending on the plan for production of ammonium nitrate, it is sent to the

final neutralizer of the ITN unit, or the collector of partially evaporated NH_4NO_3 solutions. The reactor is cleaned of sludge once every 3 months. In this case about 3 t of sludge are unloaded by hand.

When the DLM additive is obtained by the described plan, the losses of nitrogen (in the form of nitric oxides, HNO_3 vapors and liquid nitric acid) for 1 t of ammonium nitrate are 0.35-0.5 kg in conversion for HNO_3 .

Consumption Coefficients

The consumption of ammonia and nitric acid to produce ammonium nitrate is determined by their stoichiometric ratio and the losses in the process of product production.

Table II-16 presents the standards for consumption of raw material and power for 1 t of ammonium nitrate without additives and with DLM and RAP additives depending on their content in the finished product, as well as on the conditions of salt cooling.

The calculation of the consumption standards adopted the following sample (conventional) composition of dry product with DLM and RAP additives (in weight %):

Components	With DLM additive	With RAP additive
NH_4NO_3	98.1	97.5
$\text{Ca}(\text{NO}_3)_2$	0.957	1.035
$\text{Mg}(\text{NO}_3)_2$	0.8	-
CaHPO_4	-	1.315
CaSiF_6	-	0.0845
$\text{R}(\text{NO}_3)_3$	0.163	0.065
N (total content), kg/ t	346.73	343.12

After complete mastery of the ammonium nitrate production process which satisfies all the GOST 2-65 requirements, the standard of consumption of raw materials, auxiliary materials, steam, water, electricity and air is stipulated.

TABLE II-16. SAMPLE CONSUMPTION STANDARDS OF RAW MATERIAL AND POWER FOR 1 T OF AMMONIUM NITRATE

(1)	(2)	(3)	(4)	(4)	(2)	(3)	(4)
Статья расхода	На 1 т 100%-ной NH_4NO_3	На 1 т продукта с 98.7% NH_4NO_3	На 1 т 100%-ной NH_4NO_3	На 1 т продукта условного состава	На 1 т 100%-ной NH_4NO_3	На 1 т продукта с 98.7% NH_4NO_3	На 1 т продукта условного состава
	(5)		(6)		(7)		
	Без добавок		С добавкой ДЛМ		С добавкой РАП		
(8) Аммиак, т	0.2155	0.2127	0.213	0.211	0.2143	0.2116	0.20101
(9) Азотная кислота (100% HNO_3), т	0.794	0.784	0.80	0.793	0.7956	0.7855	0.780
(10) Доломит, кг	—	—	11	10.9	—	—	—
(11) Апатит (39.4% P_2O_5), кг	—	—	—	—	18.7	18.48	18.2
(12) Вода обратная, м ³	30	29.6	30	29.7	30	29.6	29.4
(13) Пар, млн. ккал	0.3	0.296	0.3	0.297	0.3	0.296	0.294
(14) Электроэнергия, квт·ч							
(15) без охлаждения соли в кипящем слое	15	15	15	14.85	15	14.8	14.7
(16) с охлаждением соли в кипящем слое	21	21	21	20.7	21	20.6	20.5

Key:

1. Articles of consumption
2. Per 1 T of 100% NH_4NO_3
3. Per 1 T of product with 98.7% NH_4NO_3
4. Per 1 T of production of conventional composition
5. Without additives
6. With DLM additive
7. With RAP additive
8. Ammonia, T
9. Nitric acid (100% HNO_3), T
10. Dolomite, kg
11. Apatite (39.4% P_2O_5), kg
12. Circulating water, м³
13. Steam, million kcal
14. Electricity, kw x h
15. Without cooling of salt in fluidized bed
16. With cooling of salt in fluidized bed

Wastes of production of ammonium nitrate per 1 T of finished product are up to 0.6 T of condensate of liquor steam and about 0.4 T of steam condensate. The output of nitrogen contained in ammonium nitrate, in relation to nitrogen entering for neutralization in the form of ammonia and nitric acid is about 99%.

Water-Resistant Ammonium Nitrate

Water-resistant ammonium nitrate is produced by applying a hydrophobic film on the granules or small salt crystals. This film is formed on the surface of the particles of ammonium nitrate from ferric sulfate and from a mixture of synthetic fatty acids and paraffin.

When an aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ is added to a melt of ammonium nitrate, during crystallization of salt a so-called ferruginous nitrate is obtained. The solution of iron sulfate is added to the melt in a quantity so that the content of $\text{Fe}_2(\text{SO}_4)_3$ in the finished product is 0.06-0.07% (in conversion for iron). After treating the ferruginous ammonium nitrate with a mixture of fatty acids and paraffin, a thin layer of "metal soap" (iron salts of fatty acids) is formed on the surface of the salt particles. The required quantity of mixture of fatty acids and paraffin is 0.35-0.40% of the weight of the nitrate.

One of the versions of the process for obtaining water-resistant ammonium nitrate is the following. The melt of ammonium nitrate with concentration of 98.2-98.5 NH_4NO_3 enters from the separators through the hydraulic gate and the trough into the buffer tank that is separated into two parts by a partition that does not reach the bottom. Gaseous ammonia is fed into one part of the tank to neutralize the acidity of the melt. A solution of iron sulfate is poured into the other part from the pressure tank. The "ferruginous" and neutralized melt are sent from the buffer tank to granulation in the tower (the granulator is turned at a rate of 450 rpm). The granules formed in the granulation tower are transferred by conveyer to a rotating drum-mixer. A previously prepared mixture of fatty acids with paraffin is simultaneously sent by gravity flow from the tank. The granules are coated with this mixture, and a film of iron salts of fatty acids is formed on their surface.

For more uniform coating of the granules with the hydrophobic

film, the mixture of fatty acids and paraffin is separated into fine streams by a rack installed above the stream of granules. The product is sent from the drum on a conveyer to the packing section.

Domestic and foreign industry also uses other methods of giving ammonium nitrate water resistance, but the basic fundamentals of the method for applying the hydrophobic film on the particles of salt are similar to those described above.

Practice has shown that fine-crystalline ammonium nitrate is best suited for production of a film of iron salts of fatty acids on the surface of its particles, since these salts link more strongly to the fine nitrate crystals.

Granulated water-resistant ammonium nitrate must not contain visible foreign inclusions or pieces of noncrystallized melt. The color of the product must be from yellow to light chestnut.

The basic requirements for the granulated water-resistant ammonium nitrate (MRTU-6-03-162-64) are presented below:

Water resistance (according to hydrodynamic method), mm wat. col., no less	20
Moisture content (after drying of 2 g at 100°C), %, no more	1.4
NH ₄ NO ₃ content (in conversion for dry substance), %, no less	98
Content of mixture of fatty acids with paraffin, %	0.3-0.4
Content of iron (Fe), %	0.06-0.09
Acidity of aqueous solution of nitrate, %, no more	0.09
Content of substances that are insoluble after calcination in HCl, %, no more	0.09

Of the ammonium nitrate-based fertilizers, one should note lime-ammonium nitrate (melt of ammonium nitrate with limestone)⁴⁰⁻⁴² which has become fairly popular in certain countries of West Europe. The manufacture of this fertilizer in the capitalist countries is roughly 1.5 million T per year (in conversion for nitrogen).

Improvement in the Production of Ammonium Nitrate

The specific consumption of steam, water, and electricity in the production of ammonium nitrate is comparatively low. However, with the current scales of ammonium nitrate production and the planned increase in its volume, even a small reduction in the specific energy outlays has very great economic significance.^{43,45}

In addition, with the extant methods of ammonium nitrate production, large heat-exchange surfaces are required for evaporation of its solutions and a significant quantity of auxiliary equipment (collectors, tanks, pumps, etc.). This significantly increases the capital investments for the construction of new industries.

Increase in the output of the ammonium nitrate shops results in a decrease in the specific capital expenditures,⁴⁴ but they are still high since weak solutions of NH_4NO_3 have to be reprocessed. Consequently, intensive development is underway of methods to produce ammonium nitrate using 58-62% nitric acid, with conducting the stage of neutralization at high temperatures, etc. Realization of these methods makes it possible to partially or completely exclude the process of concentration of ammonium nitrate solutions in the evaporators and improve the quality of the finished product.

So-called evaporation-free methods of ammonium nitrate production^{30,46} have been developed by now, as well as a method of continual vacuum-crystallization of solutions⁴⁷ that was used for the first time to produce ammonium-nitrate. Individual units abroad have used the evaporation-free method of L. Shtengel', that was later perfected by him jointly with D. Dorsi.

The essence of this method is reduced to the following. Gaseous ammonia and 58-60% nitric acid are preheated to 160-165°C by steam, and are fed in a stoichiometric ratio to the reactor-neutralizer which operates at gage pressure of 3.5 atm. Because of the physical heat of the preheated original components, and the heat that is released

during neutralization, the temperature in the reactor reaches 205-238°C. In this case, almost all the water that enters with the nitric acid is evaporated, and a steam-liquid emulsion is formed that consists of a melt of ammonium nitrate, liquor vapors and a slight amount (traces) of ammonia. This emulsion is further separated in the separator of the centrifugal type.

For 1 T of ammonium nitrate (counting on 100% NH_4NO_3) obtained according to this plan, 218 kg of ammonia, 806 kg of nitric acid (100% HNO_3), 21 kW x h of electricity, 305 kg of steam (9 atm.) and 8.4 m³ of cooling water are consumed.

The safety of the process using the described method is guaranteed because of the short time that the formed melt stays in the reactor-neutralizer, and the small quantity of reaction mass that is present at one time in the neutralization unit, as well as because of the automatic regulation of the regime.

The production of ammonium nitrate with the use of a vacuum-crystallizer is done in the United States. According to this method, the solutions of ammonium nitrate are obtained at atmospheric pressure in two stages: initially in a neutralizer to pH of the solution 6.7, then in a buffer tank to pH of 6.4. Evaporation of the solutions to a concentration of 79% NH_4NO_3 is done in units with forced circulation that is created by a pump. The evaporated solutions are sent to a vacuum-crystallizer that also operates with forced circulation of the liquid. Crystallization occurs at a temperature of 40°C. It is automatically regulated by the appropriate supply of water to the barometric condenser. The suspension of ammonium nitrate crystals in a liquor solution that is formed in the vacuum-crystallizer is separated on centrifuges.

The crystals are further dried by hot air in a drum to moisture content of 0.05% and are mixed with 4% aluminum oxide to improve the physical properties of the finished product.

Roughly two times less steam is consumed for the production of ammonium nitrate according to this method with the use of vacuum-crystallization than in other methods of production. This method is used on small units.

The general trend towards increase in the unit output of units that is characteristic for modern chemical industry and other rapidly developing areas of technology has been reflected in the production of nitrogen fertilizers as well. Thus, for the production of ammonium nitrate, the group of colleagues from GIAP developed a unit with daily output of 1400-1500 T of product whose quality completely satisfies the standards of GOST 2-65.

The process of neutralization in this unit is done in an apparatus of new design at atmospheric pressure with the use of 58-60% nitric acid. In this case, 90-93% solution of ammonium nitrate is formed which is evaporated in a film evaporator (with "falling" film) to the state of a melt which contains 99.5-99.7% NH_4NO_3 . The nitrate of this melt is granulated in a tower with subsequent two-stage cooling of granules in the fluidized bed. The cooled granules after screening into fractions are dusted with a talc-magnesia mixture and are sent for packing. Trapping of salt dust from spent air is provided for in the large output unit.

In order to improve the physical properties of ammonium nitrate, a number of methods have been suggested. Some of them have become widespread, and others are more limited in use. These methods can be arbitrarily divided into the following groups:*

- 1) granulation of ammonium nitrate from a highly-concentrated melt;
- 2) introduction into the ammonium nitrate of additives of water-soluble inorganic salts;
- 3) treatment of particles of ammonium nitrate with incombustible hydrophobic substances;
- 4) dusting of the granules with substances insoluble in water.

*The previously mentioned procedures for improving the properties of the product by cooling it, the use of granulation devices of new designs, etc. are not examined here.

It has been recognized both in the USSR and abroad that with separate use of the listed methods, it is not possible to manufacture ammonium nitrate that maintains 100% friability for many months. Consequently, a combined plan was developed for production of noncaking ammonium nitrate. According to this plan which by now has been realized at the active enterprises, crystallization of salt from a highly concentrated melt (99.6-99.7% NH_4NO_3), cooling of granules in the fluidized bed, their screening with selection of fractions of particles with sizes 2-3 mm, dusting of the granules with substances that are insoluble in water are stipulated.

In order to produce a highly concentrated melt of ammonium nitrate, it is necessary to evaporate its solutions at 175°C, but since partial thermal breakdown of ammonium nitrate is possible at this temperature, the evaporation is done in two stages. Initially the solutions are evaporated in standard evaporators until a melt is obtained which contains 93-98.5% NH_4NO_3 . Then this melt is additionally evaporated in evaporators of special design by preheated air at 175-180°C in the presence of a small quantity of ammonia that prevents thermal breakdown of the ammonium nitrate.

Crystallization of the melt stipulates the use of static granulators instead of centrifugal, and cooling of the granules uses a two-stage fluidized bed.

When a 99.6-99.7% melt is crystallized in the granulation towers, granules are formed with glassy surface that determines their high mechanical strength.

In order to obtain a product of uniform granulometric composition that does not contain dust-like or large particles, the cooled granules are sent to the vibration sieves. Here the commercial-grade particle fractions of size 2-3 mm are removed. Particles of smaller and larger dimensions are returned to the production cycle (they are added to the solutions of ammonium nitrate that are sent for evaporation).

Granules of dimension 2-3 mm enter the rotating drum to which the dusting additive is added (2-3% kieselguhr or talc-magnesium mixture from the quantity of nitrate). The finished product is further packed into paper bituminized bags or bags made of polyethylene film.

2. Calcium Nitrate

Physical-Chemical Properties of Calcium Nitrate⁴⁹

Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$ is a white crystalline salt. A grayish hue is permissible for the technical-grade product. Calcium nitrate can be crystallized in the form of hydrates: $\text{Ca}(\text{NO}_3)_2 \times 2\text{H}_2\text{O}$; $\text{Ca}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$; $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$.

Certain physical-chemical constants of the anhydrous salt and hydrates are presented in table II-17.

TABLE II-17. PROPERTIES OF CALCIUM NITRATE

(1) Соль	(2) Температура плавления °C	(3) Теплота образования из простых веществ ккал/моль
$\text{Ca}(\text{NO}_3)_2$	561±6	225
$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	49—51	368.5
$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	40—51.1	440
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	42.7	510

TABLE II-18. HYGROSCOPICITY OF $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$

(1) Температура °C	(2) Давление водяных паров над насыщенным раствором мм рт. ст.	(3) Равновесная влажность воздуха над насыщенным раствором %
15	7.16	55.9
20	9.73	55.4
25	12.04	50.5
30	14.88	46.7
40	~ 20	35.5

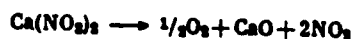
Key:

1. Salt
2. Melting point, °C
3. Heat of formation from simple substances, kcal/mole

Key:

1. Temperature, °C
2. Pressure of steam above saturated solution, mm Hg
3. Equilibrium humidity of air above saturated solution, %

When heated above 561°C, anhydrous salt $\text{Ca}(\text{NO}_3)_2$ is broken down with the release of oxygen and the formation of calcium nitrate, which is further broken down into CaO and NO_2 :



(II-12)

Tetrahydrate $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ melts at 42.7°C , forming a solution that boils at 150°C with the formation of dihydrate $\text{Ca}(\text{NO}_3)_2 \times 2\text{H}_2\text{O}$. It is completely dehydrated at 172°C .

Calcium nitrate has high hygroscopicity.² Figure II-31 presents the curves that characterize the pressure of water vapors above the saturated solutions of certain salts. It is apparent from the figure that calcium nitrate is even more hygroscopic than ammonium nitrate. (p. R127).

TABLE II-19. SOLUBILITY OF CALCIUM NITRATE IN WATER⁵⁰

(1) Температура °C	(2) Растворимость вес. %	(3) Твердая фаза	(1) Температура °C	(2) Растворимость вес. %	(3) Твердая фаза
-4.7	12.5	(4) Лед	0	50.5	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
-9.0	22.9		20	56.0	
-16.1	33.2		25	59.0	
-28	43.9		40	66.3	
			42.7*	66.7	
			42.6	70.6	$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
			51.1*	75.2	$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
			50.6	77.0	
			51.6	78.0	$\text{Ca}(\text{NO}_3)_2$
			151**	79.0	

Key: 1. Temperature, °C
2. Solubility, weight. %
3. Solid phase
4. Ice

* Melting point

** Boiling point of solution

TABLE II-20. DENSITY OF AQUEOUS SOLUTIONS⁵ OF $\text{Ca}(\text{NO}_3)_2$ (in g/cm^3)

(1) Концентрация $\text{Ca}(\text{NO}_3)_2$ вес. %	(2) Температура, °C						
	50	60	70	80	90	100	110
40	1.3600	1.3478	1.3365	1.3255	1.3175	1.3090	1.2990
45	1.4175	1.4055	1.3950	1.3850	1.375	1.3655	1.3590
50	1.4750	1.4630	1.4535	1.4440	1.4340	1.4250	1.4150
55	1.5325	1.5220	1.5125	1.5025	1.4925	1.4830	1.4730
60	1.5900	1.5800	1.5625	1.5610	1.5515	1.5425	1.5320
65	1.6490	1.6390	1.6300	1.6202	1.6100	1.6015	1.5920
70	1.7070	1.6975	1.6885	1.6805	1.6705	1.6608	1.6510
75	1.7650	1.7570	1.7475	1.7403	1.7309	1.7200	1.7103
80	1.8245	1.8155	1.8075	1.8000	1.7910	1.7810	1.7708
85	1.8840	1.8750	1.8675	1.8600	1.8515	1.8415	1.8325

Key: 1. Concentration of $\text{Ca}(\text{NO}_3)_2$, weight. %
2. Temperature, °C

Because the solutions of calcium nitrate do not freeze at low temperatures, they are used as cooling liquids. The characteristics of aqueous solutions of $\text{Ca}(\text{NO}_3)_2$ are presented in table II-20-II-26 and in fig. II-32-II-34.

TABLE II-21. DENSITY OF AQUEOUS SOLUTIONS OF $\text{Ca}(\text{NO}_3)_2$ WITH ADDITION⁵ OF 5% NH_4NO_3^*

(1) Концентрация $\text{Ca}(\text{NO}_3)_2$ вес. %	(2) Температура, °C								
	50	60	70	80	90	100	110	120	130
50	1,5420	1,4950	1,4890	1,4785	1,4680	1,4585	1,4522	1,4445	1,4380
55	1,5660	1,5570	1,5480	1,5410	1,5305	1,5200	1,5120	1,5080	1,5005
60	1,6282	1,6195	1,6105	1,6030	1,5945	1,5840	1,5780	1,5700	1,5635
65	1,6905	1,6820	1,6730	1,6660	1,6570	1,6480	1,6410	1,6340	1,6260
70	1,7530	1,7440	1,7360	1,7290	1,7200	1,7105	1,7040	1,6985	1,6900
75	1,8140	1,8060	1,7990	1,7920	1,7840	1,7745	1,7670	1,7600	1,7520
79	1,8660	1,8580	1,8500	1,8420	1,8340	1,8260	1,8180	1,8110	1,8025

Key:

1. Concentration of $\text{Ca}(\text{NO}_3)_2$, weight. %
2. Temperature, °C

* In relation to content of $\text{Ca}(\text{NO}_3)_2$ in solution.

TABLE II-22. VAPOR PRESSURE⁵ ABOVE AQUEOUS SOLUTIONS OF $\text{Ca}(\text{NO}_3)_2$ (in mm Hg)

(1) Концентрация $\text{Ca}(\text{NO}_3)_2$ вес. %	(2) Температура, °C							
	70	80	90	100	110	120	130	140
50	135	220	330	485	730	—	—	—
55	120	185	280	420	640	—	—	—
60	100	150	240	360	550	—	—	—
65	90	120	195	300	460	640	—	—
70	—	80	140	235	375	520	720	—
75	—	—	90	175	285	390	525	740

Key:

1. $\text{Ca}(\text{NO}_3)_2$ concentration, weight. %
2. Temperature, °C

Methods of Calcium Nitrate Production^{2,3}

The following methods are known for calcium nitrate production:

TABLE II-23. BOILING POINT OF AQUEOUS SOLUTIONS OF $\text{Ca}(\text{NO}_3)_2$ (in °C) AT DIFFERENT PRESSURE⁵

Концентрация $\text{Ca}(\text{NO}_3)_2$, вес. %	(2) Давление, мм рт. ст.													
	760	700	650	600	550	500	450	400	350	300	250	200	150	100
32.4	104.8	103.1	101.5	99.0	96.8	93.9	91.0	87.9	84.2	80.7	76.2	71.0	65.2	58.0
38.3	106.4	104.7	102.5	100.8	97.6	95.7	92.8	89.8	86.0	82.5	77.6	72.2	66.6	59.2
43.6	108.5	106.2	104.5	102.3	99.8	97.0	94.8	91.8	87.5	84.0	79.2	74.0	68.7	60.7
48.5	109.8	108.0	106.4	104.5	102.0	99.4	97.0	94.5	91.0	87.0	82.3	76.2	71.2	62.3
53.0	112.4	110.6	108.2	106.9	104.5	102.5	100.0	97.5	94.5	90.0	85.5	79.0	73.0	63.4
58.9	117.0	115.4	113.7	111.7	109.5	107.0	104.3	100.7	97.6	94.5	90.0	84.7	78.0	69.6
65.5	124.0	122.2	120.4	118.0	115.0	112.5	110.0	106.6	103.1	98.8	95.0	90.6	84.4	76.0
77.9	143.3	141.8	140.0	137.8	135.5	132.5	130.0	126.4	122.0	117.0	112.5	107.5	101.5	—

Key:

1. Concentration of $\text{Ca}(\text{NO}_3)_2$, weight. %
2. Pressure, mm Hg

TABLE II-24. VISCOSITY OF AQUEOUS SOLUTIONS OF $\text{Ca}(\text{NO}_3)_2$ (in centipoise)

Температура °C	(2) Концентрация $\text{Ca}(\text{NO}_3)_2$, %					
	30.55	40	46.99	60	70	80
50	1.26	2.05	3.80	—	—	—
60	—	1.72	3.13	7.73	51.29	—
70	0.91	1.45	2.70	6.13	35.47	—
80	0.79	1.25	2.26	4.65	24.90	—
90	0.69	1.09	1.95	4.09	14.32	105.62
100	0.61	0.96	1.71	3.71	15.43	78.04
110	—	—	—	2.85	12.73	51.65

Key:

1. Temperature, °C
2. Concentration of $\text{Ca}(\text{NO}_3)_2$, %

- 1) direct interaction of chalk or limestone with nitric acid;
- 2) absorption of nitrous gases by milk of lime with subsequent inversion of obtained solutions by nitric acid;
- 3) nitric acid breakdown of phosphates. In this method, the main products produced are such fertilizers as dicalcium phosphate,

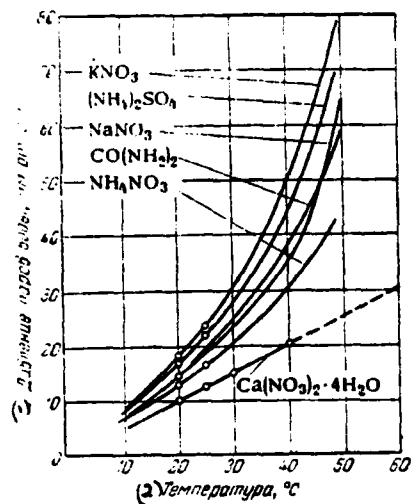


Figure II-31. Pressure of Water Vapors above Saturated Solutions of Pure Substances

Key:

1. Pressure of water vapors, mm Hg
2. Temperature, °C

nitrophos or nitrophoska; calcium nitrate is a by-product.

4) interaction of calcium oxide with nitrogen peroxide at 300-400°C, the so-called dry method which has limited application.

Production of Calcium Nitrate from Limestone and Nitric Acid

The plan for production of calcium nitrate by this method is shown in fig. II-35.

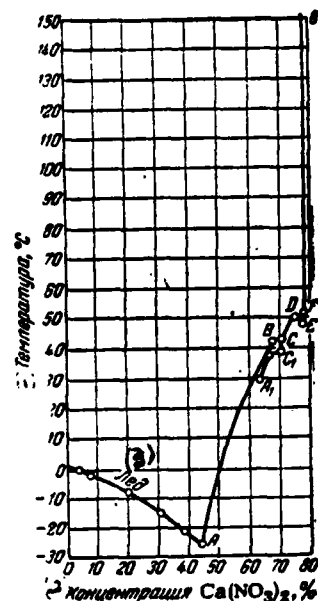


Figure II-32. Curves of Calcium Nitrate Solubility in Water

Key:

1. Temperature, °C
2. Concentration $\text{Ca}(\text{NO}_3)_2$, %
3. Ice
- A. Eutectic point (-28°C) corresponds to concentration of 43.9% $\text{Ca}(\text{NO}_3)_2$ in solution
- ABC. Solubility curve of stable α -form of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
- B. Melting point of tetrahydrate (42.7°C)
- A₁C₁. Solubility curve of metastable β -form $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
- CDE. Solubility curve of $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
- D. Melting point of trihydrate (51.1°C)
- EF. Solubility curve of metastable dihydrate $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
- FG. Solubility curve of anhydrous salt $\text{Ca}(\text{NO}_3)_2$, solubility almost does not increase with rise in temperature
- G. Boiling point of saturated solution (151°C) containing ~79% $\text{Ca}(\text{NO}_3)_2$

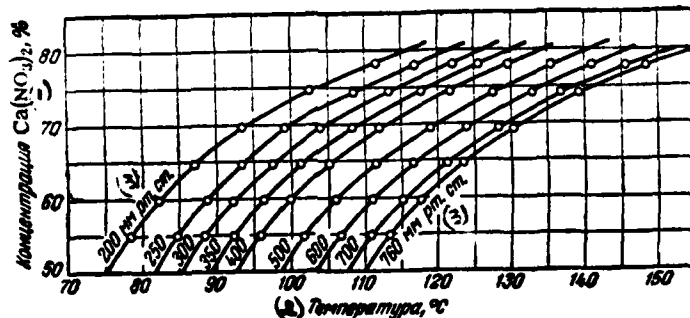


Figure II-33. Boiling Point of Aqueous Solutions of $\text{Ca}(\text{NO}_3)_2$ at Pressure 200-760 mm Hg

Key:

1. Concentration
2. Temperature, °C
3. mm Hg

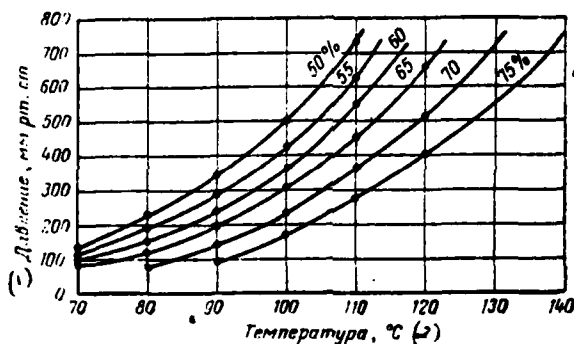


Figure II-34. Boiling Point of Aqueous 50-75% Solutions of $\text{Ca}(\text{NO}_3)_2$ and Vapor Pressure above Solutions

Key:

1. Pressure, mm Hg
2. Temperature, °C

Nitric acid (40-48%) flows by gravity flow from a pressure tank into reaction tower 3 that is filled with limestone (pieces 100-150 mm in size). The limestone (CaCO_3 content 94-97%) is loaded into the tower with the help of a charging ladle hoist. The lower part of the tower has a grating on which the limestone rests.

The carbon dioxide that is released in the tower is sucked out by fan 1. The spray trapped by the gas is held in spray-trap 2 and drains into settling tanks 5 and 6. A vacuum in limits of 15-25

TABLE II-25. VISCOSITY OF AQUEOUS SOLUTIONS OF $\text{Ca}(\text{NO}_3)_2$ WITH ADDITION OF 5% NH_4NO_3 *

(1) Температура °C	(2) Концентрация $\text{Ca}(\text{NO}_3)_2$, %					
	31,84	41,8	51,65	60	70	80
50	1,47	3,22	5,76	10,12	—	—
60	—	—	—	7,85	—	—
70	1,08	1,59	3,85	6,30	—	—
80	0,94	1,38	2,73	5,25	22,80	—
90	0,82	1,22	—	4,40	17,20	—
100	0,72	1,07	2,13	3,65	14,20	—
110	—	—	—	3,20	11,40	—
120	—	—	—	2,40	9,05	46,00
130	—	—	—	1,80	7,50	30,40

Key:

1. Temperature, °C
 2. Concentration of $\text{Ca}(\text{NO}_3)_2$, %
- *In relation to the content of $\text{Ca}(\text{NO}_3)_2$ in solution.

TABLE II-26. SPECIFIC HEAT CAPACITY OF AQUEOUS SOLUTIONS⁴⁹ OF $\text{Ca}(\text{NO}_3)_2$ AT 21-51°C

Концентрация (1) $\text{Ca}(\text{NO}_3)_2$ %	Теплоемкость (2) кал/(г·град)	Концентрация (1) $\text{Ca}(\text{NO}_3)_2$ %	Теплоемкость (2) кал/(г·град)
47,9	0,6255	15,4	0,8463
37,8	0,6856	8,4	0,9116
26,75	0,7597	4,4	0,9510

Key:

1. $\text{Ca}(\text{NO}_3)_2$ concentration, %
2. Heat capacity, cal/(g x deg)

mm wat. col. is maintained in the tower. The acid solution of calcium nitrate that flows from the tower remains in vessels 5 and 6 where particles of sand and other insoluble admixtures are precipitated. Part of the solution is again fed for sprinkling the reaction tower through tank 4, while the remaining solution is removed for final neutralization in apparatus 8. Ammonia or slaked lime is used for final neutralization. When ammonia in calcium nitrate is added to the solution, admixtures of ammonium nitrate are formed. Crystallization of $\text{Ca}(\text{NO}_3)_2$ from the melt is facilitated in their presence. The towers, final neutralizer, settling tanks and pumps are made of stainless steel brand Kh18N9T. The neutralization solutions of

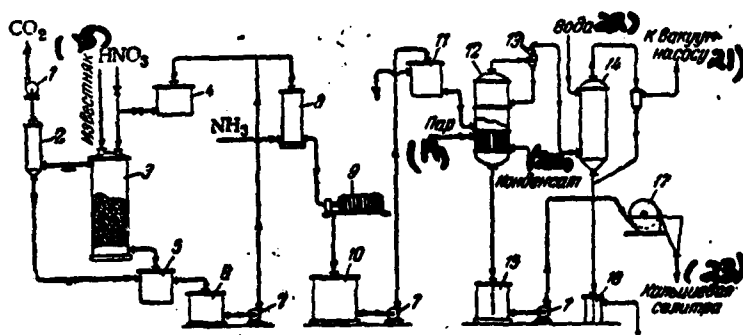


Figure II-35. Plan for Production of Calcium Nitrate from Limestone and Nitric Acid

Key:

- | | | |
|------|--|---------------------|
| 1. | Fan | |
| 2. | Spray trap | |
| 3. | Reaction tower | |
| 4. | Pressure tank for acid solution of calcium nitrate | |
| 5,6. | Settling tank of acid solution of calcium nitrate | |
| 7. | Centrifugal pumps | |
| 8. | Final neutralizer | |
| 9. | Filter press | |
| 10. | Collector of filtered solution | |
| 11. | Pressure tank | |
| 12. | Evaporator | |
| 13. | Trap | |
| 14. | Barometric condenser | |
| 15. | Collector of melt of calcium nitrate | |
| 16. | Barometric container | |
| 17. | Cooling rollers | 21. To vacuum pump |
| 18. | Limestone | 22. Water |
| 19. | Steam | 23. Calcium nitrate |
| 20. | Condensate | |

calcium nitrate are usually very contaminated with the admixtures contained in the limestone. It is very difficult to separate them. Filter presses are usually used to filter the formed viscous solutions of $\text{Ca}(\text{NO}_3)_2$, although their output is low.

The solution that is filtered on filter press 9 enters collector 10 and is further fed for evaporation. The solution that arrives for evaporation contains 49% $\text{Ca}(\text{NO}_3)_2$ and 3% NH_4NO_3 . In evaporator 12, the concentration of solution is increased to 75-82% $\text{Ca}(\text{NO}_3)_2$. The melt of calcium nitrate that is obtained in this case is sent for crystallization. This can be done on cooling rollers 17

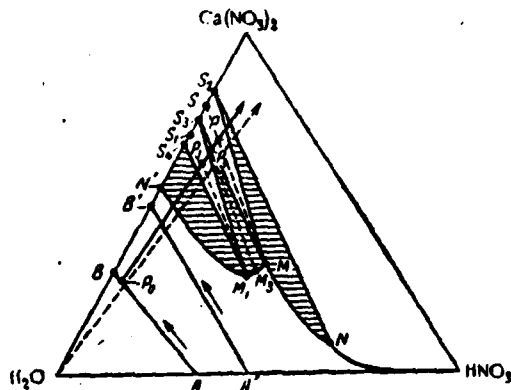


Figure II-36. Diagram of Equilibrium of $\text{Ca}(\text{NO}_3)_2$ - HNO_3 - H_2O System at 25°C

or in the granulation tower.

Figure II-36 presents the equilibrium diagram in the $\text{Ca}(\text{NO}_3)_2$ - HNO_3 - H_2O system at 25°C . Points S_2 , S_3 and S_4 correspond to di-, tri- and tetrahydrate $\text{Ca}(\text{NO}_3)_2$. The areas of existence of these crystal hydrates are in limits of the hatched curvilinear triangles: tetrahydrate in triangle S_4M_1N' , trihydrate in triangle S_3MM_1 , and dihydrate in triangle S_2MN . These regions are limited by curve $N'M_1MN$ of crystal hydrate solubility in acid solutions and by the lines for conversion of the forms of the corresponding crystal hydrates. Below and to the left of the solubility line there is a region of unsaturated acid solutions. With neutralization by limestone of 30% (point A) or 48% (point A') nitric acid, the change in solution composition as neutralization occurs is illustrated by straight lines AB and A'B'. They do not intersect the saturation curve $N'M_1MN$. Consequently, a solid salt can only be obtained after evaporation of the neutralized solution.

We assume that as result of neutralizing 30% acid by limestone, we obtain a slightly acid solution whose composition is illustrated by point P_0 . With evaporation of this solution, the figurative point of the system from which water is removed will be shifted along the ray P_0P . The interval P_1P of this ray corresponds to the content in the system of 75-78% $\text{Ca}(\text{NO}_3)_2$. If the solution composition after evaporation is depicted by point P, then when it

is cooled to 25°C, the mixture of di- and trihydrate is crystallized. The composition of this mixture is depicted by point S, while the composition of the liquor solution is illustrated by point M.

If the composition of the evaporated solution corresponds to point P₁, then after cooling of the solution to 25°C, a mixture of crystals of tri- and tetrahydrate is obtained. The composition of the mixture is illustrated by point S₁. The composition of the liquor solution is indicated by point M₁. With evaporation of the solution to a composition corresponding to point P₃, crystals of the trihydrate Ca(NO₃)₂ x 3H₂O precipitate out after cooling.

The USSR does not produce calcium nitrate used as a fertilizer from nitric acid, but from the waste nitrous gases. This permits a less expensive product to be produced.

Production of Calcium Nitrate by the Method of Alkaline Absorption of Nitrous Gases

When nitrous gases are washed by milk of lime, an alkali is formed which contains calcium nitrite with an admixture of a certain quantity of calcium nitrate:



The nitric oxides are absorbed by milk of lime (fig. II-37) in towers sprinkled by circulating solution in which the surplus alkalinity is maintained to 30 g/l by adding milk of lime (100-130 g/l) or dry lime to it. This makes it possible to obtain more concentrated alkali. The temperature of the alkali that arrives for sprinkling is in limits of 30-35°C. No less than 92% of the nitric oxides are recovered from the exhaust nitrous gases in alkaline absorption.

The alkali that flows out of the absorption towers is treated

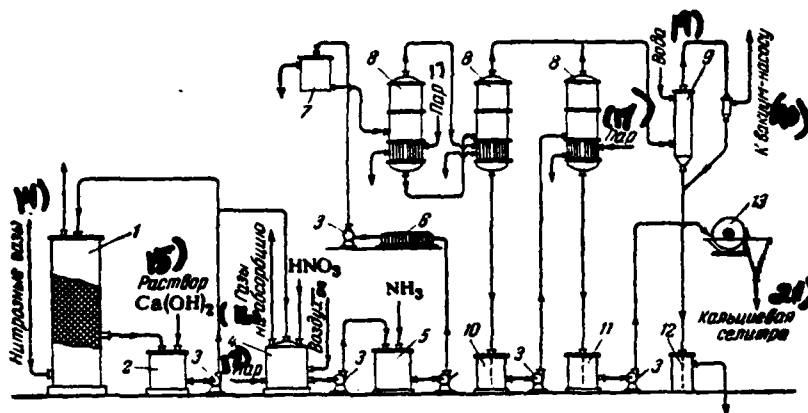
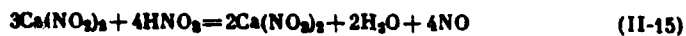


Figure II-37. Plan for Production of Calcium Nitrate by Method of Alkaline Absorption of Nitrous Gases

Key:

1. Absorption tower
2. Collector of nitrite-nitrate alkali
3. Centrifugal pumps
4. Inverter
5. Final neutralizer
6. Filter press
7. Pressure tank for filtered solution
8. Evaporators
9. Barometric condenser
10. Collector of evaporated solution of calcium nitrate
11. Collector of melt of calcium nitrate
12. Barometric container
13. Cooling rollers
14. Nitrous gases
15. Solution
16. Gases to absorption
17. Steam
18. Air
19. Water
20. To vacuum pump
21. Calcium nitrate

with nitric acid to convert (invert) the nitrite into nitrate:



The nitric oxide that is released during inversion is returned to the absorption system for the production of diluted (weak) nitric acid. Inversion is done in unit 4 with heating by live steam and intensive mixing of the solution by compressed air.

A surplus of nitric acid remains in the inverted solution. It is neutralized by ammonia in apparatus 5. In this case, a certain quantity of ammonium nitrate is formed. Its presence has a favorable effect on the process of subsequent crystallization of the calcium nitrate. The solution is further filtered on filter press 6, heated to 60-70°C, and sent for evaporation to one- or multihousing evaporation units. Vertical type evaporation units are usually used with inner or extension heating chamber. The solution is evaporated with the following conditions for the one-stage plan of evaporation (one-housing unit):

Pressure of the heating steam, atm.	5
Vacuum in the apparatus, mm Hg	500
Composition of solution for evaporation, %	
$\text{Ca}(\text{NO}_3)_2$	25%
NH_4NO_3	1.4%
Composition of melt at outlet from unit, %	
$\text{Ca}(\text{NO}_3)_2$	77-82%
NH_4NO_3	5-6%
Temperature of melt at outlet from unit, °C	120
Temperature of liquor vapor, °C	105

If a three-stage plan of evaporation is used (see fig. II-37), the first and second evaporators 8 operate continuously, while the third operates in batches. The first evaporator on the course of the solution is heated by live steam (pressure 6-8 atm.) In the zone of solution evaporation, the pressure of the liquor vapor can be 1.5-3-4 atm. In the second evaporator, the solution is evaporated with vacuum (residual pressure in the evaporation zone 0.2 atm.). Heating of the second housing uses liquor vapor that is collected from the first evaporator. The solution that emerges from the second evaporator is collected in tank 10. From here it is fed to final evaporation in the third evaporator which operates at vacuum of 600 mm Hg and is heated by live steam (pressure 6-8 atm.). With the indicated vacuum, the boiling point of the solution is about 110°C. The concentration of the melt at the outlet from the unit reaches roughly 85-86% with regard for the presence of NH_4NO_3 . At atmospheric pressure, this solution boils at 150°C and the concentration of the melt only slightly exceeds 79%.

The operating pattern of the three-housing evaporator with evaporation of solutions of calcium nitrate is characterized by the following indicators:

	first housing	second housing	third housing
Concentration of solution, %			
at inlet to unit	25	36	60
at outlet from unit	36	60	86
Vapor pressure, atm.			
of heating	6	1.5*	6
of liquor	1.5	0.2	0.2
Boiling point of solution, °C	118-120	78-80	110-112

*Liquor vapor from first housing.

The melt pours from the third evaporator into vessel 11, and is further sent for crystallization. This is done on cooling rollers 13 or in the granulation towers.

Crystallization is the most complicated process in the production of calcium nitrate. The mechanism for the formation of calcium nitrate crystals is still not sufficiently clear. The structure of the formed salt crystals varies: sometimes in crystallization solid crystals that are easily separated from the cooling surface of the unit are formed. In other cases, a viscous syrupy-like melt is formed that does not harden into a solid crust. Even with strong overcooling of the calcium nitrate melt, crystallization sometimes does not occur. In order to cause crystallization, seed crystals of calcium nitrate are put into the melt. However, crystallization in this case does not always occur in the same way. In a number of cases, this is associated with the inconstant temperatures of salt melting (see table II-17).

Ammonium nitrate has a great effect on the process of $\text{Ca}(\text{NO}_3)_2$ crystallization. In the presence of ammonium nitrate, the rate of crystallization of calcium nitrate increases 1.5-2-fold with simultaneous increase in the crystallization temperature by 50°C. The more ammonium nitrate is contained in the solution, the better crystallization occurs. For normal occurrence of the process of crystallization of calcium nitrate, it is usually quite sufficient

to have 5-6% NH_4NO_3 of the quantity of calcium nitrate in the melt. It has been established, however, that when there is a content of 5% ammonium nitrate, 72% melt of calcium nitrate (density 1.72 g/cm^3) is not quite crystallized on the cooling rollers, while the melt that contains 73-82% $\text{Ca}(\text{NO}_3)_2$ (density $1.76-1.88 \text{ g/cm}^3$) is crystallized well, and the 83% melt (density over 1.88 g/cm^3) is crystallized poorly.

Admixtures of nitrates of iron and aluminum almost have no effect on the rate of crystallization of calcium nitrate; in the presence of silicates and sodium nitrate, its crystallization is impaired (adhesive and poorly hardening crystals are obtained).

Crystallization of calcium nitrate with the addition of ammonium nitrate occurs on cooling rollers at 90°C . In this case, a large part of the salt is crystallized in the form of dihydrate $\text{Ca}(\text{NO}_3)_2 \times 2\text{H}_2\text{O}$. The temperature of the melt in the roller pan is maintained at about 110°C .

In order to reduce the hygroscopicity of the calcium nitrate after crystallization on the cooling rollers, it can be mixed with hydrophobic substances (for example, with paraffin-base mazut). The mixing is done in a small rotating drum-mixer into which the hydrophobic additive is dosed.

Before the calcium nitrate is loaded into the packaging, it should be cooled to 30°C since hot salt is prone to conglomeration. This impairs its scatterability. The calcium nitrate is cooled in a drum through which cooled air is blown. After cooling, the calcium nitrate enters the packing section on a conveyer.

The product is packed in kraft pulp bituminized bags with holding capacity of 40-45 kg. Automatic scales are used for weighing. The bags are sewn on sewing machines and stored in covered dry warehouses.

Sample consumption coefficients for 1 T of technical-grade

calcium nitrate containing 82% $\text{Ca}(\text{NO}_3)_2$:

Solution of calcium nitrate, 25%, T	3.3
Steam (6 ₃ atm.), T	2.0
Water, m ³	75.0
Electricity, kw x h	23.5
Bags, No.	25

The production waste is 1.6 T of steam condensate for 1 T of nitrate.

A new method has been developed for granulating calcium nitrate (as well as carbamide and other substances from melts) that can be recommended instead of crystallization of it on the surface of the cooled drum or spraying of drops of melt in the tower in the stream of air. This new method consists of crystallizing the salt from drops of melt sprayed in mineral oil that contains seed crystals, with subsequent separation of the granules from the oil on centrifuges.

Use and quality of Calcium Nitrate

Calcium nitrate is a universal physiological alkaline fertilizer that is suitable for all soils of the nonchernozem zone with insufficient content of calcium. However, because of the low content of nitrogen (15.5%), its shipping great distances is not profitable, since the transportation expenditures significantly increase the cost of a unit of nitrogen in the fertilizer. Consequently, it is expedient to set up production of calcium nitrate near the regions of its consumption.

According to MRTU-6-03-195-67, the calcium nitrate that is used as a fertilizer is manufactured in the form of a flaked product of light chestnut color. The total nitrogen content in the calcium nitrate (in conversion for anhydrous substance) must be no less than 17.5%. The content of ammonium nitrate—in limits of 4-7%, and the moisture content no more than 14%.

In order to improve the agrochemical properties of calcium nitrate, its surface treatment with paraffin-based mazut (up to 1%

of the salt weight) is permitted.

Sample granulometric composition of the finished nitrate is given below:

Particle dimensions, mm	5	5-2	2
Number of fractions, %	80.2	19.5	0.3

3. Potassium Nitrate

Physical-Chemical Properties of Potassium Nitrate

Potassium nitrate, KNO_3 , is an anhydrous, practically non-hygroscopic salt of white color which is crystallized in two different forms. At low temperatures, crystals of rhombic shape are formed, and at high temperatures, rhombohedral crystals. The transition of salt from one crystal form into another occurs at 127.7°C and is accompanied by the release of heat in a quantity of 1.410 kcal/mole.

The basic physicalchemical constants⁵¹ of potassium nitrate are given below:

Molecular weight	101.107
Density, g/cm ³	2.11
Melting point, °C	337
Heat capacity at 28°C	
specific, cal/(g x deg)	0.221
molar cal/(mole x deg)	22.38
Heat of formation from simple substances, kcal/mole	117.76
Heat of dissolving in 280-560 mole of water at 15°C, kcal/mole	-8.3

When potassium nitrate is heated above 338°C , oxygen is released and potassium nitrite is formed. At higher temperatures, potassium oxide K_2O can be formed. When heated with sulfuric acid, potassium nitrate is broken down with the release of nitric oxides.

The salt is easily dissolved in water and in diluted ethyl alcohol. Dissolving of potassium nitrate in water occurs with a

noticeable decrease in temperature. The solubility of KNO_3 in water with an increase in temperature from 30 to 114°C rises roughly 7-fold (table II-27).

TABLE II-27. SOLUBILITY OF KNO_3 IN WATER²

Температура (1) °C	Растворимость (2) г/100 г воды	Твердая (3) фаза	Температура (1) °C	Растворимость (2) г/100 г воды	Твердая (3) фаза
-1	3.34	Лед(4)	40	63.9	KNO_3
-2.85	12.2	Эвтектика(5)	50	85.7	То же(6)
0	13.25	KNO_3	60	109.9	"
10	21.0	"	80	169.0	"
20	31.5	"	100	245.2	"
25	38.2	"	114	312.0	"
30	45.6	"			

Key:

1. Temperature, °C
2. Solubility of g/100 g of water
3. Solid phase
4. Ice
5. Eutectics
6. The same

Data on the solubility of potassium nitrate in nitric acid are presented in table II-28.

TABLE II-28. SOLUBILITY OF KNO_3 IN NITRIC ACID⁵²

(1) Состав раствора, вес. %							
HNO_3	KNO_3	HNO_3	KNO_3	HNO_3	KNO_3	HNO_3	KNO_3
(2) При 0 °C		(2) При 15 °C		(2) При 30 °C		(2) При 75 °C	
30.1	7.0	45.1	17.7	40.1	18.9	21.8	38.9
33.5	7.5	49.3	25.1	47.7	27.7		
39.9	9.7	51.0	32.7	49.0	33.2	32.2	36.7
48.0	16.5	51.6	38.1	50.8	42.5	38.5	37.6
50.7	23.1	50.0	49.2	49.7	49.9	42.5	39.9
52.2	30.2	—	—	—	—	45.5	43.9
57.5	34.4	—	—	—	—	46.7	50
73.0*	25.5*	—	—	—	—	46.2	52.6

Key:

1. Composition of solution, weight. %
 2. At
- * solid phase of $\text{KHN}_3 \times 2\text{HNO}_3$.

TABLE II-29. DENSITY OF AQUEOUS SOLUTIONS² OF KNO₃

(1) Концентрация KNO ₃ вес. %	(2) Температура, °C							
	10	20	30	40	50	60	80	100
1	1,006	1,004	1,002	0,998	0,994	0,989	0,978	0,964
2	1,012	1,010	—	1,004	—	0,994	0,983	0,969
4	1,025	1,023	1,020	1,016	1,012	1,007	0,995	0,980
6	1,039	1,036	1,033	1,029	1,024	1,019	1,007	0,994
8	1,052	1,049	—	1,041	—	1,031	1,019	1,005
10	1,066	1,063	1,058	1,054	1,049	1,044	1,032	1,018
12	1,079	1,076	—	1,067	—	1,056	1,044	1,030
16	—	1,104	1,099	1,094	1,089	1,083	1,070	1,056
20	—	1,133	1,128	1,122	1,117	1,111	1,097	1,083
24	—	1,162	1,157	1,152	1,145	1,139	1,126	1,111

Key:

1. Concentration of KNO₃, weight. %
2. Temperature, °C

TABLE II-30. VISCOSITY OF AQUEOUS SOLUTIONS² OF KNO₃ (in centipoise)

(1) Темпе- ратура	(2) Концентрация KNO ₃ , %				
	5	10	15	20	30
0	1.68	1.61	—	—	—
10	1.25	1.22	1.21	1.25	—
20	0.98	0.97	0.98	1.01	—
30	0.80	0.80	0.80	0.81	0.89
40	0.66	0.67	0.69	0.70	—
50	0.56	0.58	0.59	0.60	—
60	0.49	0.50	0.51	0.53	—

Key:

1. Temperature
2. Concentration of KNO₃, %

TABLE II-31. SPECIFIC HEAT CAPACITY² OF AQUEOUS SOLUTIONS OF KNO₃

(1) Темпе- ратура °C	(2) Концентрация KNO ₃ g/100 g воды	(3) Тепло- емкость кал/(g·град)
20	1.4	0.9842
	5.6	0.9421
	22.4	0.8319
18	2.8	0.966
	11.4	0.8319

Key:

1. Temperature, °C
2. KNO₃ concentration, g/100 g of water
3. Heat capacity, cal/(g x deg).

In the presence of NaCl, the solubility of potassium nitrate is considerably increased.²⁸ For example, in 100 g of a saturated solution (21.63 g of KNO₃) at 18°C, after addition of 5 g of NaCl, another 0.744 g of potassium nitrate are dissolved, and after addition of 26.85 g of NaCl, another 3.22 g of KNO₃ are dissolved.

The solubility of KNO₃ in ethyl alcohol at 15°C:

Concentration of KNO_3 , % 13.2 8.5 5.6 4.3 2.8 1.7
 Concentration of $\text{C}_2\text{H}_5\text{OH}$, % 10 20 30 40 50 60

TABLE II-32. PRESSURE OF WATER VAPORS² ABOVE KNO_3 SOLUTIONS

Температура °C 1	Концентрация KNO_3 г/100 г воды 2	Давление мм рт. ст. 3	Температура °C 1	Концентрация KNO_3 г/100 г воды 2	Давление мм рт. ст. 3
-2,82	11,52	3,62	70	138	181,8
0	13,3	4,45	80	169	282,2
10	20,9	6,86	90	202	366,9
20	31,6	10,52	100	246	499
25	37,3	12,10	110	295	660
30	45,8	14,20	115	330	760
40	63,9	19,0	120	365	852
50	85,5	25,8	125	415	958
60	110	34,94			

Key:

1. Temperature, °C
2. KNO_3 Concentration, g/100 g of water
3. Pressure, mm Hg

The saturated solution of potassium nitrate boils at 115°C.

At high temperatures, potassium nitrate acts like a strong oxidizing substance (in the presence of KNO_3 , carbon, sulfur, organic substances, etc. are easily ignited).

Potassium nitrate can be combined with HNO_3 to form acid nitrates: $\text{KNO}_3 \times \text{HNO}_3$ and $\text{KNO}_3 \times 2\text{HNO}_3$.

The properties of the aqueous solutions of potassium nitrate are presented in tables II-29-II-33.

The heat conductivity λ of aqueous solutions of KNO_3 at 20°C has the following values⁵³:

KNO_3 concentration, %	10	20	30
λ , cal/(cm x s x deg)	0.502	0.487	0.469

Methods of Potassium Nitrate Production

Industry uses the following methods for producing potassium nitrate:

TABLE II-33. BOILING POINT² OF
AQUEOUS SOLUTIONS OF KNO₃ AT 760 mm Hg

Температура кипения °С	Концентрация KNO ₃ #/100 г воды	Температура кипения °С	Концентрация KNO ₃ #/100 г воды
101	15,2	109	164,0
102	31,0	110	188,5
103	47,5	111	215,0
104	64,5	112	243,0
105	82,0	113	276,0
106	101,0	114	308,0
107	120,5	115	338,5 (3)
108	141,5		(насыщенный раствор)

Key:

1. Boiling point, °C
2. KNO₃ concentration, g/100 g of water
3. Saturated solution

1) conversion method--double decomposition of sodium nitrate and potassium chloride;

2) direct method--interaction of potassium chloride and diluted (weak) nitric acid or liquid nitric oxides;

3) cation method--exchange between ions of potassium and calcium in equivalent ratios with the help of solid sorbents-cationites;

4) neutralization method--neutralization of nitric acid or nitric oxides by potassium hydroxide with subsequent inversion of formed potassium nitrite into KNO₃.

Raw material. All the industrial methods for producing potassium nitrate (with the exception of neutralization) use potassium chloride as one of the types of raw material.

According to GOST 4568-65, two brands of potassium chloride are produced: K and F. Their quality must meet the following indicates:

Indicator	Brand K			Brand F	
	highest	1st	2nd	2nd	3rd
KCl content, %, no less in conversion for dry substance	99	98.3	95	95	92
in conversion for K ₂ O	-	-	60	60	58.1
NaCl admixtures					
In conversion for dry substance, %, no more	0.9	1.4	4.5	4.5	7.0
	270				

Moisture content, % no more	0.3	1.0	1.0	1.0	1.0
Residue insoluble in water, % no more	0.1	0.15	not standardized		

The production of potassium nitrate uses only the first and second grades of potassium chloride of brand K that is shipped in a pile in railroad cars. The salt that contains an additive of amines does not cake. In the absence of this additive, potassium chloride cakes, forming a monolithic mass that is difficult to break up.

The density of solid KCl is about 2 T/m^3 . The saturated pure solution of this salt boils at 108.6°C and contains 58.4 g of KCl in 100 g of water.

TABLE II-34. KCl SOLUBILITY IN WATER⁵⁴

(1) Температура °C	(2) Растворимость		(E) Плотность g/cm ³	(1) Температура °C	(2) Растворимость		(E) Плотность g/cm ³
	(3) вс. %	(4) s/l			(3) вс. %	(4) s/l	
-10	18.8	213	1.133	60	31.4	376	1.198
0	21.9	253	1.154	70	32.6	392	1.202
+10	23.8	277	1.165	75	33.2	399	1.203
20	25.6	301	1.174	80	33.8	407	1.205
25	26.45	312	1.178	90	34.9	422	1.208
30	27.2	322	1.182	100	35.9	434	1.210
40	28.2	341	1.188	125	38.2	483	1.213
50	30.1	359	1.194	150	40.5	492	1.215

Key:
 1. Temperature, °C
 2. Solubility
 3. Weight, %
 4. g/l
 5. Density, g/cm³

The production of potassium nitrate generally uses potassium chloride in the form of aqueous solutions of varying concentration. Tables II-34-II-38 present the basic properties of the aqueous solutions of potassium chloride.

The viscosity of concentrated KCl solutions at 18°C is:

KCl Concentration, g/l	106.4	226.7	300
Viscosity, centipoise	1.056	1.089	1.120

TABLE II-35. DENSITY OF AQUEOUS SOLUTIONS⁵⁴ OF KCl
(IN g/cm³)

(1) Концентрация KCl вес. %	(2) Температура, °C								
	0	10	20	25	30	40	50	80	100
1	1,00661	1,00627	1,00463	1,00342	1,00188	0,99847	0,99428	0,9790	0,9648
4	1,02890	1,02595	1,02391	1,02225	1,02099	1,01727	1,01294	0,9966	0,9834
6	1,04055	1,03920	1,03690	1,03544	1,03380	1,02995	1,02554	1,0092	0,9960
8	1,05431	1,05227	1,05003	1,04847	1,04675	1,04278	1,03829	1,0219	1,0088
10	1,06820	1,06609	1,06332	1,06167	1,05987	1,05578	1,05122	1,0347	1,0218
12	1,08222	1,07978	1,07679	1,07508	1,07318	1,06897	1,06435	1,0478	1,0350
14	1,09638	1,09366	1,09046	1,08865	1,08669	1,08237	1,07770	1,0611	1,0483
16	1,11068	1,10775	1,10434	1,10245	1,10041	1,09600	1,09128	1,0746	1,0619
18	1,12513	1,12207	1,11845	1,11647	1,11435	1,10987	1,10510	1,0884	1,0757
20	1,13973	1,13663	1,13280	1,13072	1,12852	1,12399	1,11917	1,1024	1,0897
22	1,15449	1,15144	1,14740	1,14521	1,14294	1,13836	1,13349	1,1166	1,1040
24	—	—	1,16228	1,15995	1,15762	1,15299	1,14807	1,1311	1,1185
26	—	—	—	1,17495	1,17254	1,16788	1,16291	1,1458	1,1333
28	—	—	—	—	—	1,18304	1,17802	1,1609	1,1483

Key:

1. KCl concentration, weight. %
2. Temperature, °C

TABLE II-36. VISCOSITY OF
AQUEOUS SOLUTIONS⁵⁴ OF KCl
(IN CENTIPOISE)

(1) Температура °C	(2) Концентрация KCl, g/l		(1) Температура °C	(2) Концентрация KCl, g/l	
	37,27	74,55		37,27	74,55
5	1,460	1,411	50	0,561	0,572
10	1,261	1,236	60	0,482	0,495
18	1,049	1,050	70	0,419	0,431
30	0,798	0,800	80	0,389	0,411
40	0,661	0,670	85	0,347	0,369

Key:

1. Temperature, °C
2. KCl concentration, g/l

TABLE II-37. SURFACE TENSION⁵⁴
OF AQUEOUS SOLUTIONS OF KCl (IN
dyne/cm)

(1) Концентрация KCl g/l	(2) Температура, °C		
	20	25	40
105.35	74.83	—	71.82
159.1	75.99	—	72.90
223.8	—	77.77	—
298.2	—	77.85	—
360.1	—	78.95	—

Key:

1. KCl concentration, g/l
2. Temperature, °C

Conversion Method for Producing Potassium Nitrate^{2,3,28,55-58}

Double decomposition of sodium nitrate and potassium chloride occurs according to the reaction:



(II-16)

TABLE II-38. SPECIFIC HEAT CAPACITY⁵⁴
OF AQUEOUS SOLUTIONS OF KCl [in kcal/
(kg x deg)]

Концентрация KCl, моль/л (1)	Температура, °C (2)			
	10	20	30	40
0.1	0.9868	0.9862	0.9856	0.9850
0.5	0.9512	0.9526	0.9539	0.9595
1.0	0.9144	0.9132	0.9148	0.9166
2.0	0.8423	0.8439	0.845	0.8474

Key:

1. KCl concentration, mole/l
2. Temperature, °C

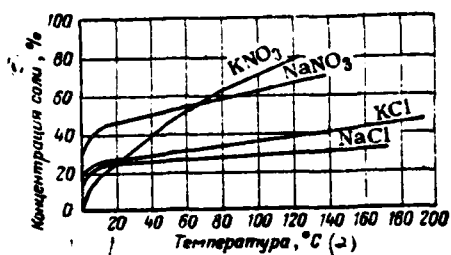


Figure II-38. Solubility of Nitrates and Chlorides of Potassium and Sodium in Water

Key:

1. Concentration of salt, %
2. Temperature, °C

The equilibrium content of salts that participate in this reaction depends very strongly on the temperature at which the process occurs.

As follows from fig. II-38, with an increase in temperature, the solubility of nitrates of potassium and sodium significantly rises, while the solubility of chlorides of these metals changes little. For example,²⁸ at 20°C, for 1000 mole of water in solution there is 74 mole of KNO₃ and 104 mole of NaCl. At 100°C, for 1000 mole of water in solution there is 438 mole of KNO₃ and the same 104 mole of NaCl.

When water is evaporated from a solution that contains equimolecular quantities of sodium nitrate and potassium chloride, a small quantity of NaCl is released into the precipitate, and the solution becomes saturated for KCl. In order to increase the quantity of NaCl in the precipitate, and consequently, to increase the output of

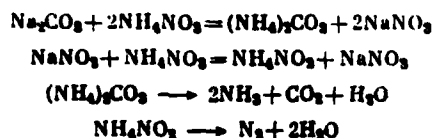
potassium nitrate, a surplus of sodium nitrate is added to the original solution.

The solubility of sodium chloride at the boiling point of its solution is almost the same as at normal temperature, while the solubility of KNO_3 at the boiling point of the solution increased many times. Therefore, roughly 70% of the NaCl that is formed in the reaction (II-16) precipitates out from the hot saturated solution of sodium nitrate and potassium chloride. It follows from here that it is expedient to conduct the reaction of double decomposition only at higher temperatures.

In addition to KCl (or its solutions), the production of potassium nitrate uses solutions of sodium nitrate that are usually obtained by inversion of nitrite-nitrate alkalis (p.299). A sample composition of inverted solutions is given below (in g/l):

NaNO_2	400—450	$\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$. .	To 0,4
NaNO_3	to 0,2	$\text{NaCl} + \text{Na}_2\text{SO}_4$. . .	2

In order to obtain potassium nitrate that does not contain admixtures of carbonates and sodium nitrates that accompany the sodium nitrate, a small quantity of ammonium nitrate⁵⁷ is added to the converted solutions. In this case, the admixture is broken down:



Gaseous products of admixture decomposition together with the steam formed during the conversion process are removed into the atmosphere.

The process of obtaining potassium nitrate by the conversion method (fig. II-39) consists of two basic stages: 1) double decomposition of sodium nitrate and potassium chloride; 2) purification of the primary ("raw material") potassium nitrate of sodium chloride and mechanical admixtures.

These two basic stages include the following operations:

dissolving of KCl in pre-evaporated solutions of sodium nitrate (if solid sodium nitrate is used as the raw material, then it is dissolved until a solution of the assigned concentration is obtained; in this case, the process of evaporation of the solutions is eliminated);

filtering of the mixture of KCl and NaNO_3 solutions of insoluble admixtures (sometimes instead of filtering, one is limited to settling of the mixture);

double decomposition of NaNO_3 and KCl;

separation of the precipitated sludge (NaCl) from the KNO_3 solution;

washing of the sludge (from KNO_3) and its dissolving (obtained solution of NaCl is used in the shops of steam supply for actionite purification of water and other purposes);

crystallization of KNO_3 from solutions and separation of crystals (obtaining of "raw material" of salt);

washing of crystals of primary crystallization;

dissolving ("steaming") of crystals and filtering of solutions of insoluble admixtures;

secondary crystallization of KNO_3 from solutions;

separation of nitrate from mother liquor and washing of crystals on centrifuge from residue of chlorides;

drying and packing of finished product.

The conversion method for production of potassium nitrate has major shortcomings: expensive sodium nitrate is used as the raw material, scarce soda is used for its production, the technological process and the equipment are cumbersome and labor intensive, and the consumption of steam is comparatively great.

The basic indicators of the technological regime are presented below.

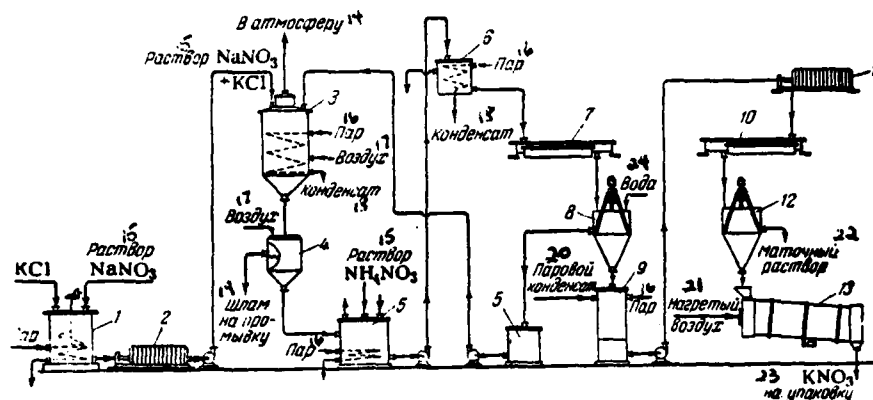


Figure II-39. Plan for Production of Potassium Nitrate by Conversion Method

Key:

1. Mixer (mixer-dissolver) for preparation of NaNO_3 and KCl solution
- 2, 11. Filter-presses
3. Reactor
4. Pressure filter or Nutsch filter for separation of NaCl precipitate
5. Collectors of solutions and wash water
6. Pressure tank of primary KNO_3 solutions
- 7, 10. Crystallizers (primary and secondary crystallization of KNO_3)
- 8, 12. Centrifuges
9. Solvent of crystals ("steamer")
13. Drying drum
- Key: 14. To atmosphere
15. Solution
16. Steam
17. Air
18. Condensate
19. Sludge to washing
20. Steam condensate
21. Heated air
22. Mother liquor
23. To packing
24. Water

Indicators

Standards

Composition of salt solution sent for conversion, g/l

NaNO_3

KCl

380-450

280-370

Pressure of heating steam feed to reactor, atm.

in mixer *Temperature of solution, °C*

at end of conversion process

6-8

70-80

125-130

Density of converted solution, g/cm³

1.65-1.68

Temperature of solution filtering, °C

90-100

KNO_3 content in sludge (NaCl), %

before washing	15-20
after washing	to 1.5
Composition of solution sent for primary crystallization, g/l	
KNO ₃	900-950
NaCl	150-170
Density of solution before primary crystallization, g/cm ³	1.54-1.56
NaCl content in "raw" salt of primary crystallization, %	
before washing	Not more than 6
after washing	1-1.5
Composition of solution after "steaming" of primary crystals, g/l	
KNO ₃	900-1100
NaCl	35-50
NaCl content in salt loaded from centrifuge, %	to 0.03
Temperature of drying KNO ₃ crystals, °C	110-115

The consumption coefficients for 1 τ of potassium nitrate obtained by the conversion method:

Sodium nitrate(100% NaNO ₃), τ	0.975-0.980
Potassium chloride (95% KCl), τ	0.910-0.960
Ammonium nitrate, kg	20-25
Electricity, kW x h	90-120
Steam, τ_3	8-9
Water, m ³	90-100
Compressed air, m ³	200-250
Paper bags, No.	23
Filter cloth (belting), running meter	0.5

Basic Equipment

Reactors. Conversion of NaNO₃ and KCl and evaporation of primary liquor and wash waters use single-stage evaporators or special batch-type reactors. The evaporators have the simplest design (heating chamber--tube with heat exchange surface about 160 m³, evaporation part with hollow volume, circulation pipe located in center). The height of these units is 8.5 m, diameter 2.5 m. Sometimes vertical evaporators are used with conical bottom and copper tube (surface of heat exchange is 150 m²). The height of the units is 6.5 m, the diameter is 2.5 m.

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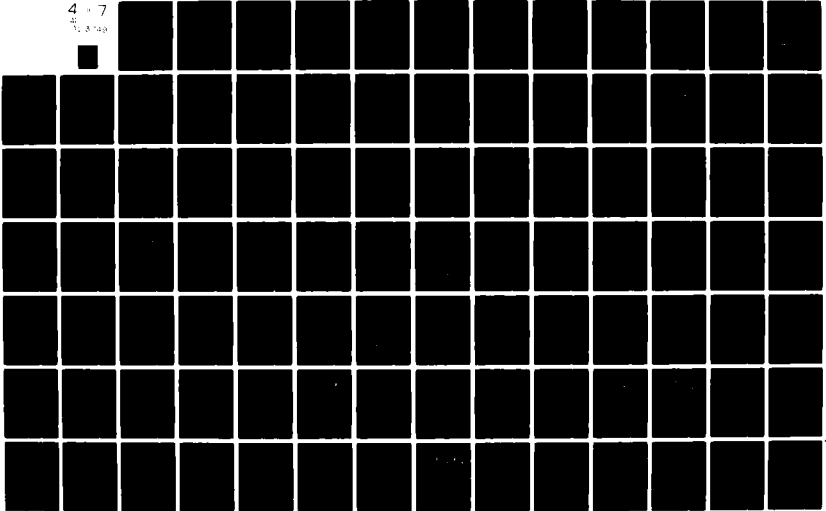
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REFERENCE BOOK FOR THE NITROGEN INDUSTRY WORKER. VOLUME 2, (U)
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The special batch-operated reactor (fig. II-40) is a cylindrical vertical vessel with conical bottom and cover that is equipped with a separator. There are coils within the reactor. Steam to heat and partially evaporate the reaction mass flows on them. Small quantities of compressed air (pressure 3 atm.) and live steam (pressure 5 atm.) are fed into the unit to prevent blocking of the lower part of the reactor with NaCl precipitate, and also to accelerate the reaction.

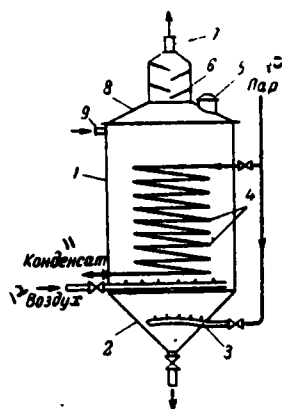
The reactors are made of carbon steel⁵⁸, the steam coils are usually made of stainless steel. The duration of the process of double decomposition in this reactor is about 5-6 h, with a surplus of sodium nitrate in the solutions in limits of 90-120 g/l NaNO₃. At the end of the reaction, the KNO₃ solution is removed from the unit together with NaCl crystals.

Nutsch filters and pressure filters are designed to separate the solutions of KNO₃ that come from the reactors from the precipitate (NaCl sludge). The filters are made of stainless, less often carbon steel, and differ little in design from each other.

For example, the Nutsch filter with capacity of 2.5 m³ is used. It is separated in height into two parts by grids. The upper cylindrical part of the filter is a receiver for the suspension and is used to separate and wash the NaCl precipitate that remains on the grid. The lower part of the filter collects and removes the filtrate to the next process. The filter surface is burlap or belting cloth that is pressed between two grids (often metal grates with fine weave are used instead of the cloth).

The sludge on the grid is first washed with mother liquors after primary crystallization, then with water, after which the sludge that mainly contains NaCl, is dissolved in water and used for different purposes (p. 275). The wash water is usually added to the converted solutions.

The suspensions are separated in the pressure filters under



NaCl suspension
in solution of
KNO₃

Figure II-40. Reactor for Conversion of NaNO₃ and KCl

Key:

1. Housing
2. Bottom
3. Perforated pipe for input of live steam
4. Steam coils
5. Manhole
6. Separator
7. Connecting pipe for removal of water vapors, air and other gases
8. Cover
9. Connecting pipe to feed mixture of solutions of NaNO₃ and KCl
10. Steam
11. Condensate
12. Air

pressure of steam or air to 4 atm. The pressure filters, like the Nutsch filters, have air pipes, trap doors for unloading the sludge, connecting pipe for input of steam, water, suspension and output of the filtrate. They are equipped with measuring instruments and safety devices.

Crystallizers. Crystallizers of drum and worm type, equipped with cooling water sleeves are used to crystallize the potassium nitrate from its solutions.

The two-stage drum-type crystallizer (length 9.5 m, outer diameter 1.2 m) is installed at an angle of 2-4° to the line of emergence of the suspension of crystals in the mother liquor from it. A toothed rim is seated on the drum. It is used (from an electric motor through a reducer) to rotate the drum with a rate of 16 rpm. In order to prevent crystals of potassium nitrate from building up on the inner surface of the drum, it has a chain that breaks up the salt crust which adheres to the walls. The drum is cooled with water fed into the sleeve of the crystallizer.

The most widespread worm crystallizers are 10 m long with diameter of 1.2 m. Blades for mixing slurry are on the central shaft of the crystallizer.

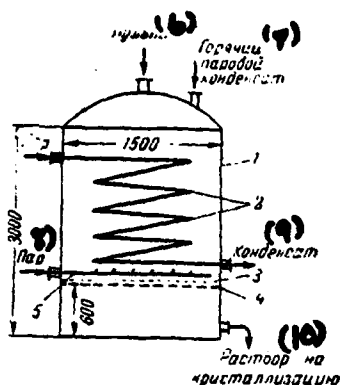


Figure II-41. Dissolver of Crystals ("Steamer")

Key:

1. Housing
2. Steam coils
3. Metal grid with small weave
4. Perforated partition (lattice)
5. Perforated pipe for input of live steam
6. Slurry
7. Hot steam condensate
8. Steam
9. Condensate
10. Solution to crystallization

Centrifuges. The production of potassium nitrate uses automatic centrifuges of continuous operation. The rotation rate of the bowl is 880 rpm.

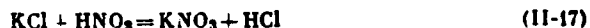
The drying drum is a horizontal welded cyclinder, 1.5 m in diameter and 9 m long. The drum is made of carbon steel (thickness of the walls 5-7 mm). It is lined on the inside with sheet aluminum. Twelve ribs (blades) are attached over the length of the drum. The rotation rate of the drum is 3-5 rpm.

Dissolver of crystals, the "steamer" (fig. II-41) is designed to separate the residues of mother liquor from the potassium nitrate crystals, and dissolve them for subsequent recrystallization.

The unit is made of stainless steel. Its volume is 6-12 m³. In individual cases, the dissolver is used as a filter to separate large-dispersed particles of insoluble admixtures from the solutions. Sometimes the "steamer" is equipped with a mixer.

Direct Methods of Producing Potassium Nitrate^{2,3,28, 59-62}

The interaction of potassium chloride with nitric acid or with liquid nitric oxides occurs according to the following reactions:



The reaction (II-18) practically does not occur at low concentrations of nitric acid and normal temperature. With a concentration of HNO_3 over 50% and temperatures above $50-60^\circ\text{C}$, as well as when liquid nitric oxides are used, the breakdown of potassium chloride is accompanied by the formation of nitrosyl chloride and chlorine.

If diluted nitric acid is used as the raw material, the formed mother liquors that contain KNO_3 and HCl are reprocessed into potassium nitrate and ammonium chloride, less often, into mixed fertilizers. When liquid nitric oxides and solid KCl are used, potassium nitrate is obtained which contains a considerable quantity of mechanical admixtures and sodium nitrate. Their removal (in the case of production for technical needs) requires two-stage recrystallization of the primary salt.

Nitrosyl chloride that is formed in the production of potassium nitrate by direct methods is oxidized by pure oxygen:



Potassium chloride which is loaded into the contact apparatus is used as the catalyst of this reaction. Since nitrosyl chloride is only oxidized by 75%, the gas mixture at the outlet from the contact apparatus is separated on a special unit.

As a consequence of the high aggressiveness of the media in which the processes of producing potassium nitrate by direct methods are performed, the apparatus has to be made of special corrosion-resistant materials (reactor of ferrosilide of special brand, the lining of diabase, etc.).

Production of Potassium Nitrate from Liquid Nitric Oxides and Solid Potassium Chloride

Potassium chloride is dried, crushed, ground and screened to produce a powdery product that further enters the reaction apparatus (converter) made in the form of a spherical mill or rotating drum. At the same time, liquid nitric oxides are fed into the converter with surplus of 10-15% of the stoichiometric quantity. A temperature of $-5 - +5^{\circ}\text{C}$ is maintained in the converter, while the nitric oxides entering it must have a temperature of -15°C .

The potassium nitrate is sent from the converter to the drying drum where it is dried by air at a temperature of $90-100^{\circ}\text{C}$. From here, the potassium nitrate is packed or recrystallized to produce a product that is suitable for technical needs.

The gas mixture that is formed in the course of the reaction comes from the converter to the liquor cooler where it is cooled to -10°C . Here the greater part of the nitric acids that were returned to the converter are condensed from the gas. The nitrosyl chloride together with other gases enters for further reprocessing.

After separation of the nitric oxides, the gases are mixed with pure oxygen, pass through two heat exchangers and are heated to 240°C . The gas mixture is further sent to the contact apparatus where the nitrosyl chloride is broken down in the presence of KCl (catalyst). At the outlet from the contact apparatus, the gases are initially cooled in water, then in liquor coolers, and enter the rectification column at $20-22^{\circ}\text{C}$.

The gases in the column are separated into nitrosyl chloride (which is returned to the contact apparatus), residue of nitric oxides (with admixture of NOCl) sent to the converter, and chlorine (with admixture of oxygen) that can be removed from the upper part of the column for liquefaction, or to the shops that process organo-chloride products.

The degree of conversion of potassium chloride into KNO_3 is ~ 98%, the degree of oxidation of nitrosyl chloride by oxygen at 240°C does not exceed 75%. In individual cases, NOCl with an admixture of nitric oxide can be used for nitrosation of certain organic substances.

The described method of producing potassium nitrate is distinguished by many stages and a number of difficulties that do not make it possible to obtain a product of the required quality. They are due to the fact that the solid potassium chloride used in this process contains admixtures (silicates, NaCl , insoluble oxides, etc.) which completely pass into the composition of potassium nitrate. In addition, since the liquid nitric oxides contain 0.3-0.5% moisture, then a certain quantity of hydrochloric and nitric acids are also present in the potassium nitrate. This makes it necessary to neutralize the primary product with alkali.

The primary product generally also contains unreacted KCl and sodium nitrate which is formed from sodium chloride that is always present in the original potassium chloride. Since the product is contaminated with the listed admixtures, it is suitable for use only as a fertilizer. If it is necessary to manufacture potassium nitrate for industrial consumers, the primary product should be recrystallized, and this requires all the technological equipment of a salt industries (evaporators, crystallizers, centrifuges, etc.).

Production of Potassium Nitrate from Diluted Nitric Acid and Solid Potassium Chloride

The raw material used is 45-50% nitric acid and solid potassium chloride. The process of KNO_3 production occurs in a reactor with mixer at $20-30^\circ\text{C}$. When potassium chloride breaks down by nitric acid, reaction (II-17) occurs. The hydrochloric acid that is formed in this case and the surplus of nitric acid are neutralized by ammonia.

When nitric acid, potassium chloride, wash waters (see below) and mother liquors containing KNO_3 and NH_4Cl are loaded into the

reactor, the duration of the process is about 1 h. In the reactor, 2/3 of the potassium nitrate of its formed quantity is precipitated, 1/3 is released from the mother liquors during their cooling.

For more complete conversion of KCl into potassium nitrate, a concentration of chlorine ions must be maintained in the reaction solution on the level of 170 g/l. The concentration of chlorine in the solution is regulated by adding steam condensate or mother liquor and wash water to the reactor.

At the end of the process of conversion, the suspension of potassium nitrate crystals in the mother liquor is transferred from the reactor into the intermediate collector with mixer. At the same time, cooled slurry comes from the vacuum-cooling unit. It consists of 1/3 potassium nitrate particles that precipitated out from the mother liquors. The mixture of KNO_3 crystals and mother liquor is further pumped into the Nutsch filter for separation of the salt from the liquid. The filter salt is poured over with a weak solution of caustic soda and then washed with water. The salt is dried in a drying drum at 105-115°C.

The wash waters are sent to a separate collector, from which they are returned to the reactor. The mother liquors after separation of the salt on the Nutsch filter are sent for cooling in the vacuum-cooling units. Here the mother liquors are cooled by self-evaporation from 30 to minus 5-7°C.

The cooled solutions which contain a suspension of precipitated salt, from the evaporator unit are poured into a collector from which they are pumped into the salt-separator. The crystals with small quantity of mother liquor are sent from here through the intermediate collector for reprocessing into commercial-grade potassium nitrate.

The mother and wash liquors that are accumulated in different stages, after neutralization by ammonia, are reprocessed into

crystalline ammonium chloride. These solutions are evaporated in evaporators with extension chambers. The precipitate of ammonium chloride that is released in the process of evaporation is separated from the mother liquor in Nutsch filters.

The mother liquors ("final alkalis") and wash waters (after washing of the ammonium chloride crystals) are sent to the reactor. The crystalline ammonium chloride enters the shop for the production of mixed nitrogen-containing fertilizers. A total of 0.645 T of ammonium chloride are obtained per 1 T of generated potassium nitrate. the NH_4Cl content in the product does not exceed 90%.

The consumption coefficients for 1 T of of commercial-grade potassium nitrate (without consideration for the outlays for ammonium chloride):

Potassium chloride (98% KCl), T	0.803
Nitric acid (100% HNO_3), T	0.700
Steam (7 ₃ atm.), T	5.2
Water, m	140
Electricity, kw x h	220

According to another version of this method, potassium nitrate is produced as follows (fig. II-42). A quantity of 56-58% nitric acid (surplus of 15% HNO_3 as compared to the stoichiometric quantity) as well as the wash waters and the mother liquors from the previous operations (see below) are poured into reactor 1 that is a cylindrical vessel lined with a double layer of diabase plate. Then elevator 2 feeds into the reactor individual portions of solid potassium chloride, and live steam and compressed air for heating to 75-85°C and mixing of the solution. During the first hour of the reaction, the breakdown of potassium chloride occurs comparatively rapidly, then the rate of decomposition slows down. The process is completely finished in 4 h. The water vapors, hot air and gases (mainly NOCl) that is released in the reaction is sucked out of the reactor by an air injector and sent for reprocessing (not described here).

The solution obtained in the reactor which contains 450-520

g/l of KNO_3 , 35-65 g/l of HNO_3 and 120-140 g/l of HCl , is separated from the mechanical contaminants. Then the clarified solution enters

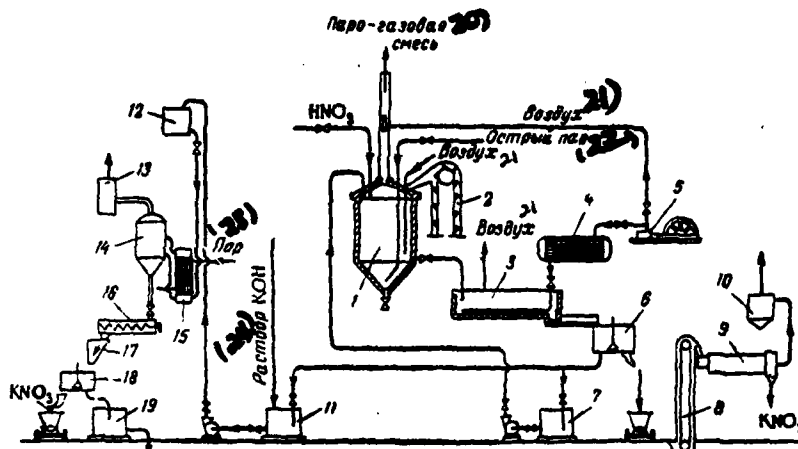


Figure II-42. Plan for Production of Potassium Nitrate by Direct Method from Diluted Nitric Acid and Solid Potassium Chloride

Key:

1. Reactor
2. Elevator for KCl supply
3. Crystallizer
4. Air cooler
5. Air compressor
- 6,18. Centrifuges
7. Collector of mother liquors
8. Elevator for supply of KNO_3
9. Dryer
10. Cyclone
11. Collector of wash water (neutralizer)
12. Pressure tank for wash water
13. Separator
14. Evaporation chamber of evaporator
15. Boiler of evaporator
16. Worm crystallizer
17. Bin
18. Centrifuge
19. Collector of secondary mother liquors
20. Steam-gas mixture
21. Air
22. Live steam
23. Steam
24. Solution

crystallizer 3 where it is cooled to 25-30°C by air that is pre-cooled to 8-10°C in apparatus 4. The mixture of crystals with mother

liquor (90-110 g/l KNO_3 , 20-40 g/l HNO_3 , 70-80 g/l HCl) enters from the crystallizer to the diabase-lined trough (not shown in the figure). Here a large part of the solution is separated from the KNO_3 crystals which are further washed with water and in the form of an aqueous suspension enter the rubberized centrifuge 6 where they are additionally washed of the chloride admixtures.

The salt is loaded from the centrifuge into a cart, from which it is fed by elevator 8 into the drying drum 9, then sent for packaging.

If it is necessary to produce technical-grade potassium nitrate, the salt is doubly recrystallized.

The wash water that contains a certain quantity of HCl and HNO_3 is neutralized in collector 11 by a solution of potassium hydroxide and enters for evaporation in apparatus 14 and 15. The evaporated solution is sent for crystallization in cooling worm 16. The potassium nitrate crystals that are precipitated here are separated from the mother liquor in centrifuge 18. Part of the mother liquor is returned to the reactor, the remaining is removed from the cycle.

According to another version, the mother liquors are neutralized by ammonia and evaporated. In this case, a mixed fertilizer is obtained with various ratios of KNO_3 , NH_4Cl and KCl .

The output of potassium nitrate according to the described version of the method does not exceed 70-75%.

Production of Potassium Nitrate by Method of Cation Exchange^{2,63,64}

The USSR has developed a method for producing potassium (sodium) nitrate by the method of cation exchange using concentrated original solutions and domestic ionites, for example, of brand KU-1 (Espatite) and others. The original raw material in this process is 45-47% nitric acid, wastes of limestone (rubble), and potassium chloride.

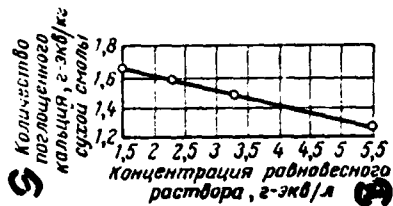


Figure II-43. Effect of Concentration of Saturated Solution on Quantity of Calcium Absorbed by Cationite KU-1

Key:

1. Quantity of absorbed calcium, g-equiv/kg of dry resin
2. Concentration of equilibrium solution, g-equiv./l

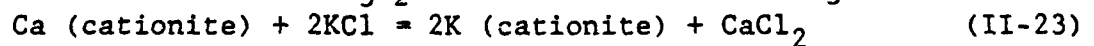
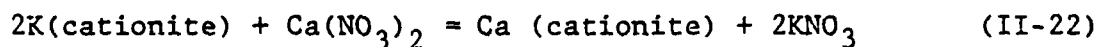
The majority of researchers view the interaction with ions of dissolved substances as a chemical reaction of double exchange which is subordinate to the law of mass action, with certain deviations.

During the exchange of two equivalent ions, the quantity of each ion that is absorbed by the ionite changes little during dilution of the equilibrium solution of salts, and changes significantly if the exchanging ions are equivalent. In the latter case, the degree of sorption of the ion of high valency increases with dilution of the equilibrium solution.

Thus, with a change in the concentration of solutions of calcium nitrate from 5.5 to 1.5 g-equiv/l, the quantity of calcium that is absorbed by cationite KU-1 considerably increases (fig. II-43). It follows from here that with high concentrations of the original solution of calcium nitrate even on the cationites that have comparatively low exchange capacity, a fairly high degree of conversion of $\text{Ca}(\text{NO}_3)_2$ into potassium nitrate can be attained.

These and certain other laws governing ion exchange⁶⁴ were used in developing the process of obtaining commercial-grade potassium nitrate from solutions of calcium nitrate and potassium chloride.

The reactions that occur during cationization are schematically described by the following equations:

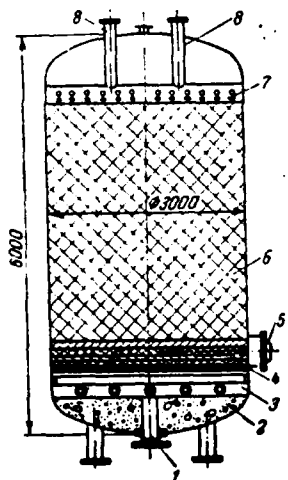


When solutions of potassium nitrate are obtained by the

method of cation exchange, initially a solution of potassium nitrate is prepared (from limestone rubble and weak nitric acid) and a solution of potassium chloride. After purification from mechanical admixtures on frame filter presses, these solutions are sent to the cationite reactors where exchange of ions occurs.

This reactor (fig. II-44) is a cylindrical steel unit with spherical bottom and cover. The apparatus is lined on the inside with an anticorrosion coating. The reactor is filled with cationite almost the entire height (with grains of size 1-2 mm). Within the reactor there is a lower and upper distribution device that is designed for uniform supply to the cationite of solutions of salts and water, and to prevent removal of the grains of cationite by the liquid stream.

Figure II-44. Cationite Reactor



Key:

1. Connection pipe for supply of solutions to lower distribution device
2. Bottom, poured concrete
3. Lower distribution device
4. Layers of crushed quartz (quartz "pillow")
5. Manhole
6. Cationite
7. Upper distribution device with caps
8. Connection pipes for outlet of solutions

The process of cationization is separated into two cycles: charging of the cationite (regeneration) and production of production solutions (conversion).

In the charging cycle, the solution of potassium chloride is sent through the cationite reactor. In the next cycle of conversion, partially converted solutions of potassium nitrate (the solutions contain a certain quantity of KNO_3), then fresh solutions of potassium

nitrate, and finally, water are successively sent through the cationite. When partially converted solutions of potassium nitrate are sent through the cationite, a production solution is obtained which contains about 200 g/l of KNO_3 and 60-100 g/l of $\text{Ca}(\text{NO}_3)_2$,

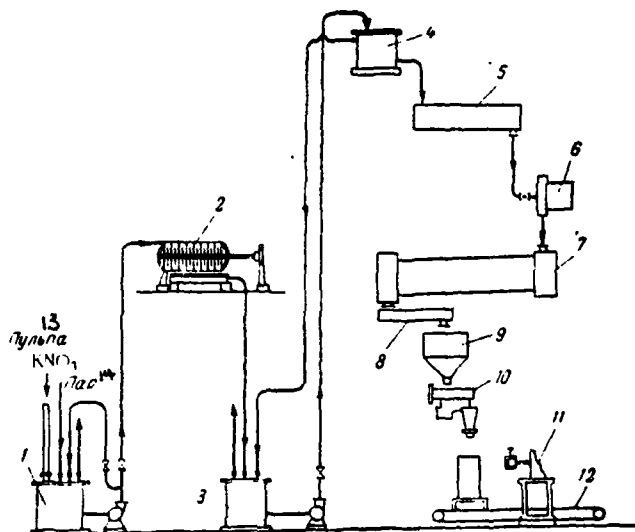


Figure II-45. Plan for Process of Recrystallization, Drying and Packing of Potassium Nitrate Obtained by the Method of Cation Exchange

Key:

1. Salt dissolver ("steamer")
2. Filter press for purification of hot solutions of potassium nitrate from mechanical admixtures
3. Collector of filtered solutions
4. Pressure tank
5. Worm-crystallizer
6. Centrifuge
7. Drying drum
8. Worm
9. Bin
10. Automatic scales
11. Sewing machine
12. Conveyer
13. Slurry
14. Steam

This solution is sent for evaporation and crystallization for the production of primary crystals of potassium nitrate. After one

recrystallization of them, a product of the first grade is obtained (fig. II-45).

After separation of the primary salt, the liquor solutions are united with the partially concentrated solutions of $\text{Ca}(\text{NO}_3)_2$, and after separation of the finished (commercial-grade) product, the mother liquors are added to the production solutions.

All further stages in reprocessing of the production solutions into crystalline potassium nitrate are done according to standard salt technology. The spent solutions of potassium chloride are removed from the production cycle.

The process of obtaining potassium nitrate by the method of cation exchange is simple in technology and design. This method is distinguished by a number of advantages over the conversion and other methods of producing KNO_3 (scarce raw material is not required, the outlays of steam are lower, part of the apparatus can be made of ferrous metals, etc.).

Currently in the USSR and abroad, the method of cation exchange is only used in the production of potassium nitrate for the production of a technical-grade product. A study is being made of the possibility of using this method for the production of potassium nitrate that is designed for use as a fertilizer.

The consumption coefficients for 1 T of potassium nitrate obtained by the method of cation exchange:

Nitric acid (100% HNO_3), T	0.75-0.80
Potassium chloride (98% KCl), T	1.0-1.1
Limestone(wastes), T	0.8-0.9
Slaked lime, kg	6-8
Steam, ($\frac{7}{3}$ atm.), T	6-6.5
Water, m ³	125-140
Electric power, kW·h	130-150

The losses of cationite (wear) during a year of operation does not exceed 3-4% of its initial quantity.

Neutralization Method of Potassium Nitrate Production^{2,28,56}

The process of producing potassium nitrate by this method consists of two basic stages: 1) absorption of nitric oxides from waste nitrous gases by solutions of potassium hydroxide or potash; 2) inversion (oxidation) of potassium nitrate formed in solutions of alkaline absorption into potassium nitrate (R. p. 54).

In certain cases, the potassium nitrate is obtained by direct neutralization of solutions of potassium hydroxide or potash by diluted (weak) nitric acid.

The potassium hydroxide or potash used as the raw material contains a lot of admixtures, therefore, in order to obtain a sufficiently pure potassium nitrate, we have to recrystallize the primary ("raw") salt.

The solution of potassium hydroxide that is used in this method of production of potassium nitrate (melted solid KOH is used less often), contains 600-750 g/l of KOH, 4-7 g/l (KCl + NaCl), 6-12 g/l K₂CO₃, 20 g/l NaOH and other admixtures. The technical-grade potash, depending on the method of its production, contains from 85 to 97% K₂CO₃, as well as admixtures of chlorides, sulfates, etc.

During absorption of nitric oxides by a solution of potassium hydroxide from exhaust nitrous gases, the following reactions occur:



In practice, solutions are obtained with a ratio of potassium nitrate and nitrite of roughly 1:4.

When nitric oxides are absorbed by solutions of potassium hydroxide and potash, it is very important to maintain a small surplus of alkali in the solutions (30-40 g/l). With increased alkalinity, the ceramic attachment of the absorption scrubbers is rapidly destroyed and the solutions are contaminated with gel-like

admixtures of silicates.

The solutions that are obtained as a result alkaline absorption contain: 350-400 g/l of KNO_2 , 80-90 g/l KNO_3 , 2-3 g/l of K_2CO_3 , admixtures of chlorides, sulfates, etc.

The process of inversion of nitrite-nitrate solutions (alkalis) or direct neutralization of the alkali nitric acid should be done with a small surplus of HNO_3 (30 g/l). Otherwise, the inverters and neutralizers made of stainless steel rapidly malfunction as a consequence of intensified corrosion of the welded seams (in the more acid medium, the chlorides present in the solution form HCl and NOCl , which rapidly destroy the welded seams at 70-80°C).

The inverted solutions of potassium nitrate are purified of mechanical admixtures by filtering on a frame filter press (filter cloth--belting), after which they are sent for evaporation. A small quantity of ammonium nitrate is sometimes added preliminarily to the solutions to destroy the admixtures of nitrites and carbonates of potassium (p.274).

The solutions of potassium nitrate are concentrated in vacuum evaporators that operate at a vacuum of 500-550 mm Hg. The solutions that have been evaporated to density of 1.5-1.6 g/cm³ enter the worm crystallizer that is cooled by water. The crystals that precipitate here at a temperature of 35-45°C are separated on a centrifuge and exposed to recrystallization according to the standard salt technology.

After several cycles of reprocessing the solutions of potassium nitrate, a large quantity of admixtures (chlorides, sulfates, carbonates, etc.) is accumulated in the mother liquors. Consequently, it is impossible to obtain a product that corresponds in quality to the potassium nitrate of first grade even after two recrystallizations of salt. These mother liquors have to be removed from the production cycle and processed separately into fertilizer.

The consumption coefficients for 1 t of potassium nitrate of the first grade that is obtained by neutralization method:

Nitric acid (100% HNO_3), t	0.85-0.9
Potassium hydroxide (100% KOH), t	0.73-0.85
Electricity, kw x h	105-115
Steam, t_3	8-8.5
Water, m^3	110-125

Use and Quality of Potassium Nitrate

Potassium nitrate is used in many branches of industry and agriculture.

The product of first grade is included in certain powders and pyrotechnic compositions. Potassium nitrate is widely used in the food industry to preserve meat and other products, and in metallurgy to harden metals, etc.

Potassium nitrate is a valuable inert material-free fertilizer which simultaneously contains two nutrients, nitrogen and potassium (13.85% nitrogen, 46.58% K_2O). They are practically nonhygroscopic and do not cake. As a consequence of the high cost, potassium nitrate is still only put under garden and flower crops, and in small quantities under citrus crops and tobacco. Potassium nitrate is packed in five-layer kraft-pulp bags impregnated with bitumen-motor oil mixture. The bag with salt weighs 40-45 kg (net).

The quality of the potassium nitrate (GOST 1949-65) must correspond to the following indicators:

Indicators	Grade		
	1st	2nd	3rd
KNO_3 content in conversion for dry product, %, no less,	99.8	99.5	98
Moisture content, %, no more	0.1	0.2	2
Admixtures, %, no more chlorides (in conversion for NaCl)	0.03	0.1	not normed
carbonates (in conversion for K_2CO_3)	0.02	0.04	the same
residue insoluble in water	0.03	0.03	"
substances oxidized by KMnO_4 (in			

conversion for KNO ₂) salts of potassium ² and man- ganese (in conversion for Ca)	0.01 0.02	Not normed 0.025	 not normed
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Note: Potassium nitrate that is intended for production of powders must contain no more than 0.002% salts of potassium and manganese.

4. Sodium Nitrate and Nitrite

Physical-Chemical Properties of Sodium Nitrate and Nitrite⁵⁰

Sodium nitrate, NaNO₃, has the appearance of a colorless, transparent crystals (grayish or yellowish hue is permitted). The density of sodium nitrate is 2.257 g/cm³ at 30°C and 2.265 g/cm³ at 20°C. The melting point of pure NaNO₃ equals 309.5°C. At 380°C, this salt is broken down into sodium nitrite and oxygen. The heat of formation of solid sodium nitrate from simple substances is 111.25 kcal/mole.

Sodium nitrite, NaNO₂, is colorless or slightly yellowish crystals of a rhombic system. The density is 2.17 g/cm³ at 20°C. The melting point is 271°C. The heat of transformation of solid sodium nitrite from simple substances equals 88.3 kcal/mole.

Data on the solubility of sodium nitrite and nitrate in water are given in tables II-39 and II-40.

The polytherm of solubility⁵⁰ of the system NaNO₃-NaNO₂-H₂O is shown in fig. II-46, and the viscosity of aqueous solutions of sodium nitrate--in fig. II-47.

The heat conductivity λ of aqueous solutions of sodium nitrate⁵⁰ at 32°C is presented below:

Concentration of NaNO ₃ , weight. %	44	40	22	20
λ , cal/(cm x s x deg) ³	0.0013	0.0014	0.0014	0.0014

The joint solubility of NH₄NO₃ and NaNO₃ in water is shown in table II-41, and the pressure of vapors above the aqueous solutions.

TABLE II-39. SOLUBILITY OF NaNO_3 IN WATER (In g/100 g of water)

Температура °C (1)	Растворимость (2)	Твердая фаза (3)	Температура °C (1)	Растворимость (2)	Твердая фаза (3)
-6.7	20	Лед ⁽⁴⁾	119*	209.0	NaNO_3
-12.7	40	*	120	213.0	*
-18.1	61.5	Эвтектика ⁽⁵⁾	140	255.0	*
0	70.7	NaNO_3	160	301.0	*
20	88.0	*	180	383.0	*
25	92.7	*	200	432.0	*
40	104.9	*	224.7	724.0	*
60	124.7	*	253.6	1250.0	*
80	148.0	*	289.2	4494	*
100	176.0	*			

Key:

1. Temperature, °C
2. Solubility
3. Solid phase
4. Ice
5. Eutectics

* Boiling point of solution at 736 mm Hg.

TABLE II-40. SOLUBILITY OF NaNO_2 IN WATER⁵⁰
(in g/100 g of water)

Температура °C (1)	Растворимость (2)	Твердая фаза (3)	Температура °C (1)	Растворимость (2)	Твердая фаза (3)
-28	6.3	Лед ⁽⁴⁾	20	81.8	NaNO_2
-8.7	19.5	*	40	95.7	*
-19.5	39.1	Эвтектика ⁽⁵⁾	60	112.3	*
-10	57.5	$\text{NaNO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	80	135.5	*
-5.1	71.4	NaNO_2	100	163.0	*
0	73	*	128*	219.5	*

Key:

1. Temperature, °C
2. Solubility
3. Solid phase
4. Ice
5. Eutectics

* Boiling point of solution at 761.5 mm Hg.

of sodium nitrates and ammonium nitrates in tables II-42-II-44.

Methods of Production of Sodium Nitrate^{66,67}

Sodium nitrate is extracted from natural deposits and produced by plant method which is based on the absorption of nitric oxides

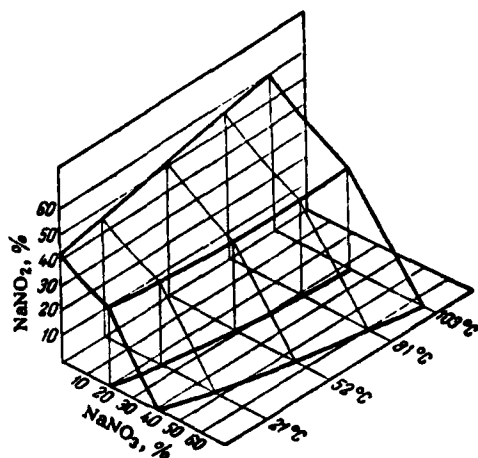


Figure II-46. Polytherm of Solubility of NaNO_3 - NaNO_2 - H_2O System

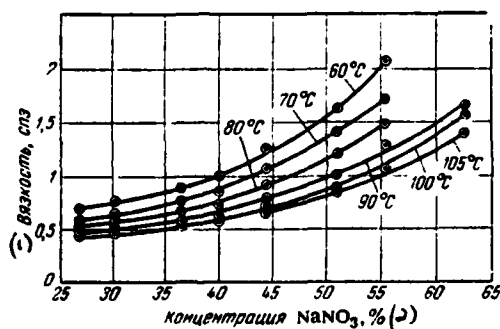


Figure II-47. Viscosity of Aqueous Solutions of NaNO_3

Key:

1. Viscosity, centipoise
2. Concentration of NaNO_3 , %

by solutions of soda, or on double decomposition of certain nitrates with other sodium salts, or on cation exchange (this method has been described in the previous section, p. 286). The simplest method for producing NaNO_3 is neutralization of nitric acid by soda or by sodium hydroxide, but it is not used in industry because of its inefficiency.

TABLE II-41. SOLUBILITY IN $\text{NH}_4\text{NO}_3\text{-NaNO}_3\text{-H}_2\text{O}$ SYSTEM^{65a}
(in weight.%)

Состав насыщенного раствора (1)		Твердая фаза (2)	Состав насыщенного раствора (1)		Твердая фаза (2)
NH_4NO_3	NaNO_3		NH_4NO_3	NaNO_3	
At 0°C			At 80°C		
52.40	0	NH_4NO_3 β -rhomb. (IV) the same + NaNO_3 NaNO_3	80.41	0	NH_4NO_3 α -rhomb. (III) the same + NaNO_3 NaNO_3
52.46	2.08		78.60	2.24	
50.42	4.25		75.30	6.87	
49.05	7.18		73.82	9.02	
41.37	20.02		64.59	20.34	
38.71	24.63		0	55.58	
0	42.34				
At 10°C			At 80°C		
64.0	0	NH_4NO_3 β -rhomb. (IV) the same + NaNO_3 NaNO_3	86.44	0	NH_4NO_3 α -rhomb. (III) the same + NaNO_3 NaNO_3
62.54	2.72		80.13	8.73	
61.51	5.30		75.58	15.09	
55.01	12.64		72.06	19.25	
52.24	16.47		61.48	25.37	
49.60	22.40		31.89	42.03	
33.48	30.27	10.83	51.60		
22.85	35.25	0	59.90		
10.95	41.34				
0	46.80				
At 40°C			At 98°C		
74.64	0	NH_4NO_3 α -rhomb. (III) the same + NaNO_3 NaNO_3	91.15	0	NH_4NO_3 tetragonal rhombohedr. (II) the same + NaNO_3 NaNO_3
72.98	2.7		88.89	2.78	
60.47	21.68		86.98	5.38	
41.47	31.02		85.97	7.23	
13.01	44.88		85.81	8.79	
0	51.30		78.26	18.45	
		0	60.04		

Key:

1. Composition of saturated solution
2. Solid phase

Note: The Roman numerals indicate the crystalline modifications of ammonium nitrate according to table II-1.

TABLE II-42. PRESSURE OF WATER VAPORS ABOVE NON-SATURATED SOLUTIONS OF NaNO_3 (in mm Hg)

Температура °C (1)	Концентрация NaNO_3 , г/100 г воды (2)										
	10	20	30	40	50	60	70	80	90	100	110
0	4.42	4.28	4.15	4.04	3.93	3.83	3.73	3.64*	—	—	—
25	22.03	22.14	21.39	20.69	20.04	19.42	18.83	18.29	17.77	17.4*	—
50	89.2	86.1	83.1	79.8	77.5	74.9	72.56	70.25	68.1	66.1	—
75	278.9	268.8	259.1	249.8	241.1	232.9	225.1	217.8	210.8	204.3	199.4
100	732.5	705.6	679.8	654.8	631.3	609.0	588.1	568.2	549.4	531.6	514.8
125	1167	1015	955.4	896	842	790	741	694	650	603	560

Key:

1. Temperature, °C
2. Concentration of NaNO_3 , g/100 g of water

* Supersaturated solutions

(continuation of table II-42)

(continuation of table

(1) Температура °C	(2) Концентрация NaNO ₃ , г/100 г воды									
	120	130	140	150	160	170	180	190	200	220
75	192.1	186.5	181.2*	—	—	—	—	—	—	—
100	498.9	483.7	469.4	455.7	442.8	430.1	418.3**	—	—	—
125	1135	1097	1064	1032	1002	973	945	919	893	846

Key:

1. Temperature, °C
 2. Concentration of NaNO₃, g/100 g of water
- * Saturated solution
** Supersaturated solution

TABLE II-43. PRESSURE OF WATER VAPORS ABOVE SATURATED SOLUTIONS⁶⁵ OF NaNO₃

(1) Температура °C	(2) Давление мм рт. ст.	(1) Температура °C	(2) Давление мм рт. ст.	(1) Температура °C	(2) Давление мм рт. ст.
10	7.1	60	97.2	110	567
15	9.8	65	119.7	115	654
20	13.0	70	146.4	120	749.2
25	17.4	75	181.2	125	854
30	22.9	80	213.9	130	968
35	29.9	85	255.9	135	1091
40	38.6	90	303.9	140	1225
45	49.2	95	358.6	145	1368
50	62.3	100	418.3	150	1520
55	78.2	105	490.1		

Key:

1. Temperature, °C
2. Pressure, mm Hg

TABLE II-44. VAPOR PRESSURE ABOVE AQUEOUS SOLUTIONS⁶⁵, SATURATED WITH NH₄NO₃ AND NaNO₃ (in solid phase for both salts)

(1) Температура °C	(2) Давление мм рт. ст.	(1) Температура °C	(2) Давление мм рт. ст.	(1) Температура °C	(2) Давление мм рт. ст.
10	5.3	50	34.0	90	81.4
15	7.0	55	40.2	95	82.3
20	9.1	60	47.0	100	79.8
25	11.8	65	53.9	105	72.6
30	15.0	70	60.9	110	59.3
35	18.8	75	67.6	115	38.5
40	23.2	80	73.4	120	8.2
45	28.3	85	77.9	121.1*	0.0

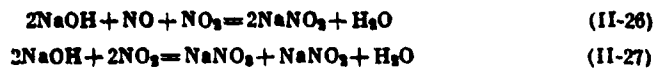
Key:

1. Temperature, °C
 2. Pressure, mm Hg
- * Eutectic point (79.5% NH₄NO₃+20.5% NaNO₃)

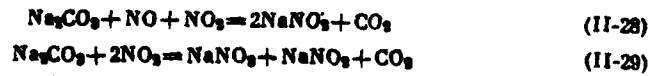
Production of Sodium Nitrate by the Method of Alkaline Absorption of Nitrous Gases

This is the most popular industrial method of producing sodium nitrate and is based on alkaline absorption of nitric oxides from exhaust gases from the production of diluted nitric acid (R. p. 52).

When nitric oxides are absorbed by a solution of sodium hydroxide, the reactions occur



when it is absorbed by the solutions of calcined soda, the reactions



The solutions that are obtained as a result of the alkaline absorption of nitrous gases, nitrite-nitrate alkalis, are reprocessed. Its plan is shown in fig. II-48. The ratio between sodium nitrate and nitrite in the alkalis depends on the temperature and the degree of oxidation of the nitrous gases.

A sample composition of "raw" nitrite-nitrate alkalis after alkaline absorption (in g/l):

NaNO_2	320-350	NaCl	2-4
NaNO_3	To 50	H_2O	850-820
$\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$	10-15		

The solution that is filtered out on filter press 4 enters inverter 6 of batch-type or continuous action. Here conversion (inversion) of the sodium nitrite into sodium nitrate⁶⁸ occurs.

The process of NaNO_2 inversion into NaNO_3 occurs when the solution is treated with a weak nitric acid:

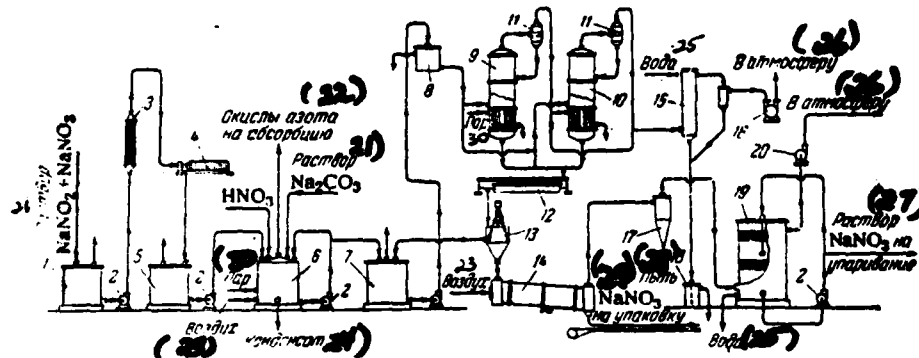
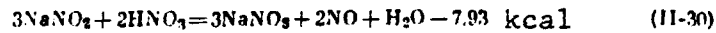


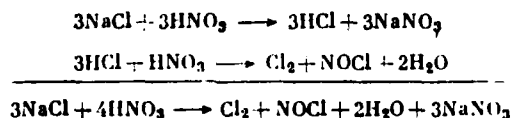
Figure II-48. Plan for Production of Sodium Nitrate from Nitrate-Nitrite Alkalis

- Key:
1. Reception tank
 2. Centrifugal pumps
 3. Preheater
 4. Filter press
 5. Collector of filtered solutions
 6. Inverter
 7. Collector of inverted solution
 8. Pressure tank
 9. Evaporator of first stage
 10. Evaporator of second stage
 11. Traps
 12. Worm crystallizer
 13. Centrifuge
 14. Drying drum
 15. Barometric condenser
 16. Vacuum-pump
 17. Cyclone
 18. Barometric container
 19. Scrubber for trapping NaNO_3 dust from drying drum
 20. Fan
 21. Solution
 22. Nitric oxides to absorption
 23. Air
 24. Condensate
 25. Water
 26. To atmosphere
 27. NaNO_3 solution to evaporation
 28. Dust
 29. NaNO_3 to packing
 30. Steam

In order for the process of inversion to occur with the greatest completeness, the nitric acid is dosed in the inverter in such a quantity that its concentration in the solution at the end of

the reaction is roughly 1.5%. Inversion occurs at 80-90°C and with constant mixing of liquid in the unit with the help of a circulation pump. The solution in the inverter is heated by saturated steam that enters the coil located in the lower part of the apparatus. The inversion process (including loading and unloading) lasts about 4 h.

One should indicate that an increase in temperature above the indicated limits results in an increase in the losses of nitric acid and intensification of corrosion of the welded seams of material of which the inverter is made. In the nitrite-nitrate alkalis that are obtained during absorption of nitric oxides by a solution of calcined salt, there generally is a content of sodium chloride that interacts with nitric acid, forming such aggressive substances as hydrochloric acid, chlorine and nitrosyl chloride:



The nitric oxides that are formed as a result of inversion are removed from the solution by air that is injected into the inverter by an air blower, and further is sent through a trap for reprocessing in the absorption section for the production of diluted (weak) nitric acid. The nitric oxides contain admixtures of chlorine and its compounds (see above), therefore in the nitric acid, whose concentration corresponds to roughly 25-30% HNO_3 , chlorine is accumulated. As a consequence, this solution has a strong corrosive effect on the equipment. Therefore, as 1.5-2 g/l of chlorine are accumulated in the nitric acid, it needs to be removed from the appropriate plate of the absorption column. The removed acid is further used in the production of ammonium nitrate.

At the end of the inversion process, the solution is neutralized by soda, then the neutralized solution which contains 40-50% NaNO_3 , is sent at temperature 40-60°C for evaporation.² Evaporation of solutions of sodium nitrate usually uses a two-housing unit that operates in a vacuum. The evaporator 9 of the first stage is heated by live steam (pressure 6-8 atm). In the evaporation zone, the

pressure of the liquor steam is 1.5-3 atm. Housing 10 of the second stage is heated by liquor steam that comes from the first housing. A vacuum to 600 mm Hg is maintained in the evaporation zone.

Evaporation occurs in steel or pig iron evaporators of the vertical type with central circulation pipe or with extension heating chamber. When one of the units stops for repair or cleaning, the evaporator can operate as one-housing. In this case, heating steam with pressure of 6-8 atm. is fed into the evaporator, and vacuum of 600 mm Hg is maintained in the evaporation zone.

The solution is evaporated to the condition of a suspension in which the total content of NaNO_3 is roughly 75%. In this case, the solution contains 62% sodium nitrate. Its remaining quantity is in a suspended state in the form of crystals.

The liquor steam that emerges from the evaporator of the second stage is condensed in barometric condenser 15. The uncondensed gases with the help of vacuum-pump 16 are removed into the atmosphere. The steam condensate is used in the boiler plant or to obtain a soda solution, or to warm up the solutions.

From the evaporator, the suspension enters the pig iron worm crystallizer 12 of batch-operation with water sleeve. Here when the suspension is cooled to 40-45°C, further crystallization of the salt occurs. The NaNO_3 crystals are separated from the solution in the continuously operating centrifuge 13 with automatic unloading of the salt. The mother liquor from the centrifuge is combined with the inverted solution that is sent for evaporation.

After the centrifuge, the wet crystals of sodium nitrate enter the rotating drying drum 14 where they are dried by air heated to 100°C until they contain 1.5-2% moisture. The drying drum is rotated at a rate of 5 rpm. The dried sodium nitrate is sent for packing.

In order to trap the sodium nitrate dust, the air from the

drying drum is sent to cyclone 17 where a large part of the dust is settled out. It is unloaded and joined with the dried salt. The dust that did not settle in the cyclone is trapped in scrubber 19 that is sprinkled by a continually circulating solution of sodium nitrate. As the concentration of the solution rises, it is removed for evaporation. The air is suctioned from the scrubber by fan 20 and removed into the atmosphere.

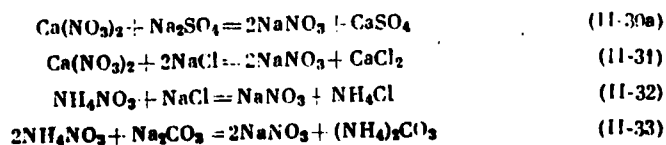
When 1 τ of sodium nitrate (100% NaNO_3) is obtained, the following quantities of raw material and energy are consumed:

Nitric acid (100% HNO_3), τ	0.455
Soda, τ	0.03
Saturated steam (8 atm.), τ	2.5
Water, m^3	65
Electricity, kw x h	120

The wastes from production of 1 τ of NaNO_3 are 0.38 τ of nitric oxides (in conversion for HNO_3) sent for absorption.

Conversion Method of Sodium Nitrate Production

Sodium nitrate can also be obtained from reactions of double decomposition:



etc.

Each of these reactions has specific features. Thus, when double decomposition occurs between calcium nitrate and sodium sulfate, a surplus of calcium nitrate is necessary. Part of it enters the composition of the product and makes it hygroscopic.

The precipitate of gypsum that settles out in this case results in strong thickening of the reaction mass. So that it remains sufficiently fluid, the mass should be diluted with a solution of

sodium nitrate after removal of CaSO_4 , i.e., part of the solution should be returned to the reactor.

The rate of the process of double decomposition depends on the temperature. For example, the reaction (II-30) at 50°C occurs considerably faster than at 70°C . In 1 h at 50°C , the degree of conversion reaches 96%, and at 70°C , only 11%. In order to obtain a large-crystal, easily filtered gypsum precipitate, a seed crystal (crystalline gypsum) is introduced into the reactor.

Production of Sodium Nitrite

One of the methods for producing sodium nitrite is its separation from nitrite-nitrate alkali until inversion of NaNO_2 . In this case, the process of absorption of nitric oxides occurs so that alkali is obtained with the greatest possible content of nitrite with the least content of sodium nitrate. This is attained by reducing the concentration of oxygen in the nitrous gas that enters for alkaline absorption, so that at the entrance of the gas into the alkali towers, the degree of oxidation of the nitric oxides contained in it corresponds to the equimolecular mixture ($\text{NO} + \text{NO}_2$).

Sodium nitrite can also be obtained from nitrite-nitrate alkalis that are formed in a normal regime of nitric oxide absorption by a solution of soda, but with a small change in the plan for re-processing the alkali. In this case, the "raw" nitrite-nitrate alkali (p.299) is heated to $80-90^\circ\text{C}$ for conversion of the soluble admixtures, bicarbonates of magnesium and calcium, into insoluble carbonates. Then the alkali is filtered or clarified by settling and is sent to the evaporator that is similar to the unit used for evaporation of the inverted solution. The evaporation is done at $118-125^\circ\text{C}$. The NaNO_2 content in the solution in the evaporator is brought to roughly 63%.

Further when the temperature of the solution is dropped to $40-45^\circ\text{C}$, in the cooling work, part of the sodium nitrite precipitates out. Complete separation of NaNO_2 from the solution in one cycle of

crystallization is impossible. This is apparent from the diagram of solubility of the $\text{NaNO}_3\text{-NaNO}_2\text{-H}_2\text{O}$ system (see fig. II-46)^(R. p. 186). The eutonic solutions at any temperatures contain considerable quantities of sodium nitrite. The crystalline precipitate of NaNO_2 is separated on centrifuges from the solution, washed with steam condensate for removal of the chlorine that is usually contained in the water, and dried in a rotating drum by air that is heated to 100°C .

The finished product, containing 1.5% moisture, goes for packing and further to the storehouse.

The mother liquor which after separation of the sodium nitrite crystals contains roughly 45% NaNO_2 and 10% NaNO_3 , is sent together with the wash waters to the inverter, where the sodium nitrite is oxidized into nitrate. Further reprocessing of the inverted solution is done according to the previously described plan (p.299).

Use and Quality of Sodium Nitrate and Nitrite

Sodium nitrate is a valuable physiological alkaline fertilizer which contains 16.47% nitrogen. Its use is most expedient on acid soils^{2,69}. It is very effective to put sodium nitrate under sugar-beets and especially under fodder beets.

Sodium nitrate is also used in the food, glass and metal-working industries. It is used in the conversion method of producing potassium nitrate (p. 272) and to produce certain other substances.

Sodium nitrate of two grades are manufactured. According to GOST 828-54, they must correspond to the following requirements:

Indicators	1st grade	2nd grade
NaNO_3 content (in conversion for dry substance), %, no less	99	98
Moisture content, %, no more	1.5	2.0
Admixtures, %, no more		
substances insoluble in water	0.1	Not standardized
chlorides (in conversion for NaCl)	0.5	the same
Sodium nitrite and other oxidizable substances	0.02	0.25

Technical-grade sodium nitrate is also produced which contains 94% NaNO_3 (MRTU 90-45-66).

Sodium nitrate is packed in wooden dry-packed boxes (net weight 100-200 kg) or in paper bituminized five-layer bags (net weight 40-50 kg). The product is stored in the packed form in dry, covered rooms.

Sodium nitrite is mainly used in the processes of diazotization (for example, in the synthesis of azo dyes), as well as in the food and textile industry, in the production of certain rubber items and in medicine. Sodium nitrite is a toxic substance, therefore in its production, storage, shipping and handling, the appropriate safety measures should be strictly observed.

According to GOST 6194-52, two grades of sodium nitrite are manufactured. They must correspond to the following indicators:

Indicators	1st grade	2nd grade
NaNO_2 content (in conversion for dry substance), % no less	98.5	96.0
Moisture content, %, no more	2.5	3.0
Admixtures, %, no more		
NaNO_3	1.0	2.5
substances, insoluble in water	0.07	0.1

The product is packed in wooden boxes of capacity to 150 l, veneer drums and wooden containers with capacity of 75-100 l (the packaging is lined from the inside with water-impermeable paper), as well as two paper four-layer bags, of which only the outer must be bituminized. The inscription "Toxic" is made on the packaging and the bags.

The solutions of sodium nitrite which contain 280 ± 10 g/l NaNO_2 are used in the production of caprolactam. According to TU 603-176-67 the solutions designed for this purpose must contain no more than 0.005 g/l of iron admixtures, no more than 7 g/l NaNO_3 , no more than 1.4 g/l of chlorine. The permissible content of sodium carbonate in solution is 15-20 g/l (presence of up to 15 g/l NaHCO_3 is permitted

with the agreement of the consumer). These solutions are shipped in rubberized aluminum tanks or in tanks made of stainless steel.

5. Ammonium Sulfate

Physical-Chemical Properties of Ammonium Sulfate

Ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ is colorless crystals of rhombic shape with density of 1.769 g/cm^3 (refraction index 1.5230). The content of nitrogen in chemically pure ammonium sulfate equals 21.2%.

Certain indicators of the physical-chemical properties of ammonium sulfate are presented below:

Molecular weight	132.139
Bulk density, T/m^3	0.7
Melting point, °C	513 (with decomposition)
Molar heat capacity at 10°C cal/ (mole x deg)	63.92
Heat of formation, kcal/mole	
from simple substances	281.46
from gaseous ammonia and sulfuric acid	65.44
Heat of crystallization from aqueous solution, kcal/mole	2.6

When heated above 100°C, ammonium sulfate is gradually broken down, becoming acid salt. At 513°C, it is completely broken down into NH_3 , H_2SO_4 , SO_3 and H_2O . The pressure of ammonia above solid $(\text{NH}_4)_2\text{SO}_4$ at 205°C equals 0.5 mm Hg; at 300°C, it is 50.8 mm Hg. Dissolving of 1 g-equiv. of salt in 1 l of water at 19.6°C is accompanied by absorption of about 1 kcal of heat. The relative equilibrium humidity of air above the solution of ammonium sulfate saturated at 30°C is 79.2%.

The solubility of ammonium sulfate in water is represented by the data in table II-45. The characteristics of its aqueous solutions are presented in table II-46-II-50.

TABLE II-45. SOLUBILITY OF $(\text{NH}_4)_2\text{SO}_4$ IN WATER^{65a}

Температура °C	Растворимость вес. %	Твердая фаза	Температура °C	Растворимость вес. %	Твердая фаза
-5	17.0	Лед ⁽⁴⁾ (5) Лед + $(\text{NH}_4)_2\text{SO}_4$ (6) (эвтектика)	15	42.45	$(\text{NH}_4)_2\text{SO}_4$
-10	28.0		20	42.85	
-15	36.0		25	43.30	
-19	39.8		30	43.75	
-10	40.5	40	44.70		
0	41.35	50	45.8		
5	41.65	60	47.0		
10	42.05	100	50.8		

Key:

1. Temperature, °C
2. Solubility, weight. %
3. Solid phase
4. Ice
5. Ice + $(\text{NH}_4)_2\text{SO}_4$
6. Eutectics

TABLE II-46. DENSITY OF AQUEOUS SOLUTIONS⁷⁰ OF $(\text{NH}_4)_2\text{SO}_4$ AT 20°C (in g/cm³).

Концентрация $(\text{NH}_4)_2\text{SO}_4$ вес. %	Плотность	Концентрация $(\text{NH}_4)_2\text{SO}_4$ вес. %	Плотность	Концентрация $(\text{NH}_4)_2\text{SO}_4$ вес. %	Плотность
1	1.0041	12	1.0691	24	1.1783
2	1.0101	14	1.0808	26	1.1496
4	1.0220	16	1.0924	28	1.1609
6	1.0338	18	1.1039	30	1.1721
8	1.0456	20	1.1154	35	1.2000
10	1.0574	22	1.2269	40	1.2277

Key:

1. Concentration of $(\text{NH}_4)_2\text{SO}_4$, weight. %
2. Density

The specific heat capacity c of aqueous solutions of ammonium sulfate at 19-51°C is given below²:

Concentration of $(\text{NH}_4)_2\text{SO}_4$, weight. %	3.5	12.8	32.8
c , cal/(g x deg)	0.9633	0.8789	0.7385

Methods of Ammonium Sulfate Production

The basic industrial methods of ammonium sulfate production are:

TABLE II-47. DENSITY OF AQUEOUS SOLUTIONS OF $(\text{NH}_4)_2\text{SO}_4$ AT DIFFERENT TEMPERATURES¹ (in g/cm³)

(1) Концентрация (NH_4) ₂ SO ₄ вес. %	(2) Температура, °C						
	10	30	40	50	60	80	100
1	1,0058	1,0015	0,9980	0,9939	0,9890	0,9777	0,9644
10	1,0600	1,0542	1,0503	1,0460	1,0412	1,0304	1,0185
20	1,1186	1,1117	1,1077	1,1033	1,0986	1,0833	1,0772
30	1,1757	1,1681	1,1640	1,1597	1,1550	1,1451	1,1346
35	1,2037	1,1960	1,1919	1,1876	1,1829	1,1731	1,1629
40	1,2314	1,2237	1,2196	1,2153	1,2107	1,2011	1,1910
45	—	—	—	1,2429	1,2384	1,2290	1,2189
50	—	—	—	—	—	1,2568	1,2466

Key:

1. Concentration of $(\text{NH}_4)_2\text{SO}_4$, weight. %
2. Temperature, °C

TABLE II-48. PRESSURE OF WATER VAPORS ABOVE SOLUTIONS² OF $(\text{NH}_4)_2\text{SO}_4$ (in mm Hg)

(1) Температура °C	(2) Концентрация $(\text{NH}_4)_2\text{SO}_4$, g/100 g воды									
	10	20	30	40	50	60	70	80	90	100
0	4,5	4,4	4,2	4,1	4,0	3,9	3,8	—	—	—
10	9,0	8,7	8,5	8,3	8,0	7,8	7,6	—	—	—
20	17,1	16,7	16,2	15,7	15,3	14,8	14,4	—	—	—
30	31,1	30,3	29,4	28,6	27,7	26,9	26,2	—	—	—
40	54,1	52,6	51,1	49,6	48,2	46,8	40,5	44,2	—	—
50	90,4	87,9	85,5	83,0	80,6	78,3	76,1	73,9	—	—
60	146,0	142,0	138,0	134,1	130,2	126,5	122,3	119,4	—	—
70	228,4	222,2	215,9	209,7	203,7	191,8	182,2	186,7	—	—
80	347,2	337,8	328,3	318,9	309,7	300,8	292,2	283,2	276,0	—
90	513,8	499,9	485,8	471,8	458,2	445,0	432,3	420,1	408,3	—
100	742,3	722,2	701,9	681,7	662,1	643,7	624,7	607,0	590,0	573,7
110	1050,0	1021,0	992,3	963,8	936,1	909,0	883,0	858,0	834,0	811,0

Key:

1. Temperature, °C
2. Concentration of $(\text{NH}_4)_2\text{SO}_4$, g/100 g of water

1) absorption by sulfuric acid of ammonia contained in the coking gas;

2) neutralization of sulfuric acid by gaseous synthetic ammonia;

3) treatment of gypsum with solutions of ammonium carbonate;

4) production from wastes of caprolactam production.

TABLE II-49. BOILING POINT OF AQUEOUS SOLUTIONS² OF $(\text{NH}_4)_2\text{SO}_4$ (at 760 mm Hg)

Концентрация ⁽¹⁾ $(\text{NH}_4)_2\text{SO}_4$ г/100 г воды	Температура кипения ⁽²⁾ °C	Концентрация ⁽¹⁾ $(\text{NH}_4)_2\text{SO}_4$ г/100 г воды	Температура кипения ⁽²⁾ °C
15.4	101	85.5	106
30.1	102	90.1	107
44.2	103	112.6	108
58.0	104	115.3	108.2
71.8	105		

Key:

1. $(\text{NH}_4)_2\text{SO}_4$ concentration, g/100 g of water⁴
2. Boiling point, °C

TABLE II-50. VISCOSITY OF AQUEOUS SOLUTIONS⁷² $(\text{NH}_4)_2\text{SO}_4$ (in centipoise)

Температура °C	Концентрация $(\text{NH}_4)_2\text{SO}_4$, вес. %					
	5.45	6.2	10.4	12.8	18.75	31.6
20	1.088	—	1.196	—	1.455	2.394
25	0.942*	0.983	—	1.08	1.44**	—
30	0.713	0.725	0.766	0.807	0.994	1.644
40	0.512	—	0.551	—	0.73	1.203
50	0.395	—	0.424	—	0.571	0.927

Key:

1. Temperature, °C
 2. Concentration of $(\text{NH}_4)_2\text{SO}_4$, weight. %
- * With concentration of 3.2% $(\text{NH}_4)_2\text{SO}_4$
 ** With concentration of 20.9% $(\text{NH}_4)_2\text{SO}_4$.

Production of Ammonium Sulfate from Ammonia of Coking Gas⁷²⁻⁷⁴

Ammonia that is contained in coking gas in a quantity of 7-10 g/m³ can be reprocessed into ammonium sulfate by indirect, direct and semidirect methods.

The indirect method means that when coking gas is cooled, resin and supernatant water are first removed from it, while the ammonia that remains in the gas is absorbed by water in the ammonia scrubbers. The ammonia that is separated from the obtained ammonia water is bound

by sulfuric acid into ammonium sulfate.

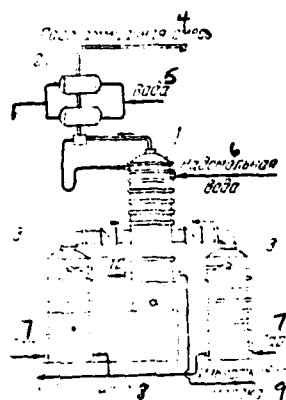


Figure II-49. Flowsheet of Supernatant Water Reprocessing

Key:

1. Distillation ammonia-lime columns
2. Fractionating columns
3. Subcolumns
4. Steam-ammonia mixture
5. Water
6. Supernatant water
7. Steam
8. To settling tank
9. Milk of lime

The direct method is based on absorption of ammonia by sulfuric acid directly from the hot coking gas. Because of the unprofitability and operating difficulties, the indirect and direct methods have not been used in industry.

The more economical semidirect method has become popular in the by-product coke industry. It consists of stages of primary gas cooling to separate the resins from it, reprocessing of the supernatant water formed during cooling of the gas, with distillation of the ammonia, and reprocessing of the ammonia into ammonium sulfate.

Reprocessing of the supernatant water consists of isolating the ammonia that has been dissolved in the supernatant water, and breaking down of ammonia salts that are formed during the interaction of NH_3 with the admixtures contained in the coking gas. Part of the salts are easily decomposed during heating. In order to break down the salts that are stable in heating, the supernatant water is treated with milk of lime.

The plan for reprocessing the supernatant water is shown in fig. II-49.

The supernatant water from the pressure tank flows by gravity into the upper plate part of the ammonia-lime column 1. Live steam

is fed into the lower part of the column. The steam bubbles through the layer of liquid on the plates. The liquid flows from the upper part of the column into the middle mixing part, is mixed with the milk of lime and is heated by live steam. In this case, a large part of the ammonia salts is broken down, while the released ammonia together with the water vapor is distilled from the upper part of the column. The liquid that contains residues of nondecomposed ammonia salts enters from the mixing part of the column into one of the subcolumns 3 with plate insertion piece. Here the ammonia is distilled by live steam and enters the upper part of column 1. The liquid from the lower part of subcolumn 3 drains through the settling tank into the sewage system. The mixture of ammonia and water vapors from the upper part of this column enters the water tubular fractionation column 2 where it is cooled from 100-102 to 95-96°C. Then the steam-ammonia mixture which contains 8-10 vol.% of NH₃ is sent for reprocessing into ammonium sulfate.

Reprocessing of ammonia into ammonium sulfate. The plan of this process is shown in fig. II-50.

The coking gas, cooled to 25-30°C and purified of resin, enters preheater 1 where it is heated by spent steam to 60-80°C. The heated gas is mixed with ammonia that is obtained during the reprocessing of the supernatant water, and is sent on bubbling pipe 5 into saturator 4.

The gas is bubbled through a 78% solution of sulfuric acid. In this case, ammonium sulfate is formed:



In the saturator, at the same time that sulfate is formed, pyridine bases are removed from the gas. They form complex compounds with sulfuric acid. They are broken down at a temperature above 65° with the release of pyridine that is removed from the saturator together with the gas.

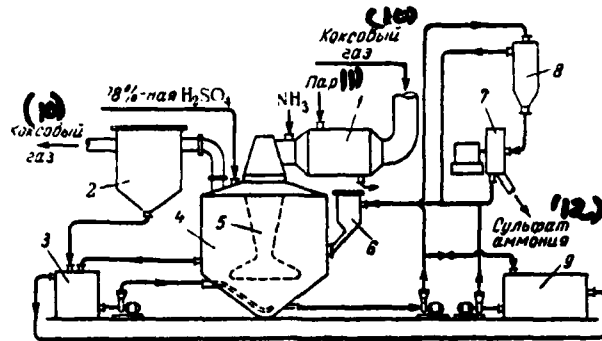


Figure II-50. Plan for Production of Ammonium Sulfate by Semidirect Method

Key:

1. Preheater of coking gas
2. Acid trap
3. Circulation tank
4. Saturator
5. Bubbling pipe
6. Reception vessel for mother liquor
7. Horizontal centrifuge
8. Crystal receiver
9. Reserve collector
10. Coking gas
11. Steam
12. Ammonium sulfate

The heat needed to evaporate the surplus moisture from the formed solution of ammonium sulfate is fed into the saturator with the coking gas that has been preheated in apparatus 1.

At the outlet from the saturator, the gas is sent to trap 2 for separation from the spray of acid, then is cooled and sent for further use. When the acidity of the solution in the saturator is decreased to 6-8% (which corresponds to the content in it of 140-170 g/l of fixed ammonia), crystals of ammonium sulfate begin to be released from the solution. The formed slurry is pumped by centrifugal pump into crystal receiver 8. The mother liquor is poured from the upper part of the crystal receiver into reception vessel 6 and is returned to the saturator. The crystals of ammonium sulfate continually enter from the crystal receiver to centrifuge 7 where they are separated from the mother liquor.

The centrifuged ammonium sulfate crystals, having moisture content of about 2%, are sent to the storehouse or for drying.

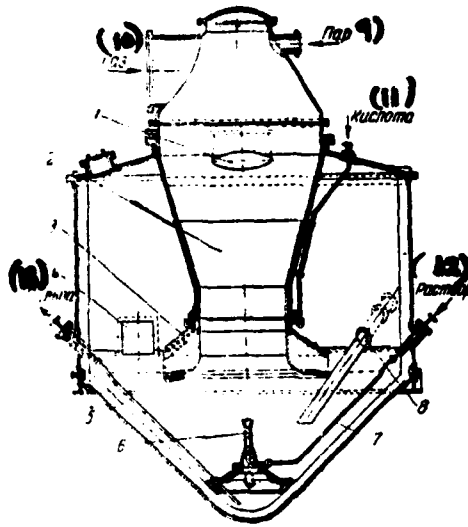


Figure II-51. Saturator with Central Bubbling Pipe and Extension Acid Trap

Key:

1. Connection pipe for outlet of gas from saturator
2. Central bubbling pipe
3. Bubbling hood
4. Connection pipe for overflow of mother liquor into circulation tank
5. Pipe for removal of slurry
6. Mixing jet
7. Pipe for supply of mother liquor into jet
8. Pipe for input of mother liquor from centrifuge
9. Steam
10. Gas
11. Acid
12. Solution
13. Slurry

Part of the solution continually circulates between the saturator and tank 3. Because of the circulation and the continuous repumping of the slurry from the saturator into the crystal receiver with return of the mother liquor to the saturator, a constant level of liquid is guaranteed in it and its thorough mixing. The salt crystals therefore are always in the suspended state, and the growth of crystals occurs uniformly in the entire mass of the solution.

The content of free sulfuric acid in the mother liquor that is

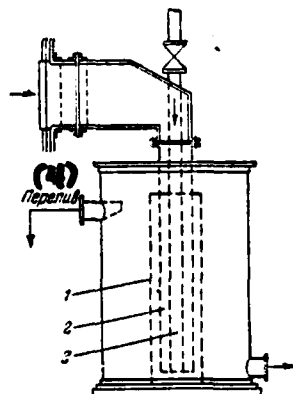


Figure II-52. Circulation Tank

Key:

1. Vessel of hydraulic gate
2. Pipe for drainage of solution from saturator
3. Pipe for drainage of solution from spray trap
4. Overflow

circulating in the saturator must be in limits of 6-8%. When the acidity drops (to 1-2%), larger crystals precipitate out of the solution. This may cause clogging of the saturator with salt. In this case, the absorption of ammonia from the gas is also impaired. With an increase in the solution acidity, the solubility of the ammonium sulfate in it increases and smaller crystals are obtained. If the solution contains over 11% acid, ammonium bisulfate NH_4HSO_4 which is easily soluble in water is formed.

Ammonium sulfate with moisture content of about 2% cakes during storage. With a decrease in moisture content, the product cakes to a lesser degree, and with a content of less than 0.2% moisture, ammonium sulfate practically does not cake.

Below is a description of the basic equipment used in this process.

Saturator (fig. II-51) is a steel cylindrical apparatus with conical bottom, lined on the inside with acid-resistant plates and equipped with connection pipes for input and output of reagents, solutions and slurry. There is a mixing jet 6 in the lower part of the saturator.

Circulation tank (fig. II-52) is made in the form of a vertical steel tank lined with lead or acid-resistant concrete. Vessel 1

which is present in the tank and pipe 2 which is almost lowered to its bottom for drainage of the solution form a hydraulic gate. It prevents penetration of gas from the saturator into the circulation tank. Acid from the spray trap enters the tank on inner pipe 3.

The crystal receiver is a vertical cylinder with conical bottom. The apparatus is continually filled. The surplus of solution is returned through the overflow into the saturator, and the crystals enter the centrifuge through the opening in the lower conical part. With one-time loading of the centrifuge with 250 kg (counting on dry product), the capacity of the crystal receiver is usually 0.5-0.75 m³.

Centrifuges. Centrifuges of continuous operation are mainly used. A rotating drum, as well as vibration drying transporters are usually used as the dryers.

The consumption coefficients for 1 τ of ammonium sulfate obtained by semidirect method:

Sulfuric acid (100% H ₂ SO ₄), τ	0.732-0.750
Electricity, kW x h	to 30
Steam, τ	2.7-6
Water, m ³	8

Production of Ammonium Sulfate from Sulfuric Acid and Gaseous Synthetic Ammonia^{2,3}

There are two known versions of this method: liquid and dry.

Liquid method. The plan of this process is illustrated in fig. II-53. The initial raw material is 76-98% sulfuric acid and 99% gaseous synthetic ammonia. The reaction between them occurs in a steel saturator 1 that is lined from the inside by sheet lead. Above it there are two layers of acid-resistant brick.

Ammonia is introduced into the saturator in the form of a steam-ammonia mixture (it contains roughly 15-20% NH₃) which enters the reaction space on two lead perforated pipes that are arranged on the bottom of the saturator. In the central part of the bottom there is

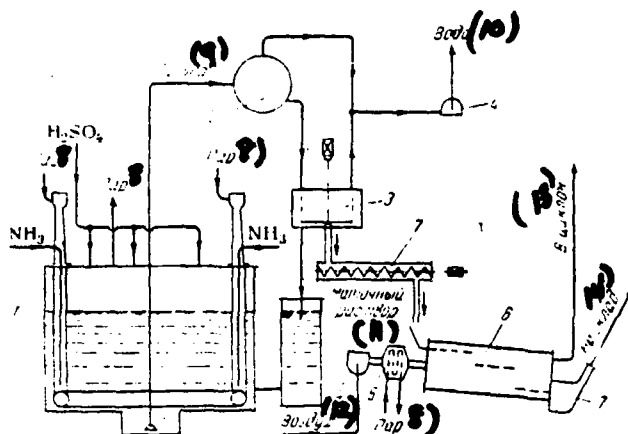


Figure II-53. Plan for Production of Ammonium Sulfate from Synthetic Ammonia and Sulfuric Acid

Key:

1. Saturator
2. Slurry collector
3. Centrifuge
4. Fans
5. Air preheater
6. Dryer
7. Worm conveyers
8. Steam
9. Slurry
10. Water
11. Mother liquor
12. Air
13. To cyclone
14. To warehouse

an areaway on whose bottom there is a ring steam pipe with holes. The steam that emerges from it intensively mixes the pulp. The steam ejector that is also placed in the areaway transfers to collector 2 the crystalline slurry that then enters centrifuge 3.

The neutralization process occurs at atmospheric pressure and 100-110°C. The acidity of the slurry is maintained in limits of 3.5-4.5%. Addition to the slurry of salts of phosphoric acid promote the formation of large crystals of ammonium sulfate.

The mother liquor is returned from the centrifuge to the saturator, while the centrifuged ammonium sulfate crystals with moisture content of 2-3% are transferred to drum dryer 6. After drying by air

heated to 120-150°C, the moisture content of the product is diminished to 0.09-0.15%. The finished product contains about 0.2% free sulfuric acid.

The consumption coefficients for 1 t of ammonium sulfate obtained by the liquid method:

Ammonia (gas 100% NH ₃), T	0.262
Sulfuric acid (100% H ₂ SO ₄), T	0.75-0.76
Electricity, kW x h	26
Steam, t	1.38
Water (circulating), m ³	1.35

Dry method. According to this method, the sulfuric acid that has been sprayed to a foggy state interacts with gaseous ammonia in the reaction chamber. Because of the reaction heat, almost all the moisture that is introduced with the acid is evaporated, and ammonium sulfate is formed as a fine crystalline powder with very low content of moisture (about 0.1%) and free acid (to 0.02%). The plan of this process is depicted in fig. II-54.

Sulfuric acid, 75-77%, is diluted with water to a concentration of 68-71% H₂SO₄, and enters by gravity flow through sprayer 1 into the conical-shaped scrubber 2 that is lined with acid-resistant plates and is equipped with an insert made of ceramic rings. In the scrubber, the ammonia of the exhaust gases that did not react in chamber 8 is absorbed by the acid. The gases freed of the ammonia are removed into the atmosphere, the acid from scrubber 2 flows along the fitting into saturator 4 which has a cylindrical shape and is lined with acid-resistant brick. A ferrosilide bubbler is installed in the saturator. Its lower edge has a toothed shape. The ammonia-containing gases that emerge from chamber 8 are bubbled through the layer of acid in the saturator. In this case, a certain quantity of ammonium sulfate is formed. The liquid that emerges from the saturator contains about 35% (NH₄)₂SO₄, 45% H₂SO₄ and 20% water.

The acid that is preheated to 135-140°C by bubbling gases in the saturator enters through measuring tank 3 into the jet tank 5 which regulates the supply of acid into reaction chamber 8, which is a

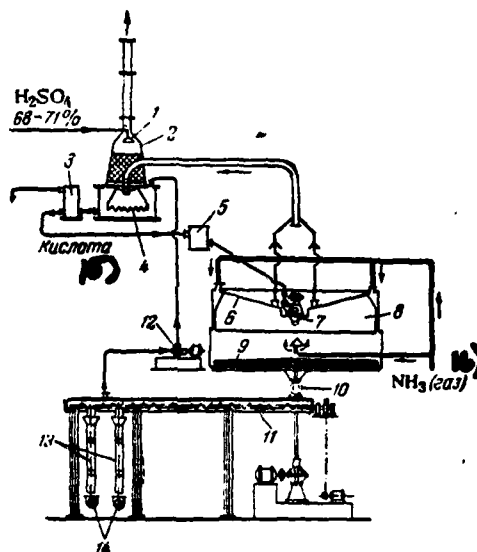


Figure II-54. Plan for Production of Ammonium Sulfate by Dry Method

Key:

1. Sprayer of acid
2. Scrubber
3. Measuring tank
4. Saturator
5. Jet tank
6. Hood
7. Acid sprayer
8. Reaction chamber
9. Scraper
10. Sprocket
11. Worm conveyer
12. Fan
13. Gravity spouts
14. Conveyers
15. Acid
16. Gas

steel cylinder. The acid enters here through ferrosilide sprayer 7 and passes into the foggy state. The ammonia is fed into the reaction chamber from the collector on several ducts. Through the gap between the vertical wall of the chamber and the steel hood 6, the ammonia enters above into the chamber and is uniformly distributed in the reaction space. The temperature in the chamber is maintained in limits of 200-220°C. The fine crystalline ammonium sulfate formed here settles on the bottom and is moved to the center by a rotating scraper 9. The crystalline product is transferred through a hole in the bottom of the chamber by a special attachment (sprocket 10)

into closed worn conveyer 11. From here it travels on gravity spouts 13 to the belt conveyers 14.

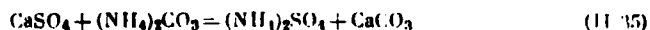
The ammonium sulfate that is obtained by this method has the appearance of loose very dusty light powder (bulk density 0.380-0.475 T/m³). This results in high losses of the product. As a consequence of this major shortcoming of the dry method, it has recently not been used industrially.

The consumption coefficients for 1 T of ammonium sulfate obtained by the dry method:

Ammonia (gas 100% NH ₃), T	0.260-0.280
Sulfuric acid (100% H ₂ SO ₄), T	0.750
Electricity, kw x h	18
Water, m ³	1

Production of Ammonium Sulfate from Gypsum^{2,3}

The essence of this method consists of processing natural gypsum by a solution of ammonium carbonate:



The plan for ammonium sulfate production from gypsum is shown in fig. II-55.

Gypsum powder and a 32-33% solution of ammonium carbonate heated to 50-55°C enters mixer 3. The gypsum powder is added in two procedures. This guarantees the formation of an easily filtered precipitate of CaCO₃. At first, about half of the consumed quantity of gypsum is mixed with the solution and the mixture is sent to reactor 4. From here, the slurry is returned to mixer 3 through collector 1. The remaining gypsum is added to mixer 3 and the obtained mixture is pumped into reactor 6. The reaction continues for roughly 8 h, after which the slurry that contains suspended particles of CaCO₃ is pumped through collector 7 into Nutsch filters 8. Filtering is done with vacuum of 360-380 mm Hg.

The sludge (calcium carbonate precipitate) is washed in the

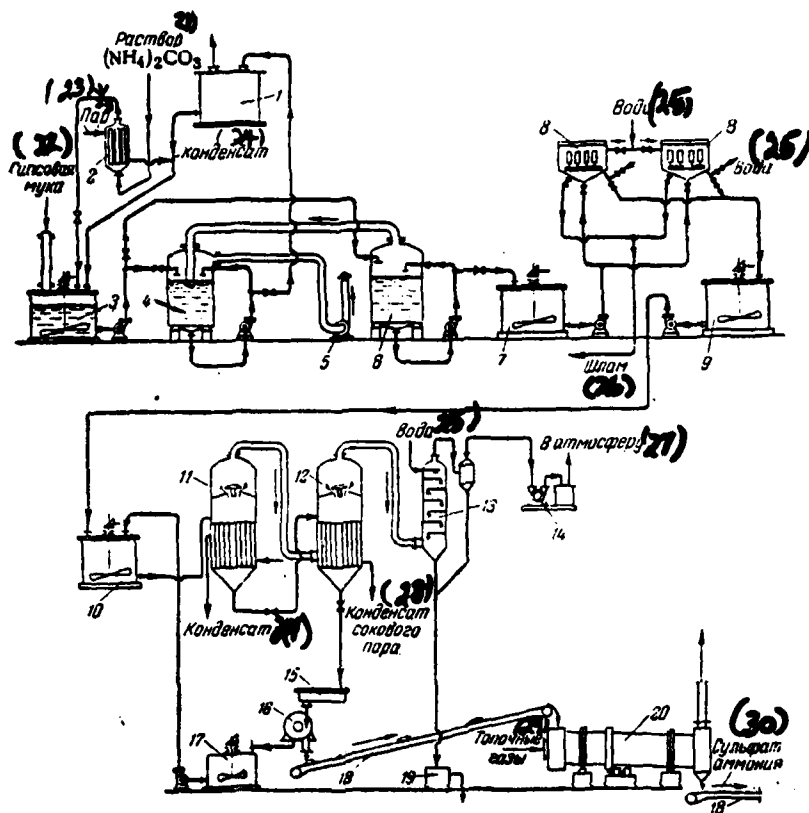


Figure II-55. Plan for Production of Ammonium Sulfate from Gypsum

Key:

1. Slurry collector
2. Preheater
3. Mixer
- 4, 6. Reactors
5. Exhauster
- 7, 9, 17. Collectors of ammonium sulfate solution
8. Nutsch filters
10. Pressure tank
- 11, 12. Evaporators
13. Barometric condenser
14. Vacuum pump
15. Trough
16. Centrifuge
18. Conveyers
19. Barometric container
20. Drying drum
21. Solution
22. Gypsum powder
23. Steam
24. Condensate
25. Water
26. Sludge
27. To atmosphere
28. Condensate of liquor steam

- 29. Furnace gases
- 30. Ammonium sulfate

Nutsch filter by water and is removed to a dump. The wash waters are used to prepare a solution of ammonium carbonate. A certain quantity of CaCO_3 particles remain in the filtered solution which contains 400-480 g/l of ammonium sulfate, therefore before evaporation, the solution is filtered once more (not shown in the plan). After repeated filtering, the solution which contains about 41% $(\text{NH}_4)_2\text{SO}_4$ and 1.5 $(\text{NH}_4)_2\text{CO}_3$ is fed for evaporation into apparatus 11 and 12 (first and second stages) made of carbon steel and lead-plated on the inside.

The evaporated slurry that contains 55% ammonium sulfate crystals and 45% solution, descends on trough 15 into centrifuge 16. Horizontal automatic or semiautomatic centrifuges are usually used. The liquor solution from centrifuge 16 is added to the solution of ammonium sulfate obtained after filters 8, and is jointly sent for evaporation.

The centrifuged ammonium sulfate which contains 1.5-2% moisture enters drying drum 20. The ammonium sulfate which has been dried to moisture content of 0.1-0.3% is further sent for packing.

The calcium carbonate sludge (760 kg per 1 τ of ammonium sulfate) that is obtained as a side product can be used in agriculture for liming acid soils or used to produce lime-ammonium nitrate (p. 247).

The consumption coefficients for 1 τ of ammonium sulfate obtained from gypsum:

Gypsum, τ	1.13	1.13
Ammonium carbonate (100% $(\text{NH}_4)_2\text{CO}_3$), τ		0.741
Electricity, kW x h		65.0
Steam (2-2.5 atm.), τ		1.109
Steam (16 atm.)*, τ		0.174
Water, m^3		25
Gaseous fuel, m^3		50.4

* For heating the air used to mix and dry the gypsum powder.

Production of Ammonium Sulfate from Wastes of Caprolactam Production

This method has begun to be used in recent years because of the development of caprolactam production. A large quantity of solutions of roughly the following composition (in %) is formed as a side product at the stages of formation of oximes and neutralization. It has roughly the following composition (in %):

Ammonium sulfate	34.0
Ammonium nitrate	1.3
Organic admixtures	0.3-0.5

After vacuum crystallization of these solutions, crystalline ammonium sulfate is obtained. The plan of this process is shown in fig. II-56.

The ammonium sulfate solution from the shop that produces caprolactam enters storage tank 1. From here it is continually pumped into mixing tank 3. The liquor solution that is circulating in the solution is also fed here. It emerges from the crystal receiver 13 and centrifuge 14. The ratio of the quantities of circulating mother liquor and fresh solution is roughly 7:1. The mixture of solutions from tank 3, successively passing several heat exchangers 4 (one of these is shown in the plan) and preheater 5, is heated from 40 to 110°C. In heat exchangers 4, the solution is preheated because of the heat of condensation of the liquor steam that enters from the vacuum-evaporator 6 and from the first two stages of the vacuum crystallizer 9. Live steam is fed into preheater 5. The heated solution enters the vacuum-crystallization unit which consists of a vertical three-stage vacuum evaporator 6 and horizontal six-stage vacuum-crystallizer 9. The vacuum in the unit is created by a steam ejector 7, and in the first stage is ~100 mm Hg. In the subsequent stages, the vacuum is gradually increased, and in the last stage reaches 710 mm Hg. In the vacuum crystallization unit, the solution boils at reduced pressure, is gradually concentrated and cooled to 40°C. The mixing of the formed suspension in the vacuum crystallizer is done by air sucked from the atmosphere.

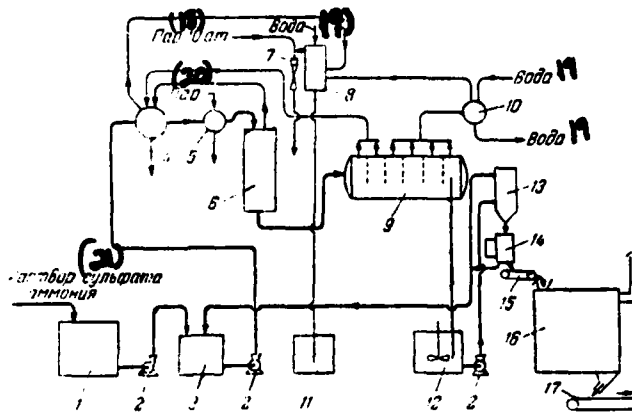


Figure II-56. Plan for Reprocessing Solutions of Ammonium Sulfate Obtained as Side Products in Caprolactam Production

Key:

1. Storage tank for ammonium sulfate solution
2. Centrifugal pumps
3. Mixing tank
4. Heat exchanger
5. Preheater
6. Vacuum evaporator
7. Steam ejector
8. Condenser of mixing
9. Vacuum crystallizer
10. Surface condenser
- 11, 12. Hydraulic gates
13. Crystal receiver
14. Centrifuge
- 15, 17. Conveyers
16. Dryer
18. Steam 10 atm.
19. Water
20. Steam
21. Ammonium sulfate solution

TABLE II-51. OPERATING PATTERN OF VACUUM-CRYSTALLIZATION UNIT

(1) Аппараты	(2) Ступени	(3) Температура °C	(4) Остаточное давление атм
(5) Вертикальный вакуум-испаритель	1-я	100—95	0.90—0.85
	2-я	90—85	0.60—0.50
	3-я	80—75	0.45—0.40
(6) Горизонтальный вакуум-кристаллизатор	4-я	70—65	0.30—0.25
	5-я	65—60	0.20—0.16
	6-я	60—55	0.16—0.13
	7-я	55—50	0.13—0.10
	8-я	50—45	0.10—0.08
	9-я	45—40	0.08

Key:

1. Apparatus
2. Stage
3. Temperature, °C
4. Residual pressure, atm.
5. Vertical vacuum evaporator
6. Horizontal vacuum crystallizer

The operating pattern of the vacuum crystallization unit is shown in table II-51.

A slow and gradual drop in solution temperature must promote the formation of large-crystal ammonium sulfate. The cooled slurry from the last stage (suspension of ammonium sulfate crystals) flows over the barometric pipe into hydraulic gate 12 that is equipped with a mixer. The slurry from here is continually repumped into crystal receiver 13 where it is partially condensed. The slurry further enters centrifuge 14. The mother liquor from the centrifuge and the clarified solution from the upper part of the crystal receiver are returned to the cycle through the mixing tank 3. The centrifuged ammonium sulfate crystals which contain 2-2.5% moisture, are sent by conveyer 15 to the tray dryer 16 of turbine type. The product is dried by air heated to 110-120°C with the help of steam coils that are arranged on the inner perimeter of the dryer. The cooled finished product (moisture content 0.1-0.3%) is transferred to the warehouse and to the packing department.

The consumption coefficients for 1 τ of ammonium sulfate that is obtained from the wastes of caprolactam production:

Solution of ammonium sulfate containing 34% $(\text{NH}_4)_2\text{SO}_4$, τ	2.97
Steam (11 atm.), τ	0.131
Steam (8 atm.), τ	1.024
Electricity, $\text{kW} \times \text{h}$	24.2
Water (28°C), m^3	55.5
Alkali* (100% NaOH), kg	2

*For neutralization of the acidity of the liquor vapor condensate.

As compared to the small-crystal product, the large-crystal ammonium sulfate (in the form of so-called rice grain) has a number of advantages: it cakes little during storage, it is scattered well by

fertilizer spreaders, and the losses of it during storage and putting into the soil are reduced.

Consequently, a lot of attention has recently been focused on developing methods for producing large-crystal ammonium sulfate. This product can be obtained when the appropriate saturation regime is observed and different additives are put into the ammonium sulfate (for example, sulfate of bivalent iron, sulfates of magnesium, aluminum, etc.).

Use and Quality of Ammonium Sulfate

Large quantities of ammonium sulfate are used in agriculture as nitrogen fertilizer (contains 20.5-21% nitrogen) for basic use on chernozem and sierozem soils under all agricultural crops.

Ammonium sulfate is a physiologically acid fertilizer, therefore the soil needs to be limed if it is used for a long time.

According to GOST 9097-65, three grades of by-product coking ammonium sulfate used as a fertilizer are produced. Their quality must meet the following requirements:

	Highest grade	first grade	second grade
Nitrogen content (in conversion for dry substance),%, no less	21.0	20.8	20.8
Free sulfuric acid,%, no more	0.025	0.050	0.050
Moisture, %, no more	0.2	0.3	0.3
Fraction with dimensions over 0.25 mm, %, no less	85	75	not normed

Ammonium sulfate (side product of caprolactam production) must meet the requirements TU AU 143-60:

Nitrogen content (in conversion for dry substance),%, no less	20.8
Moisture, %, no more	0.3
Admixtures of caprolactam, %, no more	0.5

Ammonium sulfate is packed in paper, bituminized, or polyethylene bags (capacity 45-50 kg each) and is shipped in closed

railroad cars. By agreement with the consumer, the ammonium sulfate may be shipped in a heap in clean closed cars.

6. Carbamide

Physical-Chemical Properties of Carbamide

Carbamide $\text{CO}(\text{NH}_2)_2$ (urea), or carbamic acid amide, is a colorless, odorless crystal substance. It is crystallized from solutions in the form of thin needles or rhombic prisms. The technical-grade product has a white or slightly yellowish color. Pure carbamide contains 46.6% nitrogen in the amide form.

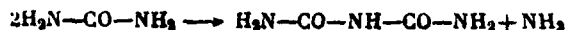
The main physical-chemical constants of carbamide:

Molecular weight	60.056
Melting point ⁷⁵⁻⁷⁷ , °C	
at 1 atm.	132.7
at 3000 atm.	150
Density ^{78,79} , g/cm ³	
at 0°C	1.335
at 25°C	1.330
at 132.7°C (liquid) ^{80,81}	1.225
Viscosity ^{80,81} (at 132.7°C), centipoise	2.58
Specific heat capacity (at room temperature), cal/(g x deg)	0.321
Molar heat capacity (at 136°C), cal/(mole x deg)	30.57
Free energy of formation ⁸² (at 25°C), kcal/mole	97.118
Heat of formation from simple substances ⁸² , kcal/mole	79.6
of melting ⁷⁵ , cal/g	57.8
of combustion ⁸² , kcal/mole	151.053
Heat of dissolving, cal/g	
in water ⁷⁵	57.8
in ethanol ^{78,83} (in methanol ^{78,83})	50.2 (46.6)
in liquid ammonia ⁸⁴	
at 26.4-31.5°C	61
at 50-108.5°C	32
Heat conductivity	
of crystals ⁷⁷ , cal/(cm x s x deg)	0.191
of liquid ⁸⁵ (at 135°C), kcal/(m x h x deg)	0.362
Entropy ⁸² (at 25°C), cal/(mole x deg)	25
Electrical conductivity of liquid ⁸¹ (at 135°C), Ohm ⁻¹ x cm ⁻¹	0.00435
Dielectrical permeability ^{86,87} (at 22°C and 4 x 10 ⁶ Hz)	3.5 ± 0.2
Dissociation constant ⁸⁸ (at 25°C)	1.5 x 10 ⁻¹⁴
Surface tension ⁸⁰ (at 132.7°C), dyne/cm	36

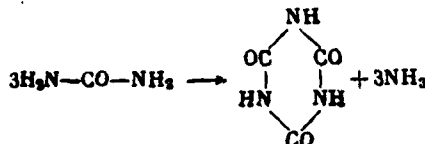
Angle of rest, °	
of crystalline product	37
of granulated product	35

Carbamide that has been heated in a vacuum to 120-130°C is sublimated without decomposition. At higher temperatures (160-190°C) it decomposes with the formation of ammonium cyanate. At atmospheric pressure and 180-190°C, carbamide breaks down with the formation of biuret, cyanuric acid and ammelide. At temperatures above 200°C, it breaks down into ammonia and cyanuric acid.

Biuret is the product of condensation of two molecules of carbamide which occurs with the splitting of ammonia:



Cyanuric acid is formed as a result of the condensation of three molecules of carbamide:



The breakdown of aqueous solutions of carbamide becomes noticeable at 60°C, significant at 100°C, and rapid at 125-130°C. Carbamide in solutions is practically stable at temperatures to 80°C.

The solubility of carbamides in water has been studied by a number of researchers. Their data is presented in table II-52.

Carbamide easily dissolves in liquid ammonia. With a rise in temperature, the solubility of carbamide significantly increases.

The pressure of ammonia vapors p_{NH_3} above the saturated solutions of carbamide in liquid ammonia $p_{90}^{\text{NH}_3}$:

t, °C	-26.4	5.8	23.9	35.9	40.9	44.7	44.9	50	61.8	81	82	101
p_{NH_3} , atm.	1.3	4.7	7.6	9.2	9.4	9.0	9.1	9.4	11.1	13.4	13.5	12.5

Carbamide dissolves in methyl, ethyl and other alcohols, and

TABLE II-52. SOLUBILITY OF CARBAMIDE IN WATER^{75,84,89}

Температура °C	Растворимость вес. %	Температура °C	Растворимость вес. %
0	40.00	65	74.11
7	44.00	70	76.28
17	50.00	75.3	77.56
20	51.83	84.4	81.42
25	54.58	93.8	85.24
30	57.18	95.0	87.00
35	59.85	104.4	89.84
40	63.80	107.0	90.00
45	64.72	109.9	91.78
50	67.23	115.3	93.78
55	69.58	120	95.00
60	71.88		

Key:

1. Temperature, °C
2. Solubility, weight. %

TABLE II-53. SOLUBILITY OF CARBAMIDE IN LIQUID AMMONIA^{84,90}

Температура °C	Растворимость вес. %	Температура °C	Растворимость вес. %
-30	17.9	44.7	73.2
-26.4	20.8	44.9	73.2
-5.0	31.8	45.0	75.6
5.8	38.8	50.0	75.9
14.5	45.1	61.8	79.3
20.5	49.2	66.0	80.7
23.9	51.8	66.5	81.4
26.0	54.3	78.0	83.6
31.5	58.1	81.0	84.8
35.9	62.8	82.0	85.0
40.9	68.0	101.0	91.1
43.0	72.3	108.5	91.9

Key:

1. Temperature, °C
2. Solubility, weight. %

TABLE II-54. SOLUBILITY OF CARBAMIDE IN CERTAIN ALCOHOLS⁷⁷
(in g/100 g of alcohol)

Спирты	Температура									
	0	10	20	30	40	50	60	70	80	90
Этанол ⁽³⁾	2,6	4,0	5,4	7,2	9,3	11,7	15,1	20,2	—	—
n-Пропанол ⁽⁴⁾	1,6	2,0	2,6	3,6	4,8	6,2	7,7	9,8	12,3	17,0
Изопропанол ⁽⁵⁾	—	—	6,2	—	—	—	—	—	23	—
Изобутанол ⁽⁶⁾	1,0	1,3	1,7	2,3	3,1	3,7	4,4	5,3	6,3	8,2
Изоамил ⁽⁷⁾	—	0,7	1,2	1,6	2,1	2,7	3,4	4,1	4,9	5,5

Key:

1. Alcohols
2. Temperature
3. Ethanol
4. n-propanol
5. Isopropanol
6. Isobutanol
7. Isoamyl

is not very soluble in ether and is insoluble in chloroform.

The solubility of carbamide in methanol is characterized by the following data²⁹⁷ (in g/100 g of alcohol):

t, °C	Растворимость ⁽¹⁾	Твердая фаза ⁽²⁾	t, °C	Растворимость ⁽¹⁾	Твердая фаза ⁽²⁾	t, °C	Растворимость ⁽¹⁾	Твердая фаза ⁽²⁾
-78	0.3	CO(NH ₂) ₂ · CH ₃ OH	0	7.7	CO(NH ₂) ₂ · CH ₃ OH	20	22.0	CO(NH ₂) ₂
-25	2.9		10	12.5		30	27.7	
-15	3.9		15	16.4		40	35.5	
-10	4.9		19	20.5		50	46.0	
						60	62.8	

- Key:
1. Solubility
 2. Solid phase

In the temperature interval from -15 to +19°C, carbamide can be dissolved in methanol, and with the precipitation of metastable solid phase⁷⁷ —CO(NH₂)₂:

Temperature, °C	-15	-10	0	10	15	19
Solubility, g/100 g of alcohol	10.9	11.0	14.2	17.7	19.7	21.4

The solubility of carbamide in certain organic solvents⁷⁷ is presented below (in g/100 g of solvent):

Solvent	t, °C	Solubility
Ethyl ether	15-20	0.0004
Glycerine	15	~ 50
Pyridine	20-25	0.96
Aqueous 50% solution of pyridine	20-25	21.53
Ethyl acetate	25	0.08

The viscosity of concentrated solutions of carbamide (above 75%) approaches the viscosity of water at low temperatures (0-10°C).

The nomogram for determining the viscosity of aqueous solutions of carbamide⁹¹ is shown in fig. II-57. On the right scale of the average line is the concentrations c of CO(NH₂)₂ solutions (in %), and on the left—the temperature t at which the solutions become saturated. After connecting the point of the assigned temperature on the left scale t with the point of solution concentration on the scale c, and after making a long straight line to the intersection with the viscosity scale η (in centipoise), we find at the intersection point the unknown viscosity of the solution. For example,

viscosity of a 50% solution of carbamide at 60°C is 0.925 cP. The saturation temperature of this solution is $t_n = 15^\circ\text{C}$.

TABLE II-55. DENSITY AND VISCOSITY OF AQUEOUS SOLUTIONS OF CARBAMIDE

Температура °C (1)	Плотность г/см ³ (2)	Вязкость спз (3)	Плотность г/см ³ (2)	Вязкость спз (3)
	(4) 15%-раствор		(4) 35%-раствор	
15	1.0423	1.250	1.0992	1.597
30	1.0367	0.904	1.0915	1.159
45	1.0302	0.705	1.0835	0.838
60	1.0218	0.576	1.0743	0.729
75	1.0140	0.491	1.0649	0.615
90	1.0050	0.425	1.0545	0.532
	(4) 55%-раствор		(4) 75%-раствор	
30	1.1530	1.786	—	—
45	1.1423	1.322	—	—
60	1.1330	1.053	—	—
75	1.1240	0.269	1.845	1.634
90	1.1145	0.746	1.1750	1.365

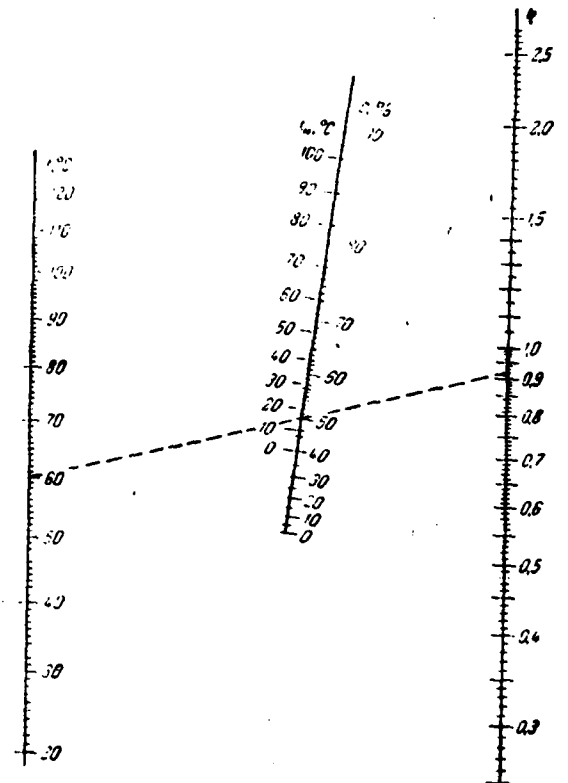
Key:
 1. Temperature, °C
 2. Density, g/cm³
 3. Viscosity, cP
 4. Solution

Figure II-57. Nomogram to Determine Viscosity η of Aqueous Solutions of Carbamide (in cP)

TABLE II-56. BOILING POINT OF AQUEOUS SOLUTIONS OF CARBAMIDE (IN °C) WITH VACUUM

Концентрация вес. % (1)	Разрежение мм рт. ст. (2)			
	710	660	560	410
20	40	51	69	81
40	43	56	71	84
60	45	61	76	90
80	Кристаллизуется (3)		87	100

Key:
 1. Concentration, weight. %
 2. Vacuum, mm Hg
 3. Crystallizes



The hygroscopic points of carbamide^{69,92} are presented below:

Temperature, °C	10	15	20	25	30	40	50
Relative air humidity above saturated solutions, %	81.8	79.9	80.0	75.8	72.5	68	62.5

Carbamide which contains 0.2-0.3% moisture practically does not cake. Cooling of the product and the introduction of additives (ground corn stalks, soy, bone, shell meal, dolomite, etc.) reduce the caking of crystalline carbamide.

The bulk density of crystalline carbamide which contains 0.5% moisture is 640 kg/m³. The bulk density of the granulated product is greater and depends on the granulometric composition of the product (table II-57).

TABLE II-57. BULK DENSITY OF GRANULATED CARBAMIDE*
(moisture content of product 0.5-1.7%)

Размерн гранул. (1) мм				(а) Насыпная плотность кг/м ³	Размерн гранул. мм (1)				(з) Насыпная плотность кг/м ³
2	2-1	1-0.5	0.5		2	2-1	1-0.5	0.5	
Содержание гранул, вес. % (2)				Содержание гранул, вес. % (2)					
4.2	87.0	5.8	3.0	682	0.6	72.4	25.7	1.3	727
3.2	88.2	6.0	2.6	688	1.9	79.4	17.0	1.7	680
6.2	82.0	7.9	3.9	692	6.6	73.0	19.0	1.4	670
6.5	90.4	—	3.1	736	2.2	80.0	16.8	1.0	670
1.9	83.1	13.5	1.5	674	1.4	72.8	23.2	2.6	710
0.6	75.6	22.1	1.7	701	5.5	78.5	14.7	1.3	678
0.9	76.7	19.4	3.0	703					

Key:

1. Granule sizes, mm
2. Bulk density, kg/m³
3. Granule content, weight. %

* According to data of N. V. Meshcheryakov.

Raw material. The initial raw material in the production of carbamide is liquid ammonia and gaseous carbon dioxide.

The physical-chemical properties of ammonia are presented in the first volume of Reference Book for Nitrogen Industry Worker (see section I).

Under normal conditions, carbon dioxide is a colorless, odorless

gas. The density of gaseous carbon dioxide (at 0°C and 760 mm Hg) equals 1.9769 kg/m³. The density of solid carbon dioxide is 1.3-1.6 kg/l, depending on the method of its production.

The triple point of carbon dioxide is -56/6°C at 5.28 atm. The heat of steam formation of CO₂ at temperatures and the appropriate pressures located between the critical and triple points, is determined from the equation (in kcal/kg):

$$r = 15.2 (304.1 - t)^{0.28}$$

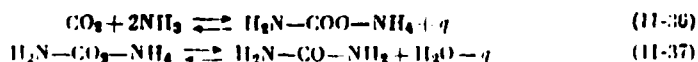
where t—temperature, °C.

Solid carbon dioxide melts at temperatures and pressures equal or exceeding its triple point. Below the triple point, solid carbon dioxide directly passes into the gaseous state (sublimates). The sublimation temperature is a function of pressure: at 1 atm. it is -78.3°C, in a vacuum -100°C and lower, depending on the depth of the vacuum.

The thermodynamic properties and the viscosity of carbon dioxide are presented in volume I of the Reference Book for the Nitrogen Industry Worker (see section I).

Physical-Chemical Fundamentals of Carbamide Synthesis

Of all the known methods for producing carbamide, the process of carbamide synthesis from ammonia and carbon dioxide according to the method developed in 1868 by the Russian chemist A. I. Bazarov⁹³ has currently obtained industrial value. Synthesis of carbamide according to this method can be viewed as the process of formation and dehydration of ammonium carbamate:



The equilibrium state of these reversible reactions, and consequently, the output of carbamide depends on the conditions of

synthesis, molar ratio of ammonia, carbon dioxide and water, temperature, pressure, quantity of inert gases in the initial mixture, duration of the process.

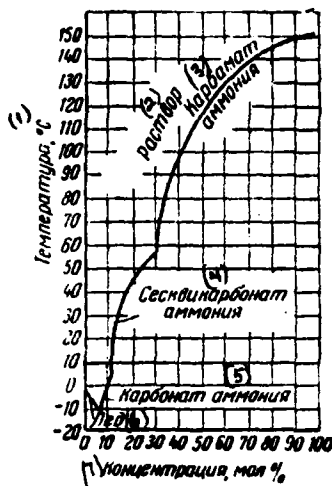


Figure II-58. Solubility of Ammonium Carbamate-Water System

- Key:
1. Temperature, °C
 2. Solution
 3. Ammonium carbamate
 4. Ammonium sesquicarbonate
 5. Ammonium carbonate
 6. Ice
 7. Concentration, mol. %

In the absence of water, only ammonium carbamate is obtained. In the presence of water, ammonium carbonate is also formed $(\text{NH}_4)_2\text{CO}_3$, ammonium bicarbonate NH_4HCO_3 , and ammonium sesquicarbonate $(\text{NH}_4)_2\text{CO}_3 \times 2\text{NH}_4\text{HCO}_3$.

Water and ammonium carbamate form a metastable system that is slowly converted into a mixture of different compounds. Their composition depends on the temperature and concentration of carbamate.

The solubility in the ammonium carbamate-water system (according to the data of Janecke) is shown in fig. II-58. It is apparent from here that the saturated aqueous solutions of ammonium carbamate exist at temperatures above 60°C. At lower temperatures, saturated solutions of other ammonium carbonates are formed.

The reaction (II-36) is exothermic. The results of determining the heat of formation of ammonium carbamate that were obtained by different researchers have discrepancies, but not very significant. Therefore, the heat of reaction (II-36) can be assumed to be equal to 152 kJ/mole (36.3 kcal/mole) with constant volume and 158 kJ/mole (37.7 kcal/mole) with constant pressure.⁹⁴

The reaction (II-37) of dehydration of ammonium carbamate with the release of carbamide is endothermic. Its thermal effect is -32.3 kJ/mole (-7.7 kcal/mole). Thus, the total heat of formation of carbamide from ammonia and carbon dioxide equals 125.7 kJ/mole (30 kcal/mole). Consequently, the process of carbamide synthesis on the whole occurs with the release of heat.

The quantity of released heat depends on the molar ratio of ammonia and carbon dioxide, the purity of the initial raw material, the water content in the reaction mass (in the column) and on the degree of conversion of ammonium carbamate into carbamide.

When carbamide is synthesized, in addition to the main reaction, side reactions may occur. The total effect of the main and side reactions determines the output of carbamide and the pressure of the process.

Matugnon and Frejacques⁹⁵ have established that the pressure of the process of carbamide synthesis with a stoichiometric ratio of $\text{NH}_3:\text{CO}_2$ is higher than the sum of pressures of water vapors and dissociation of ammonium carbamate. The dissociation pressure of ammonium carbamate was determined by Briner⁹⁶ in the interval of temperatures 77-197°C. The results he obtained are presented below:

Temperature °C	Gage pressure atm.	Tempera- °C	Gage pressure atm.
77.2	2.985	152	83.3
98.2	8.42	167	113.4
114.0	18.7	183	156.8
130.0	38.4	197	289.9

B. A. Bolotov and A. N. Popova in studying the conditions for carbamide synthesis established the dependence of the equilibrium pressure of the process on the temperature with different ratios of ammonia and carbon dioxide (fig. II-59). It is apparent from the figure that the pressure of the carbamide synthesis process significantly exceeds the pressure of ammonium carbamate dissociation

established by Briner, and only with a surplus of ammonia to 50% is the pressure of synthesis below the pressure of carbamate dissociation. According to Briner's curve for pressure of ammonium carbamate dissociation, one can determine the upper limit of the temperature in the column of synthesis at the assigned working pressure.

The reaction



is reversible, and the system is divariant. The pressure of carbamide synthesis with constant volume depends on the temperature and composition of the gas phase.

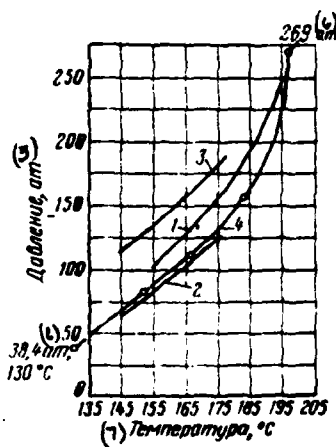


Figure II-59. Dependence of Equilibrium Pressure of Process of Carbamide Synthesis on Temperature (Filling of reaction space 0.7 g/cm³)

Key:

1. Without surplus of NH₃
2. Surplus of 50% NH₃
3. Surplus of 100% NH₃
4. Pressure of dissociation of ammonium carbamate
5. Pressure, atm.
6. atm.
7. Temperature, °C

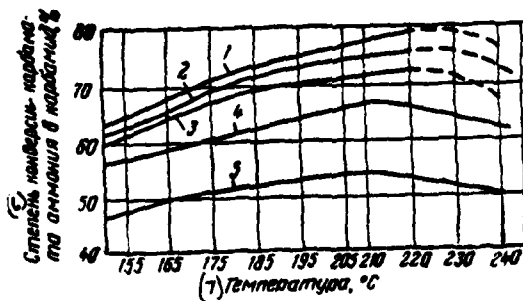


Figure II-60. Dependence of Equilibrium Output of Carbamide on Temperature and Surplus of Ammonia

Key:

1. Surplus of 300% NH₃
2. Surplus of 200% NH₃
3. Surplus of 100% NH₃
4. Surplus of 50% NH₃
5. Without surplus of NH₃
6. Degree of conversion of ammonium carbamate into carbamide, %
7. Temperature, °C

As B. A. Bolotov and V. R. Leman determined, the degree of

dehydration (conversion) of ammonium carbamate into carbamide increases with a rise in temperature and an increase in the surplus ammonia (fig. II-60). However, this increase lasts only to a certain maximum that is limited to temperature of 200-220°C. Above this temperature, it is inefficient to synthesize carbamide at the assigned pressure since with a further rise in temperature at constant pressure, the degree of conversion of ammonium carbamate into carbamide begins to decrease. This is explained by the intensive rise in pressure of dissociation of ammonium carbamate with a rise in temperature.

As follows from fig. II-61 which confirms the data of fig. II-60, with an increase in surplus ammonia to 100%, a comparatively high growth is observed in the degree of conversion of ammonium carbamate into carbamide. With a subsequent increase in the surplus ammonia, the degree of conversion increases only by 3-6%. Therefore, under practical conditions of carbamide synthesis, the $\text{NH}_3:\text{CO}_2$ ratio is assumed to be no more than 4:1.

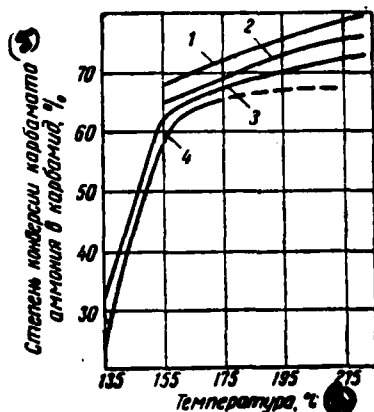


Figure II-61. Effect of Temperature on the Degree of Conversion of Ammonium Carbamate into Carbamide in the Presence of Surplus Ammonia (filling of reaction space 0.7-0.85 g/cm³)

Key:

1. At 300% NH_3
2. At 200% NH_3
3. At 100% NH_3
4. At 50% NH_3
5. Degree of conversion of ammonium carbamate into carbamide, %
6. Temperature, °C

The rate of ammonium carbamate dehydration is shown in fig. II-62. One should take into consideration that these data mainly have an illustrative nature since a whole series of factors that will be examined below influence the absolute quantities of carbamide output.

The effect of surplus ammonia and temperature on the rate of

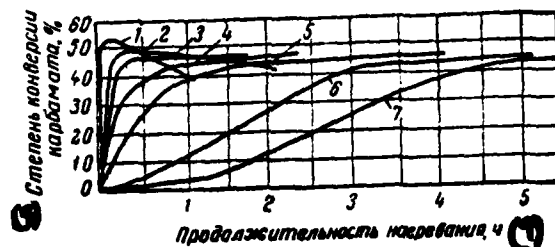


Figure II-62. Rate of Dehydration of Ammonium Carbamate

Key:

1. at 200°C
2. at 180°C
3. at 170°C
4. at 160°C
5. at 155°C
6. at 145°C
7. at 140°C
8. Degree of carbamate conversion, %
9. Duration of heating, h

conversion of ammonium carbamate into carbamide is shown in fig. II-63 (according to data of B. A. Bolotov, A. N. Popova and V. R. Leman).

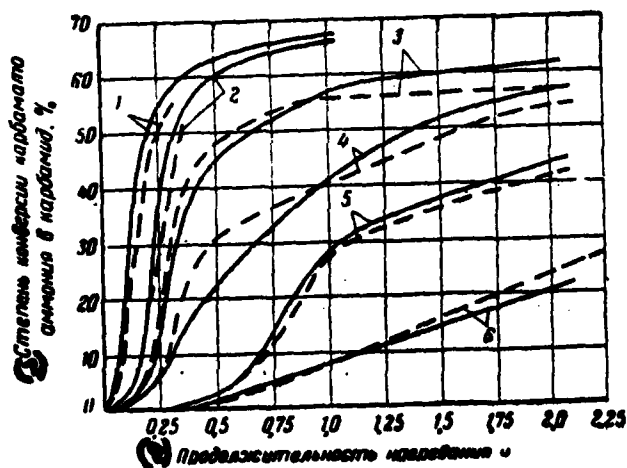


Figure II-63. Dependence of Degree of Ammonium Carbamate Conversion into Carbamide on Duration of Heating, Surplus Ammonia and on Temperature (solid lines--100% NH_3 surplus, dotted--50% surplus NH_3)

Key:

1. at 210°C
2. at 190°C
3. at 175°C
4. at 165°C
5. at 155°C
6. at 145°C
7. Degree of conversion of ammonium carbamate into carbamide, %
8. Duration of heating, h

With an increase in pressure, the degree of conversion of ammonium carbamate into carbamide increases. The specific output of the synthesis column also rises.

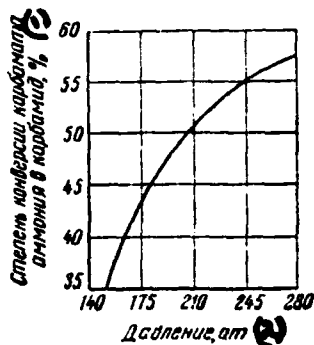


Figure II-64. Effect of Pressure on Degree of Conversion of Ammonium Carbamate into Carbamide

Key:

1. Degree of conversion of ammonium carbamate into carbamide, %
2. Pressure, atm.

At pressure of 154 atm. the degree of conversion is only 35% (fig. II-64), at 175 atm. it rises to 43%, at 210 atm.—to 51%, at 280 atm--to 57%, after which it remains on one level.

The rate of ammonium carbamate formation (with other conditions equal) rises roughly proportionally to the square of pressure. This reaction which is fairly slow at atmospheric pressure and normal temperature, under pressure on the order of 100 atm. and temperature of 150°C occurs almost momentarily. Therefore, under production conditions, in order to increase the specific output of the synthesis column, it is expedient to conduct this process at high pressure (200-280 atm.) and a temperature corresponding to this pressure.

Reaction (II-37) of the formation of carbamide from ammonium carbamate can occur with considerable output only in the liquid phase. The presence of water reduces the temperature of melting of carbamate in the initial period of the process, promoting the most rapid formation of the liquid phase. As equilibrium is reached, water has a negative effect on the course of the process of carbamide synthesis. It has been found⁹⁷ that the presence of each percentage of water above 2-3% reduces the degree of conversion of ammonium carbamate into carbamide by 1%. Frezhak and Kann have established the dependence of the equilibrium degree of CO₂ conversion into carbamide on the surplus ammonia and the water content in the reaction mixture. According to the nomogram (fig. II-65) which graphically expresses this dependence at temperatures of 130-200°C, one can compute the degree of conversion of carbon dioxide into carbamide in a broad

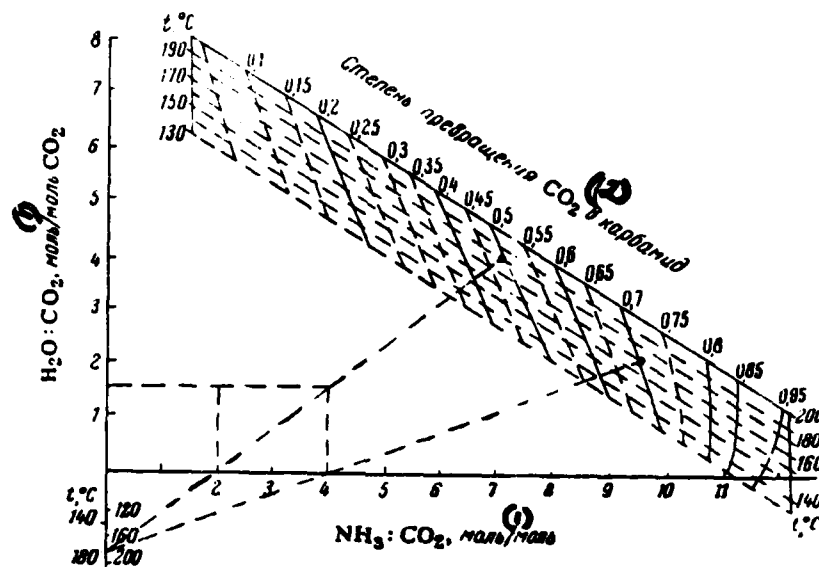


Figure II-65. The Effect of Surplus Ammonia and Water Content on Degree of Conversion of Carbon Dioxide into Carbamide

Key:

1. mole/mole
2. Degree of CO_2 conversion into carbamide

range of initial ratios of $\text{NH}_3:\text{CO}_2$ and $\text{H}_2\text{O}:\text{CO}_2$ in the reaction mass. For example, with $\text{NH}_3:\text{CO}_2=4$, addition of 1.55 mole of water and 180°C , the output of carbamide for CO_2 is 50%. With the same ratio of $\text{NH}_3:\text{CO}_2$ and 180°C , but without the addition of water, the output of carbamide rises to 73%.

A surplus of carbon dioxide does not have a significant effect on the ammonium carbamate conversion into carbamide (fig. II-66).

Figure II-67 shows a graph for the change in ammonium carbamate conversion into carbamide depending on the duration of stay of the reaction mixture in the synthesis column. It is apparent from the figure that in the space of 1 h, an almost equilibrium output of carbamide is reached. With a reduction in the time of stay of the melt in the synthesis column from 1 h to 30 min., the degree of conversion of ammonium carbamate is reduced by 6-8%, while the specific removal of carbamide from the synthesis column is increased two-fold (fig. II-68, a). Thus, with an increase in the total rate of

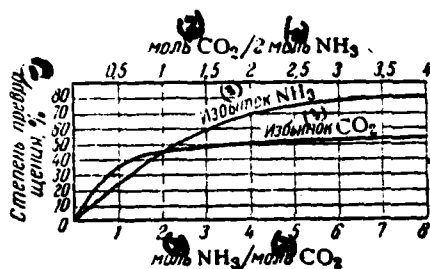


Figure II-66. Degree of Conversion of Carbon Dioxide into Carbamide with Surplus NH_3 or CO_2 and Temperature of 155°C (dotted line—stoichiometric mixture)

Key:

1. Degree of conversion, %
2. Mole
3. Surplus

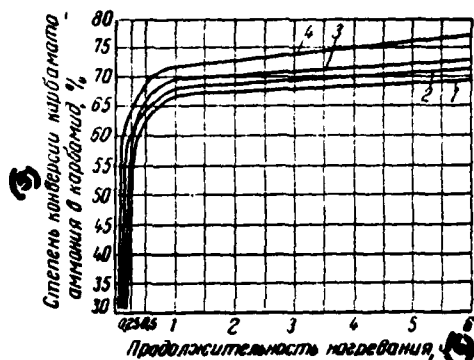


Figure II-67. Dependence of Degree of Conversion of Ammonium Carbamate into Carbamide on Duration of Heating of Reaction Mixture (Filling of Reaction Space 0.7 g/cm^3)

Key:

1. With surplus of 100% NH_3 and 190°C
2. The same at 210°C
3. With surplus of 300% NH_3 and 190°C
4. The same at 210°C
5. Degree of conversion of ammonium carbamate into carbamide, %
6. Duration of heating, h

loading the reagents into the column with a constant volume of them, the degree of CO_2 conversion into carbamide is reduced, but in this case, the output of carbamide is increased because of the reduction in time that the melt stays in the column,

The dependence of the specific removal of carbamide on the ratio of NH_3 and CO_2 is shown in fig. II-68, b.

When there are inert admixtures in the original ammonia and carbon dioxide, the partial pressure of NH_3 and CO_2 above the melt in the synthesis column is reduced, as a consequence of which there is a decline in the degree of conversion of ammonium carbamate into carbamide.

V. V. Lebedev (GIAP) [State Scientific and Planning Institute of the Nitrogen Industry and Products of Organic Synthesis]

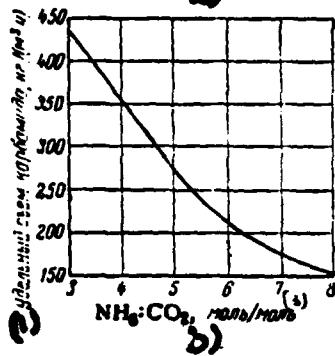
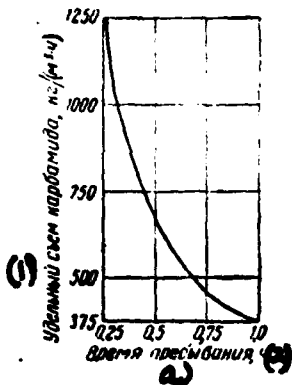


Figure II-68. Dependence of Specific Removal of Carbamide

Key:

- a. on time of stay of melt in synthesis column with $\text{NH}_3:\text{CO}_2 = 4:1$
 - b. on molar ratio $\text{NH}_3:\text{CO}_2$, with time of stay of melt in column ~ 1 h
1. Specific removal of carbamide, $\text{kg}/(\text{m}^3 \times \text{h})$
 2. Time of stay, h
 3. mole/mole

has established the dependence of decrease in degree of CO_2 conversion into carbamide on the quantity of inert gases in the initial raw material:

$$y = -2.66 \lg z + 70.06 \quad (\text{II-38})$$

$$y = -0.065 \lg z + 1.837 \quad (\text{II-39})$$

where x --content of inert admixtures in gas, vol.%;

y --degree of conversion of carbon dioxide into carbamide, weight.%.
weight.%.

Equation (II-38) refers to the equilibrium output, while equation (II-39) to the practical.

With an increase in surplus ammonia, there is a change in the density of the liquid phase (melt) and the volumetric ratios of NH_3 and CO_2 in the gas phase (fig. II-69). This has a negative effect on the specific output of the carbamide synthesis column. In order for the specific output of the column to be the greatest with the minimum energy expenditures, the $\text{NH}_3:\text{CO}_2$ ratio should be carefully

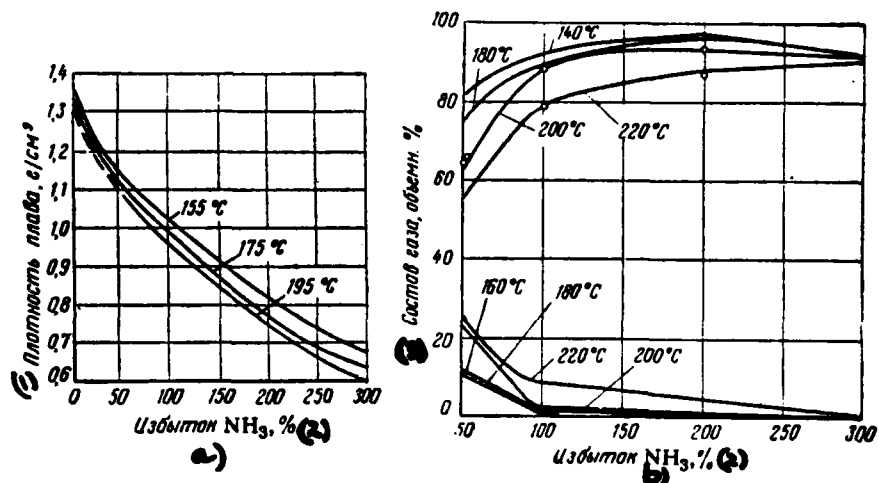


Figure II-69. Effect of Surplus Ammonia and Temperature in Synthesis of Carbamide

Key:

- a. on density of melt
- b. on composition of gas phase (descending curves-- CO₂ content, ascending--NH₃ content)
1. Density of melt, g/cm³
2. Surplus
3. Composition of gas, volume%

selected. Calculations made for a plan with complete liquid recycling (p.365) indicate that when the NH₃:CO₂ ratio rises, the consumption of electricity for 1 T of carbamide is reduced, while the specific consumption of steam is the minimum with NH₃:CO = 4:1 (fig. II-70). The total consumption of steam and electricity is also the minimum with a surplus of ammonia of about 100% .

The presented data make it possible to determine the optimal ratio of ammonia and carbon dioxide in the synthesis of carbamide under specific conditions of a chemical enterprise with regard for the cost of the steam and the electricity.

For a more complete study of the process of carbamide synthesis and to study the side processes, it is useful to know the solubility in a four-component system H₂O-CO(NH₂)₂-CO₂-NH₃, as well as the vapor pressure above the solutions and the composition of the corresponding gas phases.

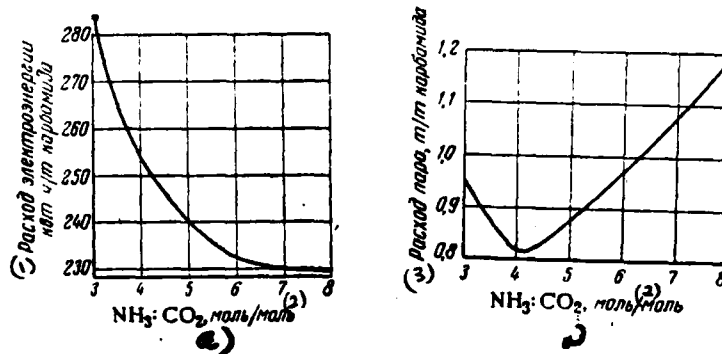


Figure II-70. Dependence of Specific Energy Expenditures in Production of Carbamide on Molar Ratio of $\text{NH}_3:\text{CO}_2$

Key:

- a. Consumption of electricity
- b. Consumption of steam during synthesis and distillation
1. Consumption of electricity, $\text{kWh} \times \text{h}/\text{t}$ of carbamide
2. mole/mole
3. Consumption of steam, t/t of carbamide

The data that refer to the metastable system of carbamide-water are presented in fig. II-71. It depicts the curve of solubility (crystallization) and the curves for the density of solutions and pressure of vapors above them with different temperatures and concentrations of solutions.

Figure II-72 illustrates the diagram for the condition of the carbamide-ammonium carbamate-ammonia⁶⁹ system. The curves of joint crystallization that demarcate the diagram into four regions correspond to the compositions of solutions that are saturated by two substances, for example, carbamide and ammonium carbamate (line OB), carbamide and its ammonia complex (line AO), etc. In the region which is adjacent to the top $\text{CO}(\text{NH}_2)_2$, there are solutions which are saturated with carbamide. Above it is a field of solutions that are saturated in relation to the complex $\text{CO}(\text{NH}_2)_2 \times \text{NH}_3$. The region of solutions saturated with ammonium carbamate is adjacent to the top of $\text{NH}_4\text{CO}_3\text{NH}_2$. In the region of stratification that is limited by ellipsoidal curve CD, two three-component solutions are in simultaneous coexistence. Their compositions are determined by the intersection

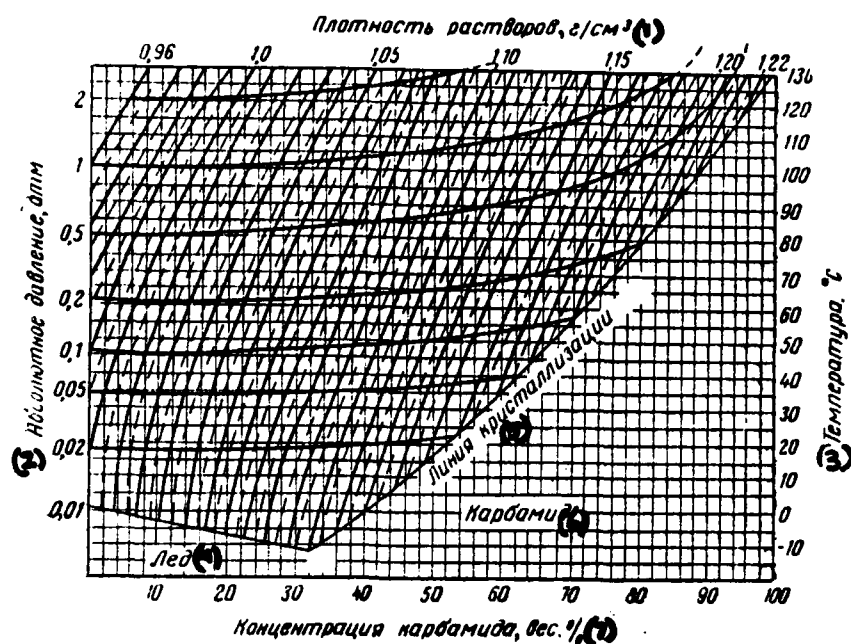


Figure II-71. Diagram of Solubility of Carbamide in Water, Density of Its Solutions and Pressure of Vapors above Solutions

Key:

1. Density of solutions, g/cm^3
2. Absolute pressure, atm.
3. Temperature, $^{\circ}\text{C}$
4. Ice
5. Line of crystallization
6. Carbamide
7. Concentration of carbamide, weight. %

points of the isotherms with boundary curve CD. The ratios of both solutions in the region of stratification correspond to the ratios of the isotherm segments into which they are divided by the assigned or unknown points of the compositions. Point O of intersection of three boundary curves characterizes the composition of the solution that is saturated with carbamate, carbamide and its ammonia complex.

By analyzing this diagram, one can draw the conclusion that in the presence of carbamide, the solubility of ammonium carbamate in liquid ammonia rises, and with an increase in the ammonia surplus, the melting point of the carbamide drops. In this case, the quantity of the liquid phase increases, and consequently, the reaction of carbamide formation is accelerated.

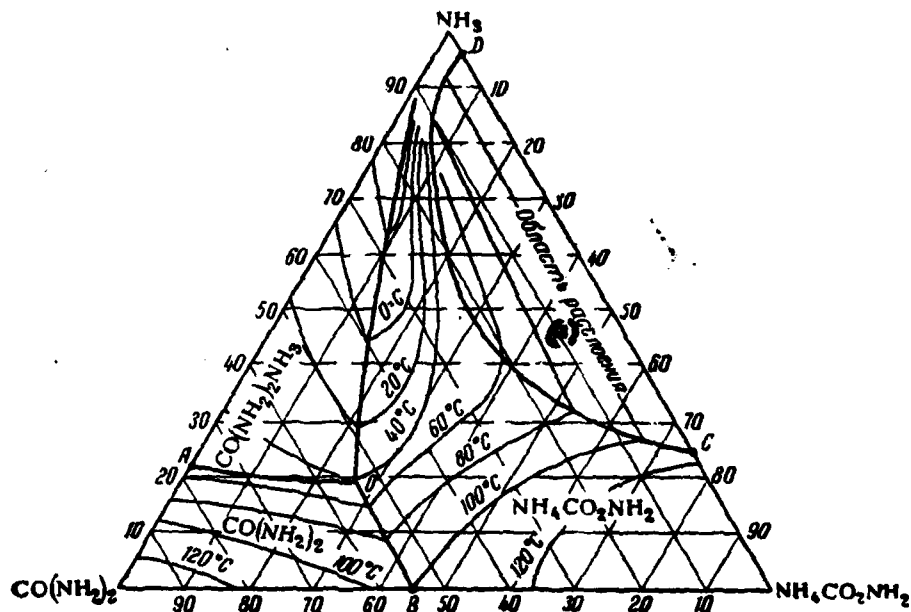


Figure II-72. Diagram of State of Carbamide-Ammonium Carbamate-Ammonia System

Key:

1. Area of stratification

Data on the melting points of the carbamide-ammonium bicarbonate and carbamide-ammonium carbonate-ammonium bicarbonate systems are presented below. ⁵⁴

System				System		
CO(NH ₂) ₂ wgt %	CO(NH ₂) ₂ -NH ₄ HCO ₃ wt %	CO(NH ₂) ₂ wgt %	t _m °C	CO(NH ₂) ₂ -NH ₄ COONH ₂ -NH ₄ HCO ₃ CO(NH ₂) ₂ : NH ₄ COONH ₂ wgt %	t _m °C	
5	95-103	50	70-88	10	80	115-134
10	82-107	60	82-84	20	60	74-113
15	79-101	70	84-85	30	40	72-108
30	80-100	80	92-112	40	20	91-100
40	83-94	90	106-125			

The equilibrium composition of the gas and liquid phases that are formed in the process of carbamide synthesis is presented in table II-58.

TABLE II-58. EQUILIBRIUM COMPOSITION OF LIQUID AND GAS PHASES IN PROCESS OF CARBAMIDE SYNTHESIS AT DIFFERENT TEMPERATURES t AND PRESSURES P

$t, ^\circ\text{C}$	P атм. ⁽¹⁾	Избыток NH_3 % ⁽²⁾	Средний состав жидк. фаз. вес. % ⁽³⁾				Средний состав парогазовой смеси, объем. % ⁽⁴⁾		
			NH_3	$\text{NH}_4\text{CO}_2\text{NH}_2$	$\text{CO}(\text{NH}_2)_2$	H_2O	NH_3	CO_2	H_2O
155	137	0	1.2	51.7	36.0	10.9	13.0	81.0	7.0
	80	50	19.4	34.5	35.5	10.6	83.6	10.6	5.4
	100	100	29.7	27.5	32.8	10.0	93.0	0	7.0
	135	200	44.0	20.6	27.2	8.2	95.7	0	4.3
	135	300	54.0	15.8	22.6	6.8	95.0	0	3.0
175	210	0	1.3	48.8	38.4	11.5	17.0	74.0	8.9
	210	50	16.2	38.2	39.2	11.8	11.0	73.4	7.6
	125	100	29.3	23.2	36.8	11.0	92.6	0.6	6.8
	160	200	45.2	17.0	29.0	8.8	95.7	8.7	3.6
	160	300	85.1	11.7	25.6	7.7	94.2	0	5.8
195	290	0	2.3	46.4	39.4	11.9	22.4	68.6	9.0
	175	50	19.1	29.1	39.8	12.0	72.0	20.0	3.0
	175	100	31.5	20.5	36.5	11.2	91.0	1.6	7.4
	210	200	45.6	14.6	30.6	9.2	93.5	1.6	5.0
	210	300	56.7	10.6	24.3	7.6	90.0	0	8.0
210	390	0	2.1	44.7	40.8	12.4	25.6	64.1	10.3
	245	50	19.1	27.1	41.4	12.4	65.4	24.5	10.1
	260	100	30.3	20.1	38.2	11.5	87.0	4.3	8.7
	290	200	47.8	13.0	30.0	8.2	89.0	3.3	7.7
	300	300	57.3	9.7	25.4	7.6	90.4	0.4	9.2
220	490	0	1.1	46.4	39.6	11.9	28.9	39.6	11.5
	295	50	18.8	28.0	40.8	12.4	65.1	25.8	9.3
	340	100	33.2	18.3	37.2	11.2	84.1	6.7	9.2
	350	200	48.9	12.3	29.8	9.0	87.2	3.6	9.2
	350	300	57.0	9.0	26.0	8.0	90.2	0.5	9.3

Key:

1. atm.
2. Surplus
3. Average composition of melt, weight. %
4. Average composition of steam-gas mixture, vol. %

Industrial Plans of Carbamide Production

World practice currently uses several industrial plans for synthesis of carbamide which are distinguished by the conditions for conducting the process and the plans for reprocessing the unreacted ammonia and carbon dioxide. All of these plans, depending on the methods of use of NH_3 and CO_2 which do not enter into the reaction of carbamide formation, can be divided into open and closed.

According to the open plans, the unreacted ammonia and carbon dioxide are not returned to the cycle, but are used for the production of nitrate, sulfate and bicarbonate of ammonia, ammonia water and other products. The breakdown of ammonium carbamate according to the

open plan may be done both in one stage (without recirculation of the gases), and in two stages (with partial recirculation of the gases).

Recirculation of the ammonia and carbon dioxide that have not be converted into carbamide and are returned to the synthesis cycle is done in closed systems. The unreacted gases can be recirculated by several methods which are roughly classified as follows:

liquid recycling of NH_3 and CO_2 in the form of aqueous solutions of ammonia salts;

recycling of an oily suspension of ammonium carbamate;

gas recycling based on extraction from the gas phase of one of its components and separate return of NH_3 and CO_2 to the synthesis cycle;

recycling of hot gases (NH_3 and CO_2).

Because of the continuous increase in the output of carbamide and the modern trend towards enlargement of the production units and decrease in the specific expenditures in production, the open plans of carbamide synthesis without recirculation of the gases are becoming less efficient and are losing their value. The units with partial recycling are used and continue to be built in many countries.

Partial Recycling

The plans with partial recycling stipulate a two-stage distillation of the melt that is obtained in the synthesis column. The ammonia that is distilled from the distillation column of the first stage is freed of carbon dioxide in the wash column, and is then condensed at 30-37°C. The pressure in the first stage of distillation is maintained in limits of 16-18 atm. The pressure in the second distillation stage is close to atmospheric.

The process of producing carbamide with partial recycling has become fairly popular since 1954 in the Soviet Union. A number of domestic enterprises use units of carbamide synthesis with output

of 100 T/day. The basis for the creation of technological plans to produce carbamide initially on an open cycle, and then with partial liquid recycling, and finally, with complete recycling was the results of extensive scientific research work done back in 1935 by B. A. Bolotov and V. R. Leman jointly with colleagues of the State Institute of High Pressures (GIVD), and subsequent work of the GIAP, Chernorechenskiy Chemical Plant and the Novomoskovskiy Chemical Kombinat.

The plan for carbamide production with partial recycling used in the USSR is shown in fig. II-73.

The process occurs as follows. Carbon dioxide under 200 atm. pressure enters synthesis column 1. Liquid ammonia from the warehouse, prepurified of oil is sent to the reception vessel, from which it is also fed into the synthesis column by a plunger pump. The process of synthesis in the column occurs at 200 atm, 180-190°C, and with molar ratio of $\text{NH}_3:\text{CO}_2=3.8-4$.

The melt formed in the column, whose composition includes carbamide, ammonium carbamate, water and ammonia, is regulated to pressure of 16-18 atm. and fed to column 2 of first stage distillation. The heat needed to distill the ammonia and break down the ammonium carbamate is supplied from extension heat exchanger 3 that is heated by steam. The gas phase which consists of ammonia, carbon dioxide and water vapors enters the fractionation column 5. Here the ammonia is freed of the carbon dioxide that is absorbed by the ammonia water that is fed to sprinkle this column.

The purified ammonia, together with inert gases goes for condensation. The condensed ammonia is further returned to the cycle, while the inert gases that contain a certain quantity of NH_3 that depends on the partial pressure of its vapors under conditions of condensation, are sent to the shop for the production of ammonium nitrate (p. 194).

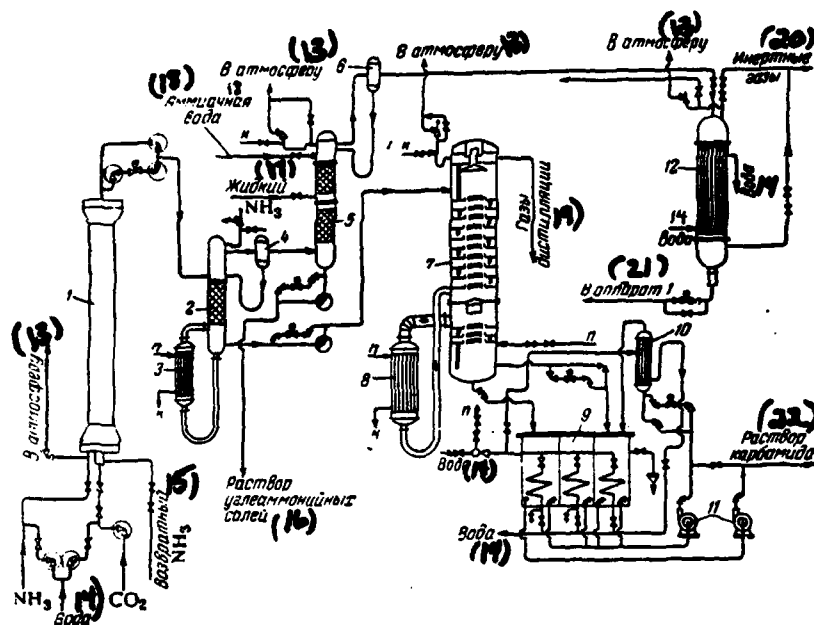


Figure II-73. Production Plan for Carbamide Production with Partial Recycling

Key:

1. Synthesis column
2. Distillation column of first stage
- 3,8,10. Preheaters
4. Spray separator
- 5,6. Fractionation columns
7. Distillation column of second stage
9. Collector of carbamide solutions
11. Centrifugal pumps
12. Ammonia condenser
- n. Steam
- k. Condensate
13. To atmosphere
14. Water
15. Return
16. Solution of ammonium carbonate
17. Liquid
18. Ammonia water
19. Distillation gases
20. Inert gases
21. To apparatus 1
22. Carbamide solution

The liquid phase (solution of ammonium carbonate) is sent from the fractionation column to distillation or to the synthesis column.

The carbamide solution from distillation column 2 of the first stage is regulated to absolute pressure of 1.5 atm. and enters column 7 of second stage distillation. Here complete breakdown of ammonium carbonate and distillation of ammonia and carbon dioxide occur. The gas mixture is sent from here to the ammonium nitrate shop, while the 68-75% solution of carbamide is sent for evaporation.

The solution is evaporated in a film type evaporator at residual pressure of 300-400 mm Hg and temperature of 125°C. In the production of crystalline carbamide that is mainly intended for technical purposes, the solution is evaporated only in one stage to a concentration of 91-93%. Then the solution enters the worm type crystallizer where crystallization and drying of the crystals simultaneously occur by blowing air through the crystallizers. A product with moisture content of 0.3% emerges from the crystallizers.

In the production of granulated carbamide that is mainly used by agriculture, the solution is exposed to two-stage evaporation. In this case, in the first stage the solution is evaporated to a concentration of 94-95%, in the second (with residual pressure of 15-60 mm Hg and temperature of 140-143°C)--to 99.5-99.8%. This melt is further sent to the granulation tower.

The difference between partial recycling and the one-pass process (without recirculation of the gases) is that the quantity of ammonia in the exhaust gases in the plan with partial recycling is about 0.8 T per 1 T of carbamide, while in the one-pass process, it rises to 1.4 T per 1 T of carbamide.

Liquid Recycling of NH₃ and CO₂ in the Form of Aqueous Solutions of Ammonium Carbonate

Plans with liquid recycling have recently been used more widely in the production of carbamide. Different versions of these plans that basically differ little from each other, have been developed abroad by the firms "Montekardini" (Italy), "Toye-Koatsu"

(Japan), "Stamikarbon" (Holland), "Inventa" (Switzerland), "Dupont" (United States), etc.

The plan of the firm "Montekatini" that was made on the basis of the results of Fauzer's work is realized in the form of a process with complete liquid recycling (fig. II-74).

Carbon dioxide, fresh liquid ammonia and a solution of ammonium carbonate are fed into the synthesis column 5 under pressure of 190-200 atm. The process of carbamide synthesis in the column occurs under mild, carefully controlled conditions. The degree of CO_2 conversion in this case is about 68%. Corrosion is almost not observed.

The melt which is obtained in column 5 and consists of carbamide, ammonium carbamate, ammonia and water is regulated to pressure of 20 atm. and is sent to preheater 7. Here the ammonium carbamate at 150°C is almost completely broken down into NH_3 and CO_2 . The steam-liquid mixture goes from the preheater to separator 13 of the first stage where the gas phase is separated from the solution of carbamide, and is further sent to condenser 14 of the first stage. Here an aqueous solution of ammonium carbamate is formed. It is fed by pump 15 into synthesis column 5.

At the exit from separator 13, the carbamide solution is regulated to pressure of 2-5 atm. and enters preheater 17, and then separator 19 of the second stage. In these units, the residue of ammonium carbamate is broken down into ammonia and carbon dioxide. The gas phase is condensed and absorbed in apparatus 18 with the formation of an aqueous solution of ammonium carbonate. It is re-pumped into condenser 14 of the first stage. Here this solution is finished saturating and also enters the synthesis column. Thus, the unreacted NH_3 and CO_2 circulate.

The solution of carbamide that is freed of ammonia and carbon dioxide, goes from separator 19 through collector 20, through filter press 22 into evaporator 21. From here, the melt is transferred

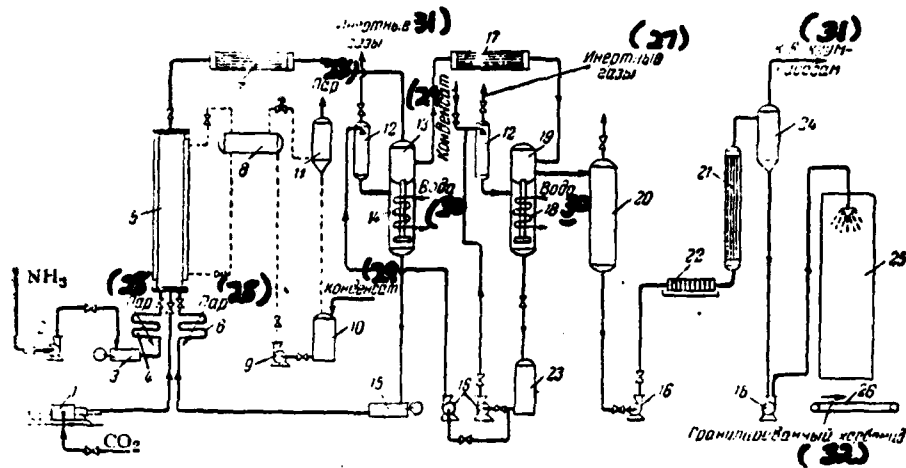


Figure II-74. Production Plan for Carbamide Production according to "Montecatini" Method

Key:

- 1. Compressor
- 2,3. Ammonia pumps
- 4,6,7,17. Preheaters
- 5. Synthesis column
- 7. Pressure tank
- 9,16. Centrifugal pumps
- 10. Collector
- 11,13,19,24. Separators
- 12. Apparatus for separation of inert gases
- 14,18. Condensers
- 15. Carbamate pump
- 20. Collector of carbamide solution
- 21. Evaporator
- 22. Filter press
- 23. Intermediate collector
- 25. Granulation tower
- 26. Conveyer
- 27. Inert gases
- 28. Steam
- 29. Condensate
- 30. Water
- 31. To vacuum pumps
- 32. Granulated carbamide

granulation tower 25. The granules are unloaded from the lower part of the tower and sent by conveyer for bagging and further to the warehouse.

The basic difference between the "Montecatini" plan and other plans with liquid recycling is that all the surplus ammonia is condensed, and jointly with the carbamate in the form of an aqueous

solution is sent to the synthesis column. In addition, in order to obtain a more concentrated solution of ammonium carbonate, the first condensation stage is done at pressure of roughly 20 atm.

The plan of the "Toye-Koatsu" firm is shown in fig. II-75. Carbon dioxide is sent by compressor 1, liquid ammonia by pump 4, and a solution of ammonium carbamate by pump 8 under pressure of 230-250 atm. to synthesis column 5. The carbamide is synthesized at 230 atm. and 180-190°C. The melt is dosed from the synthesis column to pressure of 17 atm. and enters the heated separator 6 in which almost complete breakdown of ammonium carbonate and distillation of ammonia and carbon dioxide occur at 155-158°C.

The solution of carbamide is dosed from separator 6 into separator 9 of the second stage, where at gage pressure of 1.5-2 atm. and 135°C all the ammonium carbamate is completely decomposed and the ammonia and carbon dioxide are distilled.

For final separation of ammonia and carbon dioxide, the solution of carbamide is sent to gas separator 12, from which it enters through cooler 13 for vacuum crystallization in apparatus 16. The crystals are separated from the solution in centrifuge 17, then dried and sent to the warehouse as a commercial product. If it is necessary to produce granulated carbamide, the crystals are sent to the melter in tower 19. Passing through the filter, the carbamide melt enters the stationary granulators of tower 19. The granules are collected in its lower part, cooled in the fluidized bed, and further transported to the warehouse.

The mother liquor from the centrifuge is returned to the synthesis cycle (not shown in the figure) through absorbers 10 and 7.

In these apparatus, the solution absorbs ammonia and carbon dioxide which are separated in separators 9 and 6. The concentrated solution of ammonium carbonate from absorber 7 is repumped into synthesis column 5. The ammonia which is purified from CO₂ in absorber 7 enters condenser 2, then collector 3, from which it is fed together with fresh liquid ammonia by pump 4 into the synthesis

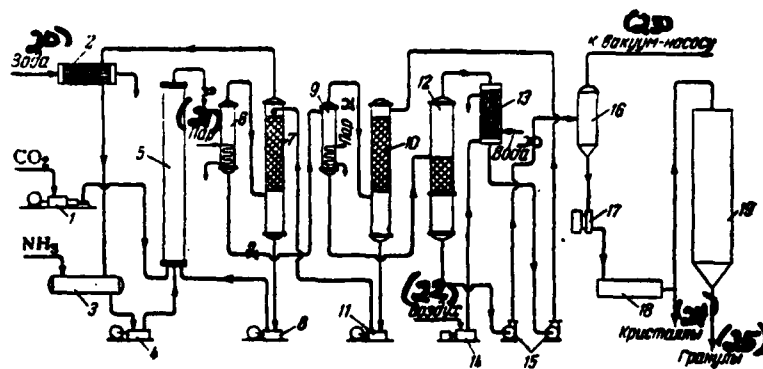


Figure II-75. Technological Plan for Production of Carbamate according to "Toye-Koatsu" Method

Key:

1. Compressor
2. Condenser
3. Ammonia collector
4. Ammonia pump
5. Synthesis column
- 6, 9, 12. Separators
- 7, 10. Absorbers
- 8, 11. Carbamate pumps
13. Cooler
14. Air blower
15. Centrifuge pumps
16. Vacuum crystallizer
17. Centrifuge
18. Dryer
19. Granulation tower
20. Water
21. Steam
22. Air
23. To vacuum pump
24. Crystals
25. Granules

column. Thus, NH_3 and CO_2 are completely recycled.

Plan of the firm "Stamikarbon." In contrast to the plan of "Montekatini" in which all the ammonia is returned to the synthesis column in the form of a solution of ammonium carbonate, and the "Toye-Koatsu" plan where the ammonia and carbon dioxide are absorbed by the mother liquor which contains up to 40% carbamide, according to the plan of the firm "Stamikarbon" (fig. II-76), the unreacted ammonia and carbon dioxide are returned to the synthesis column in the form of an aqueous solution of ammonium carbonate obtained during

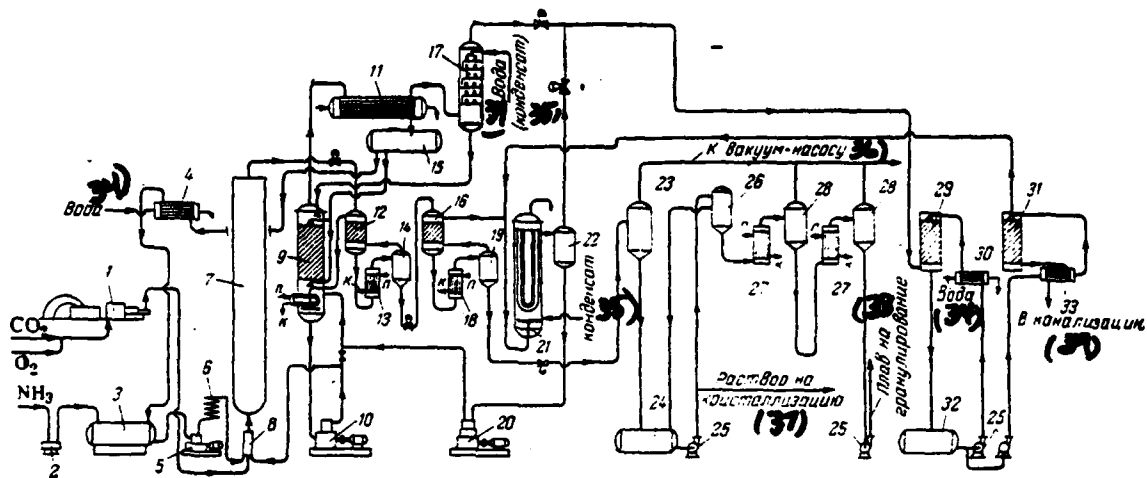


Figure II-76. Technological Plan for Production of Carbamide by "Stamikarbon" Method

Key:

- 1. Compressor
- 2. Filter
- 3,24,32. Collector
- 4,30. Coolers
- 5,10,20,25. Pumps
- 6,13,18. Preheaters
- 7. Synthesis column
- 8. Mixer
- 9. Wash column
- 11,21. Condensers
- 12,16. Rectification columns
- 14,19,28. Separators
- 15. Buffer vessel
- 17. Scrubber
- 22. Leveling vessel
- 23. Vacuum-evaporator
- 26. Pressure tank
- 27. Evaporators
- 29. Absorber
- 31. Desorber
- 33. Heat exchanger
- k. Condensate
- n. Steam
- 34. Water
- 35. Condensate
- 36. To vacuum pump
- 37. Solution to crystallization
- 38. Melt to granulation
- 39. To drain system

two-stage distillation of the melt.

In order to prevent corrosion of compressor 1, carbon dioxide is exposed to preliminary drying to moisture content of 1 g/m^3 . For this purpose, oxygen is added to the carbon dioxide fed into the synthesis column, as well as into the distillation system in such a quantity that the gas mixture contains 0.5-0.7 vol.% O_2 .

The dried carbon dioxide with admixture of oxygen is fed by compressor 1 into mixer 8 in which the same pressure is maintained as in the synthesis column, i.e., 190-200 atm. Liquid ammonia that enters from the warehouse is purified in filter 2 from the catalyst dust and partially from oil. It is then fed into collector 3. The return liquid ammonia from the water cooler-condenser 4 also enters here. The liquid ammonia is fed through preheater 6 from the collector to mixer 8. The solution of ammonium carbonate from wash column 9 is also pumped here.

Apparatus 8 is intended for preliminary mixing of ammonia and carbon dioxide. At a temperature of 175°C in the mixer, partial formation of ammonium carbamate and carbamide begins. The mixture of ammonium carbamate, ammonia, water and carbamide enters from the mixer into column 7. Here carbamide is synthesized at 190-200 atm. and $180\text{-}190^\circ\text{C}$.

The melt is regulated from the synthesis column to pressure of 17-18 atm and enters the rectification column 12 where surplus ammonia is distilled at $158\text{-}163^\circ\text{C}$ and ammonium carbamate is decomposed. The heat needed for these processes is fed to the solution from the extension heat exchanger 13.

The gas phase is separated from the liquid phase in separator 14, passes through column 12, and after combining with the gas phase released from this column, enters wash column 9. Here the ammonia is purified of carbon dioxide and sent to apparatus 11 where it is condensed, and then flows into collector 3. Part of the liquid ammonia that is obtained in condenser 11 is used to remove absorption

heat from the wash column. For final washing from ammonia, the inert gases, when they lack combustible admixtures, go from apparatus 11 into scrubber 17 that is sprinkled by condensate. In this case, ammonia water is formed in the scrubber. It is sent for sprinkling of column 9. When there are combustible admixtures, the inert gases are sent from the condenser, by-passing scrubber 17, to the ammonium nitrate shop or are recovered for other purposes.

At the outlet from separator 14, the solution is regulated to pressure 2-3 atm. and sent to column 16 of second stage rectification. The solution is heated to 140-142°C in extension preheater 18. The gas phase is separated from the liquid in separator 19.

The gas phase enters through rectification column 16 to condenser 12 of the second stage where the gases are condensed and absorbed by water with the formation of a solution of ammonium carbonate. The solution through leveling vessel 22 enters the suction line of carbamate pump 20, from which it is fed into the lower part of wash column 9. The concentrated solution of ammonium carbonate is pumped from the wash column into mixer 8.

The ammonia and carbon dioxide that are not absorbed in condenser 21 are sent to the absorption-desorption unit (apparatus 29-33). After absorption and desorption, NH_3 and CO_2 are returned to the second stage condenser.

The solution of carbamide from separator 19 enters vacuum evaporator 23 where the concentration of $\text{CO}(\text{NH}_2)_2$ in the solution increases to 74%. The solution is further sent for crystallization or evaporation.

In the production of granulated carbamide, the solution is evaporated to a concentration of 99.8% $\text{CO}(\text{NH}_2)_2$ in a two-stage vacuum-evaporator (apparatus 27, 28). The residual pressure in the first stage of evaporation is 300-400 mm Hg, in the second stage it is 40-15 mm Hg. The vacuum in the evaporation system is created

by a steam-ejection vacuum pump. The carbamide melt from the second apparatus 28 is repumped into the upper part of the granulation tower. The granules are unloaded from the tower by a special mechanism, and by a system of conveyer devices is sent for classification. In this case it is possible to obtain two fractions: fodder carbamide (granules 0.2-1 mm in size) and carbamide for fertilizer (granules 1-2.4 mm in size).

The quality indicators for the granulated carbamide obtained by the method of the firm "Stamikarbon" and domestic carbamide for agriculture (GOST 2081-63):

Indicators	Fodder carbamide	"Stamikarbon" for fertilizer	Carbamide (GOST 2081-63)
Nitrogen content, %, no less	46	46.1	46
Admixtures, %, no more			
Biuret	1	1	1
Moisture	0.3	0.3	0.3
Granule content (in %) of dimensions			
over 1 mm	less than 5	-	Two fractions*
less than 0.2 mm	less than 5	-	
over 2.4 mm	-	less than 5	
less than 1 mm	-	less than 5	

* Fraction 1--no less than 90% granules 0.2-1 mm in size (no more than 5% granules over 3 mm), fraction 2--no less than 90% granules 1-2.5 mm in size.

Recycling of Oily Suspension of Ammonium Carbamate

This process, which has been called the "Peshine" method, was developed in France and designed by the firm "Foster-Wiler" for two plants in the United States that were put into operation in 1954 and in 1956.

The feature of this process is recirculation of ammonium carbamate in the form of an easily mobile oily suspension containing up to 50% carbamate. It is injected into the synthesis column simultaneously with the fresh portions of liquid ammonia and carbon dioxide. Because of difficulties that arise in the start-up and

operation of these units, and the insufficiently good technical and economic indicators of the process, the "Peshine" method has not become popular.

Gas Recycling with Extraction of One Gas Component and Separate Return of NH₃ and CO₂ to the Process

The Swiss firm "Inventa" has developed an industrial process of gas recycling which is based on selective absorption of ammonia by an aqueous solution of ammonium nitrite and carbamide.

The firm "Chemico" (United States) has developed and implemented on an industrial scale gas recycling that is based on selective absorption of carbon dioxide by an aqueous solution of monoethanol amine. Below are the consumption coefficients for 1 T of carbamide that can be obtained by the method of the firm "Chemico":

Ammonia, T	0.58	Steam, T ₃	3.8-4.0
Carbon dioxide, T	0.78	Water, m	170-200
Electricity, kW x h	240		

The listed plans of gas recycling are inferior in technical and economic indicators to the plans with liquid recycling, therefore gas recycling has not become popular.

Recycling of Hot Gases (NH₃ and CO₂)

The plan of Bosch and Meyzer with recirculation of hot gases was previously realized by the German firm IG. The recycling is done by compression with a piston compressor of a moist mixture of ammonia and carbon dioxide to pressure of synthesis, and by feeding the mixture through a heat exchanger into the synthesis column. In this case, the degree of conversion of ammonia into carbamide reached 90%. However, the operation of the compressor was associated with great difficulties because of the need to maintain the temperature of the gas above 200°C to avoid condensation of its components and precipitation of the solid salts. This plan was not restored in the post-war period.

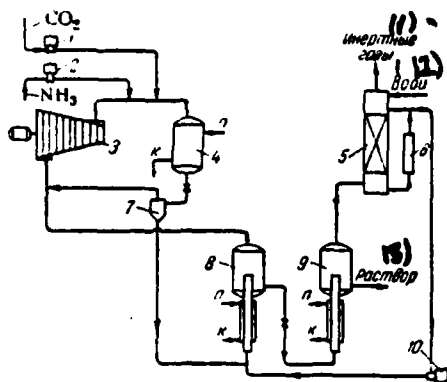


Figure II-77. Plan for Production of Carbamide by Thermal Method "Chemico" (with turbocompressor)

Key:

1. Carbon dioxide compressor
2. Ammonia pump
3. Turbocompressor
4. Heat exchanger (synthesis column)
5. Absorber
6. Cooler
7. Separator
8. Distillation column of first stage
9. Distillation column of second stage
10. Centrifugal pump
- n. Steam
- k. Condensate
11. Inert gases
12. Water
13. Solution

In 1955, the firm "Chemico" patented a process for recycling hot gases⁹⁸ (thermal process) that is based on their adiabatic compression in a turbocompressor. According to this plan, the unreacted ammonia and carbon dioxide are returned to the cycle in the form of gases and it is possible to use a large part of the heat that is released in the process of synthesis. The breakdown of ammonium carbamate in the described thermal process occurs in several stages with different pressures: for example, in the first stage at pressure 70 atm., in the second stage at pressure 14-28 atm., and in the third at pressure close to atmospheric.

The plan for production of carbamide according to the thermal method of "Chemico" is given in fig. II-77.

Carbon dioxide is compressed by compressor 1 and ammonia by pump 2 to synthesis pressure (140-420 atm.). They are mixed with the recirculating hot gas stream which has a temperature of 315-535°C. After mixing, the stream of gas at a temperature of 200-260°C enters the synthesis column-heat exchanger 4, where carbamide is formed. The reaction heat is consumed for the production of steam. The melt

that emerges from the heat exchanger is regulated to pressure of 15-30 atm. and sent to separator 7. The gas phase from the separator enters the pressure line of turbocompressor 3. The solution is sent to column 8 of first stage distillation.

The gas phase from column 8, together with the gases from separator 7 enter turbocompressor 3. The solution is regulated to gage pressure of 0.5-4 atm. and sent to column 9 of second stage distillation.

Gaseous ammonia and carbon dioxide together with the water vapors enter from column 9 to absorber 5 where they are absorbed by the solution circulating through cooler 6. Part of the solution is continually repumped into column 8. The steam obtained in the reactor is used to warm up the distillation column and for evaporation.

By now, improved systems of the thermal process have been patented with more efficient use of heat that is released in the process of synthesis and in the compression of the gas mixture. Realization of the thermal process will make it possible to significantly reduce the consumption of energy resources.

Below are the sample consumption coefficients for 1 τ of carbamide obtained according to the thermal method:

	Drive	
	electric motor	steam turbine
Ammonia, τ	0.58	0.58
Carbon dioxide, τ	0.74	0.74
Steam, τ_3	None	None
Water, m	None	42
Electricity, kW x h	250	33
Fuel (10^4 kcal)	None	15.8

Improvement in the Process of Carbamide Synthesis

The firm "Stamikarbon" has developed a stripping process⁹⁹ for production of carbamide. Synthesis occurs at pressure of 130-150 atm. temperature of 170-190°C and $\text{NH}_3:\text{CO}_2$ ratio equal to 2.5:1. The

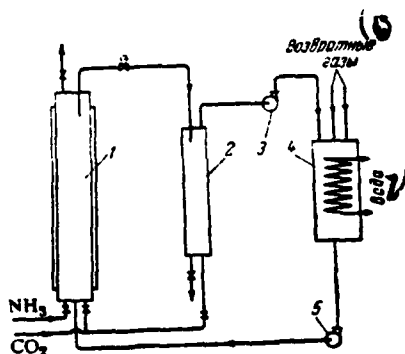


Figure II-78. Plan for Production of Carbamide according to Stripping Process of "Stamikarbon" Firm

Key:

1. Synthesis column
2. Stripping column
3. Gas blower
4. Condenser
5. Pump
6. Return gases
7. Water

ammonium carbonate is broken down in stripping column 2 at pressure close to the synthesis pressure (fig. II-78).

Carbon dioxide is fed to the lower part of the stripping column to blow through the carbamide melt. In this case, the ammonium carbamate is broken down into NH_3 and CO_2 . The gas phase is fed by gas blower 3 into condenser 4 where the ammonia and carbon dioxide are condensed with the formation of ammonium carbamate. Its melt is returned by pump 5 to synthesis column 1. The heat which is released during the formation of ammonium carbamate is used to produce steam that is consumed in the evaporator.

The solution of carbamide that contains up to 8% NH_3 and 6% CO_2 is regulated at the outlet of the stripping column to gage pressure of 2-5 atm. It is sent to the second distillation stage where it is finally freed of the carbamate and ammonia. The gas mixture (NH_3 , CO_2 , H_2O) is trapped and again returned to the cycle.

A similar process has been developed by the SNAM firm. In its version, ammonia is fed to the stripping column instead of carbon dioxide.¹⁰⁰

The Japanese firm "Toye-Koatsu" has developed a method of efficient cooperation for the production of ammonia and carbamide. In this method, the heat of the converted gas from the production of ammonia is used in the distillation assemblies for the production of carbamide to break down the ammonium carbamate and distill the ammonia and carbon dioxide. The converted cooled gas is then

compressed to pressure of ammonia synthesis and is fed to a special scrubber-washer for absorption of carbon dioxide by an aqueous solution of ammonia or ammonium carbonate. The temperature in the upper part of the scrubber is maintained below 100°C, and in the lower, in the interval of 130-180°C for more complete absorption of CO₂.

The solution of ammonium carbonate is fed from the high pressure scrubber together with fresh liquid ammonia to the column of carbamide synthesis. The purified converted gas enters for ammonia synthesis.

The production plan for the synthesis of carbamide is similar to the plan with liquid recycling, with the exception that the "Toye-Koatsu" plan lacks a carbon dioxide compressor, and the solution of ammonium carbonate is preliminarily fed to the scrubber-washer. It is sent from here together with fresh ammonia by gravity flow to the carbamide synthesis column. The solution of carbamide, after distillation, goes for evaporation and is reprocessed by the standard method.

Table II-59 presents the consumption coefficients for 1 T of carbamide that can be obtained according to the plans of certain foreign firms.

TABLE II-59. CONSUMPTION COEFFICIENTS FOR 1 T OF CARBAMIDE OBTAINED BY PLANS OF FOREIGN FIRMS

Articles of consumption	(1)	(2)		(3)		(4)		(5)
	«Монтекатини»	«Станикарбон» жидко-столб. процесс	«Тове-Коату» (жидкостной процесс)	«Хемико» жидко-столб. процесс	«Мер» жидко-столб. процесс	«Мер» жидко-столб. процесс	«Мер» жидко-столб. процесс	СШАМ (стр.-винт-процесс)
Ammonia, T	0.58	0.58	0.57	0.585	0.573	0.58	0.58	0.58
Carbon dioxide, T	0.78	0.77	0.77	0.768	0.753	0.75	0.74	0.76
Steam, T	1.5	1.5	0.3	1.85	1.0	1.65	1.65	0.9
Electricity, kw x h	160	150	120	185	180	170	250	150
Water, m ³	100	100	55	110	100	—	—	—

Key:

1. "Montekatini"
2. "Stamikarbon"

3. "Toye-Koatsu" (liquid recycling)
4. "Chemico"
5. SNAM (stripping process)
6. Liquid recycling
7. Stripping process
8. Old method
9. New method
10. Complete recycling (old method)
11. Thermal process
12. None

In the development of the domestic highly efficient plan for carbamide production, the already mastered processes were primarily improved. A check was made on the experimental-industrial units of new processes, and based on the findings, a plan was created for the production of carbamide with gas recycling. It was not inferior in technical and economic indicators to the similar foreign plans. However, it could not compete with the plan for recycling ammonia and carbon dioxide in the form of an aqueous solution of ammonium carbonate. The shops for the production of carbamide that worked with gas recycling were therefore switched to liquid recycling. Further planning of new units of carbamide synthesis is only being done on the basis of this last plan.

Complete Liquid Recycling

The plan for production of carbamide with complete liquid recycling is shown in fig. II-79.

Carbon dioxide enters through the dehumidifier - 6 into the suction line of carbon dioxide compressor 7. In order to prevent corrosion of the synthesis column, oxygen is added to the carbon dioxide (0.5 vol.% of the quantity of original gas). The carbon dioxide is sent from the compressor at pressure of 180-200 atm. to mixer 10 before synthesis column 9.

Liquid ammonia comes from the warehouse at pressure of 12-14 atm. to ammonia pumps 1. They repump it through filters 2 into storage tank 3. The return ammonia also enters here from condenser 40. The pressure in the storage tank is determined by the pressure

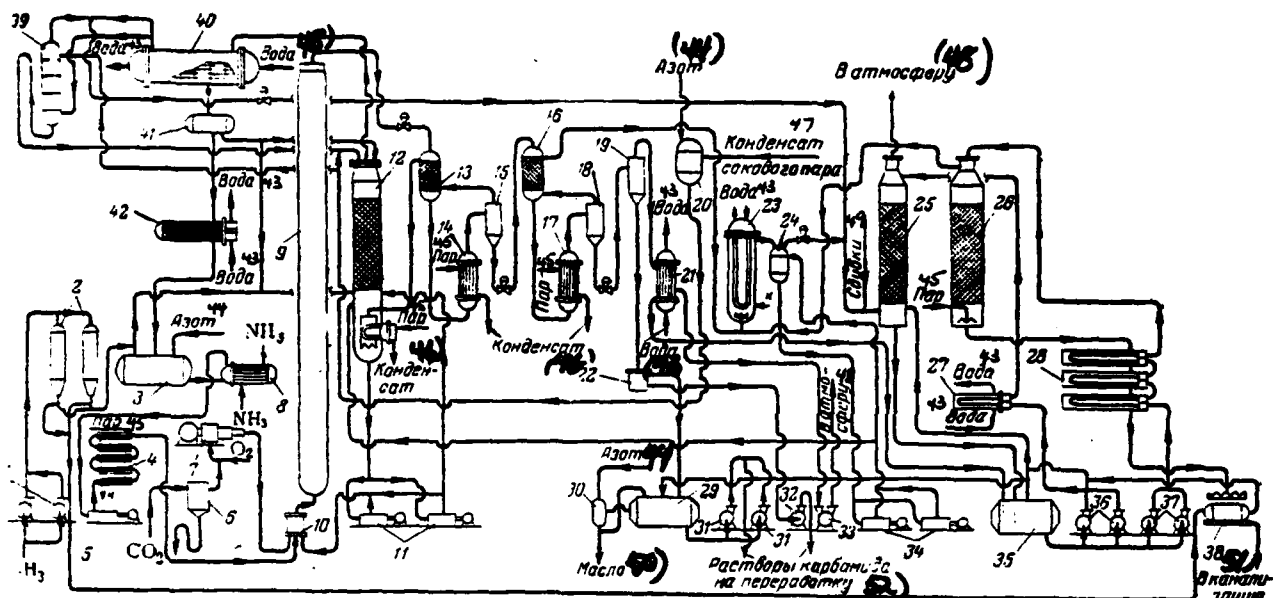


Figure II-79. Technological plan for production of carbamide with complete liquid recycling.

1 - Pumps to add liquid ammonia; 2 - Ammonia filters; 3 - Storage tank (collector) of ammonia; 4, 14, 17 - preheaters; 5 - high pressure ammonia pump; 6 - dehumidifier; 7 - carbon dioxide compressor; 8, 42 - ammonia coolers; 9 - synthesis column; 10 - mixer; 11, 34 - pumps to repump ammonium carbonate solutions; 12 - wash column; 13, 16 - rectification columns; 15, 18 - separators; 19 - vacuum evaporator; 20 - condensate collector; 21, 23 - condensers; 22, 29 - carbamide solution collectors; 24 - constant pressure vessel; 25 - absorption column; 26 - desorption column; 27 - cooler; 28 - heat exchanger; 30 - oil separator; 31, 32, 37 - centrifugal pumps; 33 - vacuum pump; 35 - collector; 38 - ammonia evaporator; 39 - scrubber; 40 - ammonia condenser; 41 - buffer vessel; k - condensate. Key: (43) Water; (44) nitrogen; (45) Steam; (46) Condensate; (47) Condensate of liquor steam; (48) To atmosphere; (49) From blower; (50) Oil; (51) To drain system; (52) Solutions of carbamide for re-processing.

of the first distillation stage which is usually 17-18 atm. In order to maintain constant pressure in the storage tank, nitrogen is added. The liquid ammonia is fed from the storage tank by plunger pump 5 under pressure of 180-200 atm. through preheater 4 into mixer 10. Ammonia and carbon dioxide that have not been converted into carbamide also enter the mixer in the form of a concentrated solution of ammonium carbonate. The molar ratio of $\text{NH}_3:\text{CO}:\text{H}_2\text{O}$ in the mixer is 4:1: (0.5-0.6).

With temperature of 175°C and pressure of 180-200 atm. in the mixer, formation of ammonium carbamate and carbamide begins. The melt which consists of carbamide, ammonium carbamate, ammonia and water, enters from the mixer into the lower part of synthesis column 9. Here at 180°C and the indicated pressure, the reactions of ammonium carbamate and carbamide formation continue.

At the outlet from the synthesis column, the melt is regulated to pressure of 18 atm. and sent to rectification column 13 of first stage synthesis. With a drop in pressure, part of the surplus ammonia is separated from the melt, and ammonium carbamate is broken down. Consequently, the temperature of the melt is reduced from 185-190°C roughly to 120°C.

The liquid phase comes from the rectification column into apparatus 14 where it is heated to 156-160°C. In this case, almost all the surplus ammonia is released from the melt and the greater part of the ammonium carbamate is broken down.

The steam-liquid mixture comes from preheater 14 to separator 15 where the gas phase is separated from the liquid. The gas phase at temperature of 156-160°C is returned to the lower part of

rectification column 13. Here heat exchange occurs between the gas and the liquid, and the gas that is cooled to roughly 120°C emerges from the upper part of the rectification column 13 into wash column 12.

The wash column is sprinkled by liquid ammonia and a condensate of liquor vapor. A solution of ammonium carbonate obtained in second stage condenser 23 is fed into its lower part. About 90% of the carbon dioxide is absorbed in column 12 by a solution of ammonium carbonate. The remaining 10% CO₂ is absorbed in the upper part of the wash column.

Liquid ammonia is fed into the wash column also to regulate the absorption temperature. It is distributed roughly as follows: 10% of the total quantity of NH₃ enters the lower part, 90% to the top of column 12. Liquid ammonia can enter the column by gravity flow from condenser 40 or be repumped by centrifugal pumps.

Ammonia water from the tail scrubber 39 or condensate of liquor vapor from collector 20 at 20-25 atm. pressure are also fed for sprinkling the wash column.

Pure gaseous ammonia at temperature of 45-50°C is sent from the wash column to the ammonia condenser 40. From here, the liquid (return) ammonia is fed to storage tank 3 where it is mixed with fresh ammonia coming from the warehouse.

The concentrated solution of ammonium carbonate from the wash column at temperature 98-100°C enters the suction line of the plunger pumps 11, and under pressure of 180-200 atm. is repumped into mixer 10.

The liquid phase from separator 15 of the first distillation stage, containing carbamide, ammonium carbamate, ammonia and water is throttled to pressure of 3 atm. and is sent to rectification column 16 of the second stage. Like the first distillation stage,

the second stage consists of a rectification column 16 in which heat exchange occurs between the liquid and gas phases of preheater 17, where the solution is heated to 135-140°C, and separator 18 where the gas phase is separated from the liquid phase.

Final breakdown of ammonium carbamate and distillation of the surplus ammonia from the solution occur in the second stage of distillation. The gas mixture which consists of ammonia, carbon dioxide and water vapors, enters from the second stage of distillation into condenser 23. Here the water vapors are condensed and the formed condensate absorbs ammonia and carbon dioxide. In this case a solution of ammonium carbonate is formed. The heat that is released during absorption is removed by the cooling water. The solution is poured from the upper part of condenser 23 into constant pressure vessel 24. From here it goes into the suction of carbamate pump 34. It feeds the solution into the lower part of wash column 12.

The liquid phase which contains about 70% carbamide is regulated from separator 18 of the second distillation stage and is sent to vacuum evaporator 19 where absolute pressure of 300 mm Hg is maintained. As a result of self-evaporation of water from the solution, its concentration is increased to 74% $\text{CO}(\text{NH}_2)_2$. Further, the 74% solution is removed through a barometric pipe into collector 29. It is pumped from here into the evaporator.

The carbamide solution is evaporated in two stages. In the first stage of evaporation, the solution with absolute pressure of 300 mm Hg and temperature of 125°C is evaporated to a concentration of 95-96% carbamide. In the second stage of evaporation, with absolute pressure of 20-50 mm Hg and temperature of 135-140°C, the solution is evaporated to a concentration of 99.8% $\text{CO}(\text{NH}_2)_2$.

A vacuum is created in the evaporator by steam-ejection devices. The liquor vapors are sent to condensers. The condensate is transferred to vessels. Part of the condensate is consumed for technological needs, The remaining condensate is used for absorption of the exhaust and blow-off gases which contain ammonia that is absorbed

TABLE II-60. MATERIAL BALANCE OF SYNTHESIS COLUMN

Components	Input						Output (melt)	
	Liquid ammonia		Carbon dioxide		Solution of ammonium carbonate			
	kg	%	kg	%	kg	%	kg	%
Ammonia	1600	99.8	-	-	503.3	40.64	1526	42.4
Carbon dioxide	-	-	745	97.9	459.6	37.49	460	12.8
Water	3.33	0.2	0.4	0.06	268.2	21.86	580	16.0
Carbamide	-	-	-	-	0.17	0.01	1014	28.4
Inert gases	-	-	15.4	2.04	-	-	15.4	0.4
Total	1603.33	100	760.8	100	1231.27	100	3595.4	100

Total input: 1603.33 + 760.8 + 1231.27 = 3595.4 kg equals output.

by the circulating cooled solution of ammonium carbonate. The circulation is done with the help of centrifugal pumps 36. The inert gases from absorber 25 are removed into the atmosphere.

The circulating solution is continually fed through heat exchanger 28 into desorber 26. At pressure of 3 atm. and temperature of 133°C, the ammonium carbonate is broken down here into ammonia and carbon dioxide. These gases are sent to condenser 23 of the second distillation stage. The water that is freed from NH₃ and CO₂ is cooled to 40°C and drained into the drainage system.

The carbamide melt is pumped from the separator of the second evaporation stage to the top of the granulation tower to the granulator. When the granulator rotates, the melt is sprayed over the tower. Falling downwards, the drops of carbamide melt harden, forming granules. The heat that is released during the formation of granules is removed by the air that can be sucked out of the tower by fans installed on the top of the tower.

The granulated carbamide is sent from the tower for bagging and storage with the help of lifting-transporting equipment.

Material Balance of Carbamide Production

The material balance is compiled for 1 T of carbamide that can

TABLE II-63. MATERIAL BALANCE OF SECOND STAGE CONDENSER

(1) Компоненты	(2) Приход						(3) Расход (раствор углекислых солей)	
	(4) газы дистилляции 2-й ступени		(5) газы из десорбера		(6) конденсат сокового сока		(7)	
	кг (7)	%	кг (7)	%	кг (7)	%	кг (7)	%
(9) Аммиак	114.4	50.4	12.3	50.0	0.19	0.5	126.89	43.5
(9) Двуокись углерода	41.5	18.2	2.1	8.5	—	—	43.6	15.1
(10) Вода	72.0	31.4	10.3	41.5	37.8	99.3	120.1	41.4
(11) Карбамид	—	—	—	—	0.07	0.2	0.07	—
(12) Инертные газы	—	—	—	—	—	—	—	—
(13) Всего	227.9	100	24.7	100	38.06	100	290.66	100

Key:

- | | |
|---|-------------------|
| 1. Components | 8. Ammonia |
| 2. Input | 9. Carbon dioxide |
| 3. Output (ammonium carbonate solution) | 10. Water |
| 4. Gases of second stage distillation | 11. Carbamide |
| 5. Gases from desorber | 12. Inert gases |
| 6. Liquor vapor condensate | 13. Total |
| 7. kg | |

Total input: 227.9+24.7+38.06=290.66 kg equals output.

TABLE II-64. MATERIAL BALANCE OF WASH COLUMN

(1) Компоненты	(2) Приход						(3) Расход					
	(4) газы дистилляции 1-й ступени		(5) раствор углекислых солей из 2-й ступени дистилляции		(6) аммиачная вода		(7) нижний аммиак (орошение)		(8) жидкая фаза		(9) газовая фаза	
	кг (7)	%	кг (7)	%	кг (7)	%	кг (7)	%	кг (7)	%	кг (7)	%
(11) Аммиак	1400	73.0	126.89	43.5	38.3	40.7	1410	100	503.3	40.84	2471.89	99.4
(12) Двуокись углерода	416	21.6	43.6	15.1	—	—	—	—	459.6	37.49	—	—
(13) Вода	92.5	4.7	120.1	41.4	55.6	59.2	—	—	268.2	21.86	—	—
(14) Карбамид	—	—	0.07	—	0.1	0.1	—	—	0.17	0.01	—	—
(15) Инертные газы	15.4	0.7	—	—	—	—	—	—	—	—	15.4	0.6
(16) Всего	1923.9	100	290.66	100	94	100	1410	100	1231.27	100	2487.29	100

Key:

- | | |
|--|--------------------------------|
| 1. Components | 6. Ammonia water |
| 2. Input | 7. Liquid ammonia (sprinkling) |
| 3. Output | 8. Liquid phase |
| 4. Gases of first stage distillation | 9. Gas phase |
| 5. Solution of ammonium carbonate from second distillation stage | 10. kg |
| | 11. Ammonia |
| | 12. Carbon dioxide |
| | 13. Water |

Tables II-60-II-69 present the material balances of the main apparatus and assemblies of carbamide production.

TABLE II-67. MATERIAL BALANCE OF VACUUM EVAPORATOR

(1) Компоненты	(2) Приход (жидкая фаза дистилляции 2-й ступени)		(3) Расход			
			(4) газовая фаза		(5) жидкая фаза	
	кг (6)	%	кг (6)	%	кг (6)	%
(7) Аммиак	11.6	0.8	52	16.5	6.4	0.5
(8) Двуокись углерода	2.5	0.2	—	—	2.5	0.1
(9) Вода	415.5	28.7	71.0	83.5	344.5	25.0
(10) Карбамид	1014	70.3	—	—	1014	74.4
(11) Всего	1443.6	100	76.2	100	1367.4	100

Key:

1. Components
 2. Input (liquid phase of second stage distillation)
 3. Output
 4. Gas phase
 5. Liquid phase
 6. kg
 7. Ammonia
 8. Carbon dioxide
 9. Water
 10. Carbamide
 11. Total
- Total output: 76.2 + 1367.4 = 1443.6 kg equals input.

TABLE II-68. MATERIAL BALANCE OF EVAPORATORS OF FIRST AND SECOND STAGES

(1) Компоненты	(2) Приход (растворы карбамида)				(3) Расход					
	(4) из отделений синтеза и дистилляции		(5) из раствори- тельной груп- пы графита и пыли		(6) газовая фаза 1-й ступени выпарки		(7) газовая фаза 2-й ступени выпарки		(8) жидкие фазы объем ступе- ней (плаз)	
	кг (9)	%	кг (9)	%	кг (9)	%	кг (9)	%	кг (9)	%
(10) Аммиак	6.4	0.47	—	—	5.2	1.6	0.48	1.1	—	—
(11) Двуокись углерода	2.5	0.15	—	—	2.5	0.8	—	—	—	—
(12) Вода	344.5	25.0	42.0	30	389.28	97.6	44.42	96.3	2.8	0.26
(13) Карбамид	1014	74.38	99.76	70	0.28	—	1.20	2.6	1113	99.74
Всего (14)	1367.4	100	141.76	100	347.26	100	46.10	100	1115.8	100

Key:

1. Components
2. Input (carbamide solutions)
3. Output

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4. From sections of synthesis and distillation
5. From solvents of large granules and dust
6. Gas phase of first evaporation stage
7. Gas phase of second evaporation stage
8. Liquid phases of both stages (melt)
9. kg
10. Ammonia
11. Carbon dioxide
12. Water
13. Carbamide
14. Total

Total input: $1367.4 + 141.76 = 1509.16$ kg equals total output.
($347.26 + 46.10 + 1115.8 = 1509.16$ kg).

TABLE II-69. MATERIAL BALANCE OF GRANULATION TOWER

(1) Компоненты	(2) Приход (плав из выпарной установки)		(3) Расход					
			(4) товарный карбамид		(5) возвратные по- тери (крупные гранулы и пыль)		(6) безвозврат- ные потери	
	кг (7)	%	кг (7)	%	кг (7)	%	кг (7)	%
(9) Карбамид	1113	99.74	1000	99.75	99.76	99.79	13.24	100
(10) Вода	2.8	0.26	2.6	0.25	0.2	0.21	—	—
(10) Всего	1115.8	100	1002.6	100	99.96	100	13.24	100

Key:

1. Components
2. Input (melt from evaporation unit)
3. Output
4. Commercial-grade carbamide
5. Return losses (large granules and dust)
6. Irreversible losses
7. kg
8. Carbamide
9. Water
10. Total

Total output: $1002.6 + 99.96 + 13.24 = 1115.8$ kg equals input.

Note: The losses of carbamide as a result of hydrolysis and the formation of biuret are ~ 1%. Irreversible losses during granulation, storage, transporting and cooling of carbamide reach 1.5%. Thus, total losses equal ~ 2.5%.

Basic Equipment

Below is a brief description of the basic production equipment of the systems of carbamide production which operate on the liquid

recycling plan.

Two types of columns of carbamide synthesis are currently in operation: columns with vessels and lined columns. They operate at pressure of 180-200 atm. and at temperature of 185-195°C.

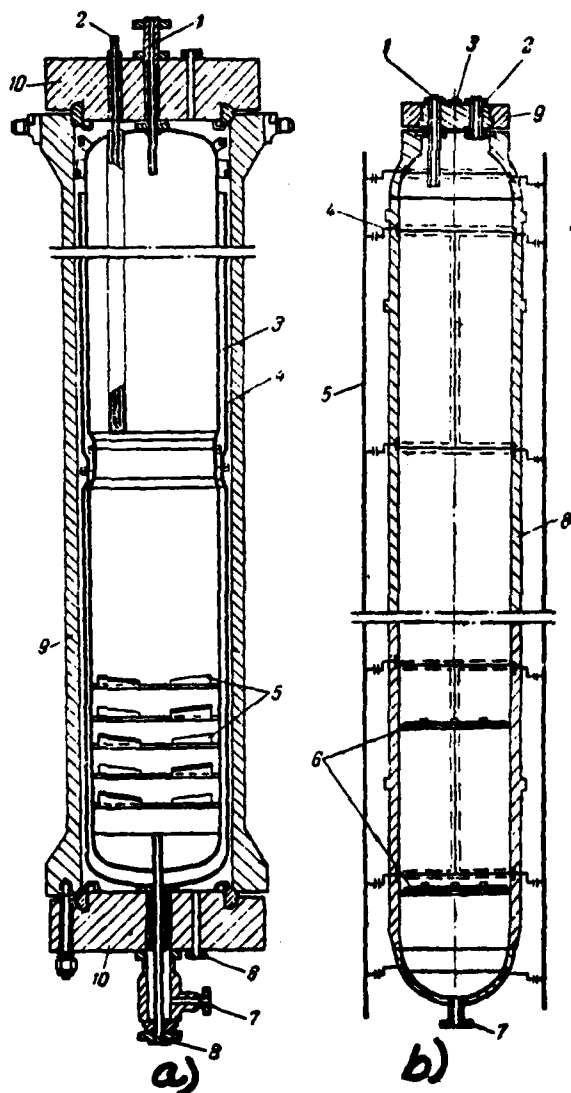


Figure II-80. Columns of Carbamide Synthesis

Key:

- a. Column with vessels
- 1. Connecting pipe for output of melt
- 2. Connecting pipe for thermocouple
- 3. Inner vessel
- 4. Outer vessel
- 5. Partitions with holes
- 6. Connecting pipe for input of fresh (protective) ammonia
- 7. Connecting pipe for input of return ammonia
- 8. Connecting pipe for input of carbon dioxide
- 9. Housing
- 10. Covers
- b. Lined column
- 1. Connecting pipe for output of melt
- 2. Connecting pipe for thermocouple
- 3. Connecting pipe for feeding melt and nitrogen
- 4. Control hole
- 5. Collector
- 6. Partitions (lattice)
- 7. Connecting pipe for input of gas-liquid mixture
- 8. Housing
- 9. Cover

Synthesis column with vessel (fig. II-80, a) for a unit with output of 100 T/day consists of high pressure housing 9 and upper and lower covers 10. Within the housing there are two vertical vessels 3 and 4 which are installed inside each other in an inverted manner. Ring gaps are formed between the housing and the vessels. The stream of liquid protective ammonia flows in them. The protective ammonia

enters through lower connecting pipe 6 into the ring space between the housing of the column and the outer vessel 4, and is lifted upwards on it. It then falls into the ring space between the outer and inner vessel 3, flows downwards and is mixed here with the return ammonia which is fed into the column through connecting pipe 7. The mixture enters the reaction zone that is demarcated by the inner vessel. Carbon dioxide is also fed here. An attachment is placed in the lower part of the column for better movement of the reaction components. It consists of several partitions 5 with holes.

The diameter of the column housing is 1.2 m, the height is 14 m. The housing is made of carbon steel, and the vessels are made of special chrome-nickel-molybdenum steel.

The volume of the column is determined by the formula:

$$V_k = V_c \tau \quad (II-40)$$

where V_k --volume of column (reaction space), m^3 ;

V_c --volume of mixture, m^3/h ;

τ --duration of reaction, h.

The lined synthesis column (fig. II-80,b) without vessels is a hollow cylindrical apparatus with spherical bottom and flat cover. With output of the unit of 250 t/day , the diameter of the column is 1.5 m, height 24 m. The volume of the reaction space of the column is 31 m^3 . High pressure housing 8 is made of carbon steel. Its inner part which comes into contact with the reaction mass is lined with chrome-nickel-molybdenum steel.

At the sites of welding the sheets of lining, there are control holes 4 over the entire height of the column. They are connected by a common collector. The hermetic sealing of the welding and the integrity of the lining are verified through these holes.

Unit of melt distillation (fig. II-81) with output of 250 t/day consists of a rectification column, heater and separator. The designs of the units of distillation of the first and second stage are similar. The difference lies only in the technological regime

of their operation. The operating regimes of the units of the first and second distillation stages are presented below:

Units	first stage	second stage
Rectification column		
pressure (gage), atm.	16-17.5	2-3
temperature of top, °C	110-120	110-120
Preheater		
pressure (gage) in pipes, atm.	16-17.5	2-3
pressure (gage) of steam in inter-pipe space, atm.	to 9	to 9
temperature of product at outlet, °C	to 160	143
Separator		
pressure (gage), atm.	16-17.5	2-3
temperature, °C	to 160	to 143
Distillation column		
pressure (gage), atm.	16-20	0.2-0.5
temperature, °C		
steam-liquid mixture after heating	110-140	-
top of column	-	to 80
bottom of column	-	to 110

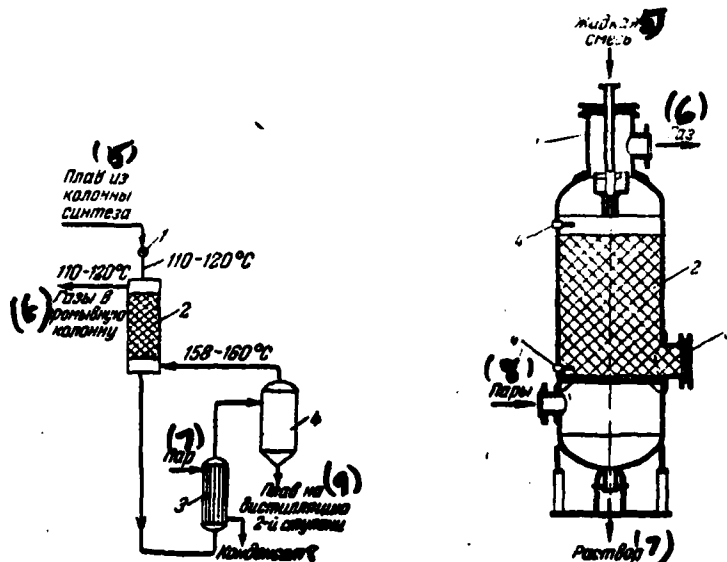


Figure II-81. Plan of Unit of First Stage Distillation

Key:

1. Throttle valve
2. Rectification column
3. Preheater
4. Separator
5. Melt from synthesis column
6. Gases to wash column

Figure II-82. Rectification Column of First and Second Stages of Distillation

Key:

1. Separating device
2. Attachment
3. Manhole
4. Connector for thermocouple

- 7. Steam
- 8. Condensate
- 9. Melt to second stage distillation

- 5. Liquid mixture
- 6. Gas
- 7. Solution
- 8. Steam

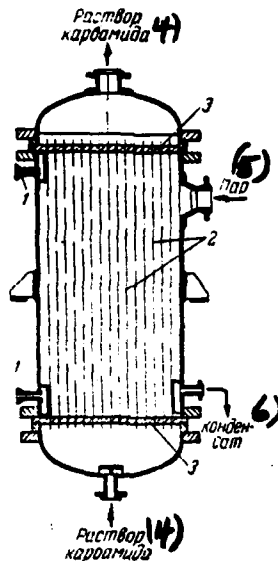


Figure II-83. Preheater of First and Second Distillation

Key:

- 1. Connection of level indicator
- 2. Heat exchange pipes
- 3. Pipe grids
- 4. Carbamide solution
- 5. Steam
- 6. Condensate

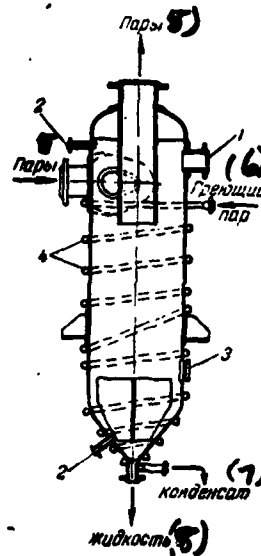


Figure II-84. Separator of First and Second Distillation Stage

Key:

- 1. Manhole
- 2. Connection of level indicator
- 3. Level gage glass
- 4. Coils
- 5. Steam
- 6. Heating steam
- 7. Condensate
- 8. Liquid

The rectification column (fig. II-82) is designed to break down ammonium carbamate and release products of breakdown and free ammonia from the carbamide solution. It is a cylindrical unit 1.4 m in diameter and 2.25 m high. It is made of chrome-nickel-molybdenum steel brand Kh17N16 M3T.

The preheater (fig. II-83) is designed to heat the melt that comes from the column of rectification. It is made in the form of a tubular heat exchanger. All of its parts that contact the melt are made of chrome-nickel-molybdenum steel. The heat exchange surface

is 170 m³.

The separator (fig. II-84) is designed to separate the steam-liquid mixture coming from the preheater into gas and liquid phases. The separator is a hollow cylinder 0.7 m in diameter and 3.03 m high with external heating. The gas-liquid mixture is fed through a connecting pipe into the apparatus tangentially. The separator is made of chrome-nickel-molybdenum steel.

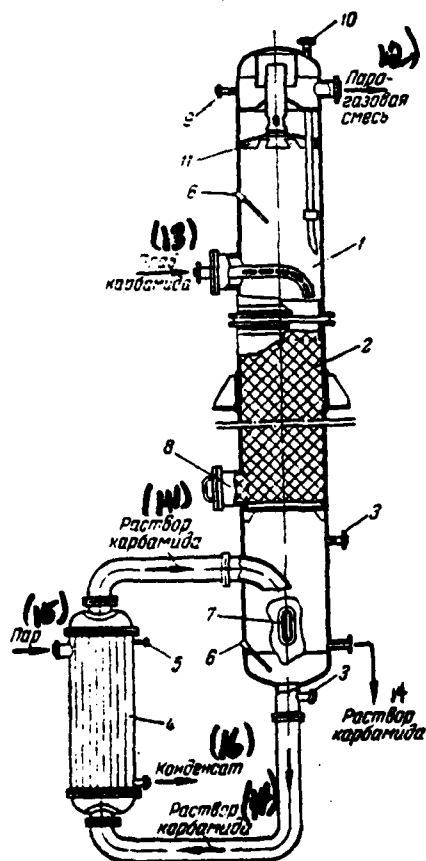


Figure II-85. Distillation Column of First Stage with Extension Preheater

Key:

1. Column
2. Attachment
3. Connection of level indicator
4. Extension preheater
5. Air blower
6. Connection for thermocouple

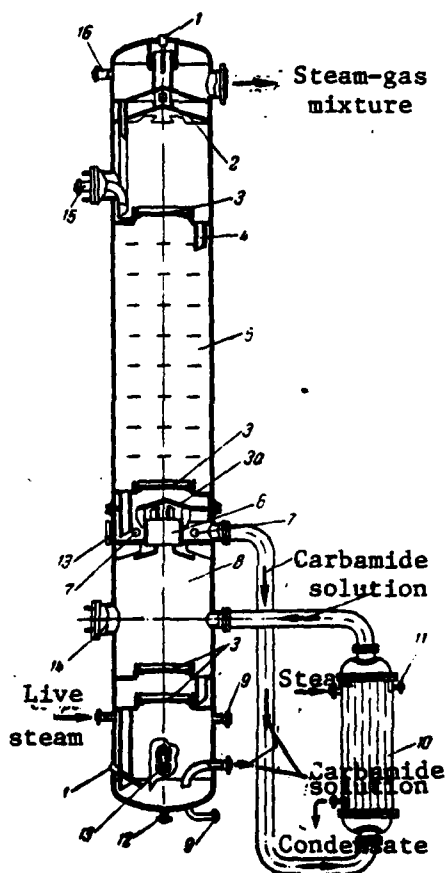


Figure II-86. Distillation Column of Second Stage with Extension Preheater

Key:

1. Connection for thermocouple
2. Separator
3. Bubble-cap plates
- 3a. Closed plate
4. Overflow pipe
5. Upper part of column

7. Level gage glass
8. Manhole
9. Connection to manometer
10. Connection to safety valve
11. Separator (spray separator)
12. Steam-gas mixture
13. Carbamide melt
14. Carbamide solution
15. Steam
16. Condensate

6. Connection sleeve
7. Connection for input of carbamide solution from first distillation stage
8. Lower part of column
9. Connection for level indicator
10. Preheater (boiler)
11. Air blower
12. Drainage connection
13. Level gage glass
14. Manhole
15. Connection for input of solution of ammonium carbonate
16. Connection to safety valve

The unit of carbamide melt distillation with output of 100 T/day consists of a vertical cylindrical column and an extension heat exchanger (preheater). The diameter of the column is 0.8 m, the height is 7.36 m.

Figure II-85 shows the unit of first stage distillation.

The housing of the column holds an attachment of height 3.16 m made of ceramic rings (50 x 50 x 5 mm). The lower part of the column is connected to the extension vertical shell-and-tube preheater. The heat exchange surface is 40 m². The steam is fed into the inter-pipe space of the preheater. The carbamide melt circulates on the pipes. The upper part of the column holds a separator device for separation of the gas from the spray of carbamide melt.

During selection of the diameter of the column, its operation in a flooding regime is checked. The limit of flooding (velocity of gas at which removal of the liquid begins) is computed from the formula*

$$\lg \left(\frac{u_0 a}{g} \cdot \frac{\rho_r \mu_a^{0.16}}{\rho_a} \right) = b - c \left(\frac{G_a}{G_r} \sqrt{\frac{\rho_r}{\rho_a}} \right)^{1/2}$$

where u_0 --linear velocity of gas (counting on the total section of the column), n/s;

a --specific surface of the attachment, m²/m³;

* Ramm, V. M. Absorptsiya gazov ["Absorption of Gases"], Izd. Khimiya 1966, p. 423.

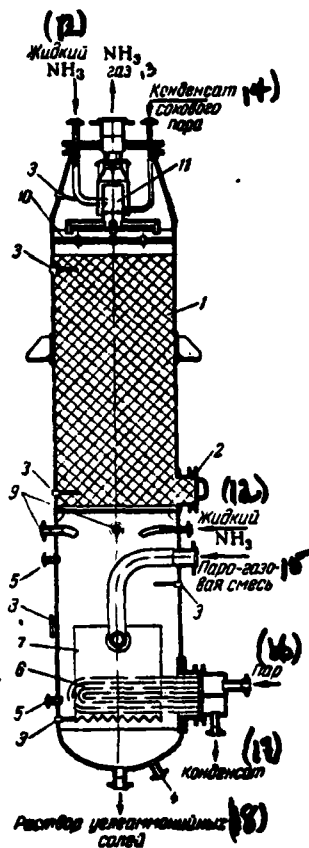


Figure II-87. Washing Column

Key:

1. Adapter
2. Manhole
3. Connection for thermocouple
4. Drainage connection
5. Connection for level regulator
6. Preheater
7. Bubbler (gas distributor)
8. Glass of level gage
9. Connection for input of solution of ammonium carbonate
10. Distributor lattice (plate)
11. Mixer
12. Liquid
13. Gas
14. Condensate of liquor vapor
15. Steam-gas mixture
16. Steam
17. Condensate
18. Solution of ammonium carbonate

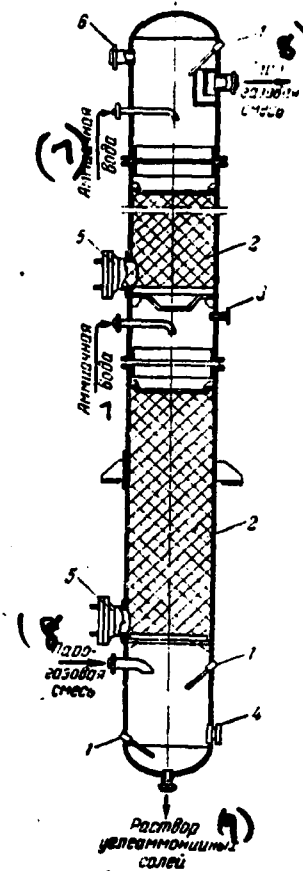


Figure II-88. Fractionation Column

Key:

1. Connection for thermocouple
2. Adapter
3. Connection for manometer
4. Glass of level gage
5. Manholes
6. Connection for safety valve
7. Ammonia water
8. Steam-gas mixture
9. Solution of ammonium carbonate

g --acceleration of gravity force, m/s^2 ;
 Σ --free volume of adapter, m^3/m^3 ;
 ρ_g, ρ_l --density of gas and liquid, kg/m^3 ;
 μ_g --viscosity of gas, cP;
 c --coefficient equal to 1.75;
 G_l, G_g --consumption of liquid and gas, $kg/(m^2 \times h)$;
 b --coefficient which depends on the shape of the adapter (for rings and wire spirals $b=0.022$, for saddle-shaped adapter $b=0.26$).

Distillation column of the second stage (fig. II-86) is also a vertical cylindrical apparatus with extension preheater (boiler).

In contrast to the first stage column, the distillation column of the second stage does not have an adapter, but has bubble-cap plates. The upper part of the column is separated from the lower part by a solid plate. This makes it possible to transmit the carbamide solution from the upper to the lower part through the extension heat exchanger in one pass.

The apparatus for purifying the ammonia of carbon dioxide in the units with output of 250 t/day is called the washing column, and in units with output of 100 t/day , fractionation columns.

The washing column (fig. II-87) is a vertical cylindrical apparatus (diameter 1.4 m, height 7 m) whose upper part is filled with an adapter, rings made of stainless steel. A heating element with bubbling device is installed in the lower part of the column. In this part, the solution of ammonium carbonate which comes from the second stage condenser absorbs about 90% of the CO_2 . In order to remove the heat of absorption, liquid ammonia is added to the lower part of the column. The remaining 10% of the CO_2 is absorbed by the concentrated ammonia water which flows from top to bottom over the adapter. The gaseous ammonia which has been purified of carbon dioxide is sent from the wash column to the condenser. The concentrated solution of ammonium carbonate is fed by pump from the lower part of the column to the synthesis column.

The column is made of chrome-nickel or chrome-nickel-molybdenum

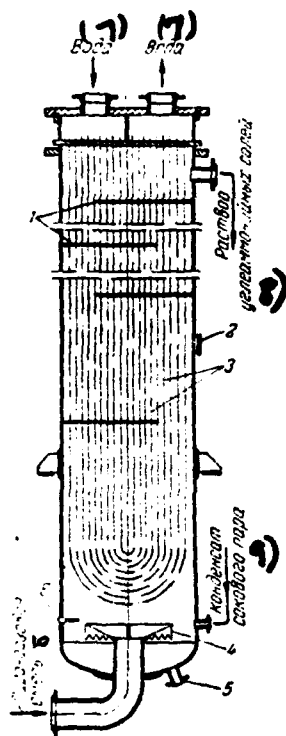


Figure II-89. Condenser of Second Stage Distillation

1. Partitions
2. Glass of level gage
3. Heat exchange pipes
4. Distributors
5. Drainage connection
6. Connection for thermocouple
7. Water
8. Ammonium carbonate solution
9. Condensate of liquor steam
10. Steam-gas mixture

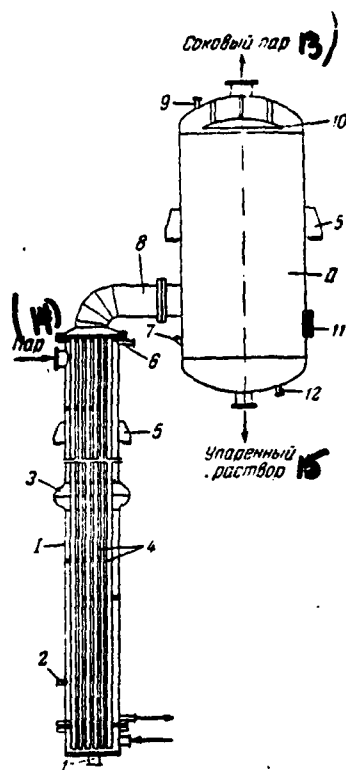


Figure II-90. Evaporator

Key:

- I. Preheater (film heat exchanger)
- II. Separator (liquor chamber)
1. Drainage connection
- 2,6. Air blowers
3. Compensator
4. Heat exchange pipes
5. Support flanges
7. Connection for thermocouple
8. Pipe for outlet of steam-gas mixture into separator
9. Connection to vacuum meter
10. Spray separator
11. Viewing glass
12. Connection for sample taking
13. Liquor vapor
14. Steam
15. Evaporated solution

steel. It operates under pressure of 16-17.5 atm., the temperature in the upper part is 45-50°C, and 92-95°C in the lower.

Fractionation column (fig. II-88) is made in the form of a vertical cylindrical apparatus with diameter of 0.8 m and height

8.26 m. The column is filled with an adapter made of porcelain rings (size 50 x 50 x 5 mm). The height of the upper layer of the adapter is 2.05 m, the lower is 2.4 m. The upper part of the column is sprinkled with ammonia water and liquid ammonia. The lower is sprinkled with liquid ammonia.

The housing of the column consists of three sheet-steel cylinders, the material of the housing is made of chrome-nickel-molybdenum steel.

The column operates under pressure of 16-20 atm.. The temperature in its upper part is up to 65°C.

The condenser of second stage distillation (fig. II-89) is designed for condensation of water vapors from gases of the second distillation stage, and absorption of ammonia and carbon dioxide by the obtained condensate with the formation of a solution of ammonium carbonate. The condenser is made of chrome-nickel-steel and is a vertical column within which a cooling element is installed with U-shaped pipes. The diameter of the housing is 1.2 m, and the high height of the tube is 4.6 m. The diameter of the pipes is 25 x 2mm and the surface of heat exchange is 260 m².

The distillation gases (steam-gas mixture) are fed into the condenser through the lower connection, pass distributor 4 and are bubbled through a layer of liquid which absorbs the ammonia and carbon dioxide. The formed solution of ammonium carbonate flows through the upper connection into the leveling vessel.

The condenser operates at gage pressure of 2-3 atm and temperature to 40°C.

The solutions are evaporated in one or two stages. The basic apparatus of the evaporation system is the evaporator (fig. II-90). It consists of preheater I and separator II. The solution enters the lower part of the tubular preheater where heating and boiling of the solution occur. The concentrated (evaporated) solution is separated from the vapors in the separator, flows downwards and

enters the second evaporation stage, from which it is sent for granulation. The liquor vapor is removed from the separators into the condenser.

The evaporator is made of steel brand Kh18N9T. The heat exchange surface of the preheater of first stage evaporation is 80 m^2 , of the preheater of the second stage, 10 m^2 .

The evaporator for the unit with output of 100 t/day has a preheater with heat exchange surface of 32 m^2 .

Control and Automation of Carbamide Production

Production of carbamide is a complicated set of individual technological processes that are strictly interlinked by material and energy flows. This process is controlled remotely from a central point at which all the instruments which regulate and indicate the load of the unit and the main parameters of the technological process installed. For convenience of observing the technological processes, a mimic flowsheet is placed above the panels of the board. It has lamps which signal emergenc deviations of the process parameters.

The means of automation and control of production are instruments and regulators of the pneumatic aggregate unified automatic control system and other instruments and regulators which are series produced by domestic industry. Each aggregate system consists of regulating and auxiliary blocks, as well as secondary recording and indicating instruments.

The assembly for liquid ammonia intake regulates the level of liquid in the buffer vessel. A wire gage of the IUVTs type is used as the sensor. It is installed directly on the unit. The assigned level in the vessel is maintained by regulating the supply of liquid ammonia from the plant network.

Pressure is also controlled and regulated in the reception buffer vessel. The assigned pressure is maintained with the help

of so-called nitrogen respiration under the influence of a regulating valve in a set with 4RB-32A regulator and recording secondary instrument of type 3RL-29V.

Before liquid ammonia is fed into the synthesis column, its temperature is regulated. Thermocouple TKhK-284 and a secondary EPD instrument with regulating valve installed on the line for feeding steam into the evaporator of ammonia are included in the temperature regulator set.

The assembly for intake and compression of the carbon dioxide has, in addition to control and measuring instruments and automatic regulators, a regulator for the $\text{CO}_2:\text{O}_2$ ratio. It is maintained and corrected according to the readings of the automatic gas analyzer for the content of oxygen that is introduced into the carbon dioxide in order to reduce corrosion of the equipment.

The column of carbamide synthesis regulates the pressure with the help of a sensor, a manometer of the MPD type and a secondary 3RL-29V instrument with 4RB-32A regulator. Constant temperature in the synthesis column with the assigned ratio of reagents is guaranteed by stabilization of the temperature of the supplied liquid ammonia.

The first stage distillation assembly uses a regulating device installed on the line of steam supply into the preheater to maintain a constant temperature. The assigned pressure in this assembly is guaranteed by a regulator that is installed at the outlet for inert gases from the assembly of ammonia condensation.

The liquid level in the separator is regulated with the help of a device and an actuator, a regulating valve which is installed on the line for removing the carbamide solution from the separator.

In the second distillation stage, as in the first stage, the required pressure is maintained by a regulator that is installed on the line for removal of gases from the second stage condenser. Constant temperature of the solution and the assigned level of liquid in the separator are also guaranteed.

In the assembly for carbamide solution reprocessing, its supply for evaporation is regulated. For this purpose, a rotametric consumption gage of the type REV, secondary instrument of the EPID type with regulating device and regulating valve are used. A constant temperature is maintained by changing the supply of steam into the preheater with the help of an EPD potentiometer and TKhK-284 thermocouples.

The assigned temperatures, pressure and levels are maintained in the assemblies of absorption and desorption of the discharge gases, collection of solution of carbamide and condensate.

The assembly for purification of the return ammonia of carbon dioxide to create the optimal technological regime that promotes more complete separation of NH_3 from CO_2 provides for temperature regulation (in the assigned limits) over the height of the washing column. The temperature regime in the washing column is stabilized by regulating the amount of liquid ammonia that is fed for sprinkling. The total quantity of sprinkling ammonia is separated into two streams.

The plans for liquid recycling stipulate regulation of the liquid level in the washing column. In the carbamate pumps of the firm "Vorktington" the actuator to regulate the system is a hydraulic coupling which correspondingly changes the number of piston strokes of the pump, and consequently, its output.

7. Liquid Nitrogen Fertilizers¹⁰¹⁻¹⁰⁵

The following are used as liquid nitrogen fertilizers: ammonia water (aqueous ammonia), ammoniates, as well as liquid (anhydrous) ammonia¹⁰⁶ which is used fairly widely in agriculture of certain foreign countries (for example, the United States) as a highly concentrated fertilizer (82.5% N). The physical-chemical properties of ammonia are examined in volume I of the Reference Book for the Nitrogen Industry Worker (p. 25 and following).

Ammonia Water

According to GOST 9-67, two brands of ammonia water are manufactured. Product of brand A is designed for agriculture, and brand B for industry. Ammonia water of both types is divided into first and second grades. Ammonia water of the first grade must contain no less than 25% NH₃, and the product of the second grade, no less than 22% NH₃.

The density of 25% ammonia water at 20°C is 0.907 kg/m³, and its freezing point is -56°C. Ammonia water with 22% density freezes roughly at -33°C.

The pressure of ammonia vapors above its aqueous solutions is presented in table II-70.

For comparison, below is the pressure p of NH₃ vapors above liquid ammonia¹⁰²:

t, °C	0	10	20	40	50	70
p, atm.	4.24	6.08	8.46	15.34	20.00	32.69

TABLE II-70. PRESSURE OF NH₃ VAPORS ABOVE AMMONIA WATER (in mm Hg)

(1) Концентрация NH ₃ вес. %	(2) Температура, °C						
	0	10	20	30	40	50	60
5	14,61	27,06	51,78	81,0	131,8	207,5	316,5
10	28,79	51,42	87,8	143,9	227,5	348,0	517,2
15	49,55	85,95	142,9	228,7	353,5	530,2	772,5
20	81,75	138,8	224,7	351,6	543,0	787,5	1123,5
25	127,5	209,5	335,5	515,3	766,9	1109,0	1566,0

Key:

1. Concentration of NH₃, weight. %
2. Temperature, °C

The total pressure of vapors P (ammonia and water) above 20 and 25% ammonia water at 20°C is presented below (in atm.)

Concentration of NH ₃ , %	20	25
P, atm.	0.2957	0.4414

The solubility of ammonia in water under pressure is shown in table II-71.

TABLE II-71. SOLUBILITY OF AMMONIA IN WATER (IN WGT.%) AT INCREASED PRESSURE^{50, 71, 167}

(1) Избыточное давление атм	(2) Температура, °C										
	-30	-20	-10	0	10	20	30	40	60	80	100
0.2	43.1	36.4	30.6	25.3	20.2	15.5	11.0	6.8	—	—	—
0.5	56.7	47.5	40.6	34.7	29.4	22.4	19.7	15.2	7.1	—	—
1.0	85.6	61.5	51.2	43.8	37.8	32.5	22.5	20.8	14.0	6.2	—
1.5	—	81.3	59.9	50.3	44.3	38.4	33.2	28.6	19.8	16.6	3.3
2.0	—	—	70.1	56.6	48.3	41.8	36.3	31.4	22.5	14.1	6.7
2.5	—	—	86.8	62.7	52.6	45.4	39.6	34.5	25.5	17.0	9.1
3.0	—	—	—	70.2	56.8	48.7	42.4	37.1	28.0	19.5	11.5
4.0	—	—	—	93.0	65.6	54.7	47.3	41.4	31.8	23.4	15.4
5.0	—	—	—	—	79.0	61.6	52.0	45.3	35.0	26.5	18.6
6.0	—	—	—	—	97.1	68.1	56.4	49.0	37.9	29.2	21.4
8.0	—	—	—	—	—	93.5	67.0	56.0	42.9	33.6	25.7
10.0	—	—	—	—	—	—	82.4	63.0	47.3	37.2	29.0

Key:

1. Gage pressure, atm.
2. Temperature, °C

The flowsheet for the production of ammonia water¹⁰⁸ is shown in fig. II-91.

The raw material in this process is gaseous ammonia that is supplied at gage pressure of 1 atm. from the shop of NH₃ synthesis (through a distributor panel) into column 3 of plate type with bubble caps. Gaseous ammonia also comes here from the liquid ammonia warehouse. This ammonia is released when poured into tanks.

The lower part of column 3 is a tubular heat exchanger that is designed to remove a considerable part of the heat of dissolving ammonia in water. Cooling water moves along the heat exchange pipes. An aqueous solution of ammonia circulates in the intertube space. Gaseous ammonia is bubbled through the layer, simultaneously dissolving in the liquid.

The residue of unabsorbed ammonia enters the upper part of the column where it passes through the bubble-cap plates. There are

coils on the plates in which cooling water circulates. In order to avoid clogging of the column with salts, the ammonia is absorbed by chemically purified water.

Production 25% ammonia water comes from the column into collector 4. From here it is pumped into storage tank 5. The ammonia water is fed from here by pump on flexible hoses to railroad or truck tanks in which it is shipped to the customers.

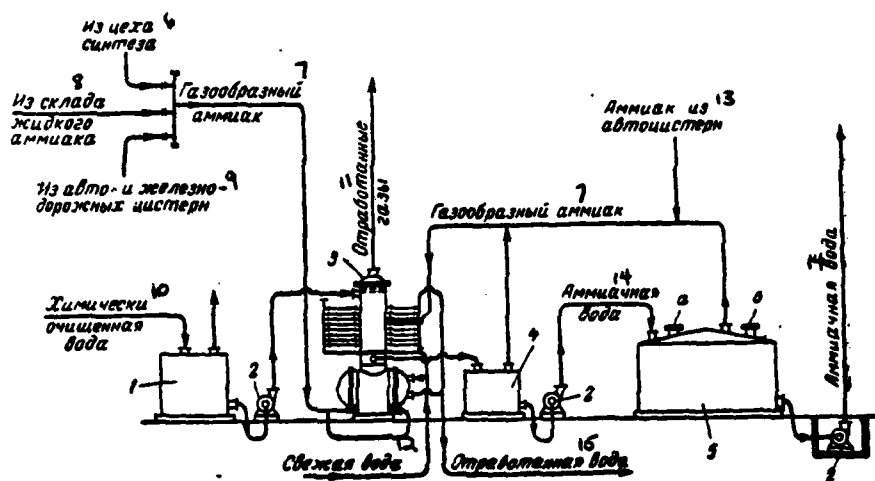


Figure II-91. Flowsheet of Ammonia Water Production

Key:

1. Collector of chemically purified water
2. Centrifugal pumps
3. Column to produce ammonia water
4. Intermediate collector
5. Storage tank
- a. Breather valve with fire-imperder
- b. Safety valve
6. From synthesis shop
7. Gaseous ammonia
8. From liquid ammonia warehouse
9. From truck and railroad tank cars
10. Chemically purified water
11. Spent gases
12. Fresh water
13. Ammonia from truck tanks
14. Ammonia water
15. Spent water

The gaseous ammonia that is released when poured into the tank as well as from the storage tank when ammonia water is stored

for a long time in them, is sent to column 3 for absorption by water.

The warehouse for ammonia water is located near the plant railroad lines. A platform for filling the tank cars is built next to them.

Ammoniates

With joint or separate dissolving in ammonia water of appropriate quantities of ammonium nitrate, potassium nitrate, carbamide, etc., solutions are obtained which are called ammoniates¹⁰² (solid ammoniates are formed during the interaction of certain solid salts with gaseous or liquid ammonia and are complex compounds of crystalline structure).

Ammoniates in the form of solutions are light liquids (a yellowish hue is also permitted) whose density depends on their composition. It fluctuates in limits of 0.9-1.25 g/cm³. The pressure of vapors above ammoniates is considerably lower than the pressure of vapors above liquid ammonia.

The composition of ammoniates that are obtained on the basis of ammonium nitrate corresponds to the formula $\text{NH}_4\text{NO}_3 \times n\text{NH}_3 \times m\text{H}_2\text{O}$. Ammoniates based on potassium nitrate and ammonium nitrate have the following formula $\text{Ca}(\text{NO}_3)_2 \times \text{NH}_4\text{NO}_3 \times n\text{NH}_3 \times m\text{H}_2\text{O}$.

Agricultural practice uses as liquid fertilizers carbon ammoniates, a mixture of aqueous solutions of ammonium carbonate, ammonia and carbamide or ammonium nitrate.

The solubility of certain nitrates in water, ammonia water and liquid ammonia is given in table II-72.

The solubility of sodium nitrate in aqueous solutions of ammonia at 0°C is presented below (in weight.%):

NH ₃	NaNO ₃	NH ₃	NaNO ₃
0	41.41	60	39.5
10	36.0	70	43.0
20	31.5	80	47.0
28	30.0	90	52.0
40	33.0	100	55.0
50	36.5		

TABLE II-72. SOLUBILITY OF NITRATES

Соль (1)	(2) Растворимость, г/1000 г			
	(3) ВОДЫ	(4) 75%-НОЙ АММИАЧНОЙ ВОДЫ	(5) 85%-НОЙ АММИАЧНОЙ ВОДЫ	(6) 100%-НОГО ЖИДКОГО АММИАКА
(7) При 0°C				
NaNO ₃	707	736.9	828.7	1274
Ca(NO ₃) ₂	1010	759.3	719.3	821.7
KNO ₃	132.5	135.3	106.1	105.2
(7) При 25°C				
NH ₄ NO ₃	2090	—	—	3587.0
NaNO ₃	927	—	—	986.7
Ca(NO ₃) ₂	1380	—	—	803.5
KNO ₃	382.5	—	—	103.4

Key:

1. Salt
2. Solubility, g/1000 g
3. Water
4. 75% ammonia water
5. 85% ammonia water
6. 100% liquid ammonia
7. At

The solubility of sodium nitrate in aqueous solutions of ammonia at 15°C is presented below (in weight.%):

Density

	NH ₃	NaNO ₃
1.258	7.3	39.8
1.233	9.0	38.7
1.212	10.5	37.8

The molar heats of dissolving nitrates of sodium and ammonia in liquid ammonia and in water have the following values (in cal/mole):

Salt	In ammonia	In water
NaNO ₃	3600	-5000
NH ₄ NO ₃	5700	-6330

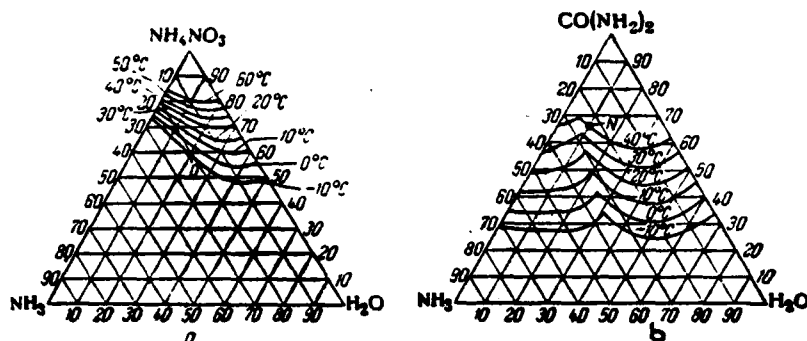


Figure II-92. Diagrams of Solubility

Key:

- a. In system $\text{NH}_4\text{NO}_3\text{-NH}_3\text{-H}_2\text{O}$
- b. In system $\text{CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_2\text{O}$

The diagrams of solubility of the triple systems $\text{NH}_4\text{NO}_3\text{-NH}_3\text{-H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_2\text{O}$ are presented in fig. II-92. The apex of the equilateral triangles corresponds to 100% content of each of the components in the system. The length of the side of the triangle is assumed to be 100%. The points that lie on the sides of the triangle correspond to the composition of the mixture of two components in the system, for example, 20% NH_4NO_3 and 80% NH_3 , or 30% NH_4NO_3 and 70% H_2O , or 40% H_2O and 60% NH_3 , etc. The straight lines that are parallel to the sides of the triangle separate segments on its sides. Their sum is equal to the side of the triangle. Consequently, the points that are located inside the triangle correspond to the composition of mixtures of three components of the system whose total concentration equals 100%. Thus, point O (fig. II-92 a) which lies on the isotherm of solubility at -10°C , corresponds to a mixture of 20% H_2O , 60% NH_4NO_3 and 20% NH_3 . At point N (fig. II-92, b) located on the isotherm of solubility at 40°C , the triple mixture contains 10% H_2O , 65% $\text{CO}(\text{NH}_2)_2$ and 25% NH_3 .

Tables II-73 and II-74 present data on the joint solubility of in the quadruple system $\text{NH}_4\text{-NO}_3\text{-CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_2\text{O}$.

Ammoniates can be produced on a unit whose flowsheet is illustrated in fig. II-93.

A certain quantity of water is poured into tank 2. Gaseous

TABLE II-73. JOINT SOLUBILITY IN SYSTEM¹⁰⁹
 $\text{NH}_4\text{NO}_3\text{-CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_2\text{O}$ AT 0°C

(1) Состав насыщенного раствора, вес. %		(2) Твердая фаза
NH_4NO_3	$\text{CO}(\text{NH}_2)_2$	
(3) При $\text{NH}_3 : (\text{NH}_3 + \text{H}_2\text{O}) = 0,2$		
6.0	34.5	} $\text{CO}(\text{NH}_2)_2$
9.97	35.5	
20.4	36.5	
35.25	35.3	
42.0	33.85	
47.8	34.0	} $\text{NH}_4\text{NO}_3 + \text{CO}(\text{NH}_2)_2$
53.0	6.75	
52.05	16.75	} NH_4NO_3
51.0	22.9	
(3) При $\text{NH}_3 : (\text{NH}_3 + \text{H}_2\text{O}) = 0,3$		
5.0	33.7	} $\text{CO}(\text{NH}_2)_2$
8.97	33.8	
19.2	34.8	
33.9	34.3	
41.6	33.6	
50.2	32.5	} $\text{CO}(\text{NH}_2)_2 + \text{NH}_4\text{NO}_3$
55.5	5.75	
53.97	14.55	} NH_4NO_3
52.85	20.15	
(3) При $\text{NH}_3 : (\text{NH}_3 + \text{H}_2\text{O}) = 0,4$		
3.98	32.50	} $\text{CO}(\text{NH}_2)_2$
7.97	33.1	
18.00	34.0	
32.50	33.40	
40.20	33.00	
46.54	27.40	} $\text{CO}(\text{NH}_2)_2 \cdot 0.11\text{NH}_3 + \text{NH}_4\text{NO}_3$
52.27	26.14	
58.05	4.75	} NH_4NO_3
56.15	12.35	
55.0	17.4	
(3) При $\text{NH}_3 : (\text{NH}_3 + \text{H}_2\text{O}) = 0,5$		
2.97	35.52	} $\text{CO}(\text{NH}_2)_2$
6.98	36.3	
16.98	35.43	
29.34	32.88	
37.30	32.50	
47.50	24.05	} $\text{CO}(\text{NH}_2)_2 \cdot 0.25\text{NH}_3 + \text{NH}_4\text{NO}_3$
55.40	23.25	
61.50	3.75	} NH_4NO_3
59.43	10.10	
58.0	14.85	

- Key:
1. Composition of saturated solution, weight, %
 2. Solid phase
 3. At

ammonia is passed through the ammonia distributor located in the lower part of the tank in order to produce 10-15% ammonia water. When ammonia is absorbed, the solution in the tank circulates with the help of centrifugal pump 3. When the concentration of ammonia

TABLE II-74. JOINT SOLUBILITY IN SYSTEM¹⁰⁹
OF $\text{NH}_4\text{NO}_3\text{-CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_2\text{O}$ at 30°C.

(1) Состав насыщенного раствора, вес. %		(2) Весовое соотношение $\text{NH}_3 : (\text{NH}_3 + \text{H}_2\text{O})$ в растворе	(3) Твердая фаза
NH_4NO_3	$\text{CO}(\text{NH}_2)_2$		
36.8	46.8	0.4	$\text{CO}(\text{NH}_2)_2$
34.8	46.1	0.501	
31.7	47.1	0.538	
39.9	49.5	0.581	
31.6	46.6	0.610	
31.8	46.6	0.600	
53.1	43.0	0.495	$\text{CO}(\text{NH}_2)_2 + \text{NH}_4\text{NO}_3$
53.1	43.2	0.498	
53.2	43.4	0.600	
53.4	43.5	0.701	
59.8	28.1	0.380	NH_4NO_3
61.1	25.1	0.457	
61.6	25.5	0.490	
57.0	37.9	0.686	
68.8	13.6	0.740	

Key:

1. Composition of saturated solution, weight. %
2. Weight ratio $\text{NH}_3 : (\text{NH}_3 + \text{H}_2\text{O})$ in solution
3. Solid phase

TABLE II-75. COMPOSITION AND CERTAIN PHYSICAL-CHEMICAL PROPERTIES OF CARBON AMMONIATES¹⁰⁹

$\text{CO}(\text{NH}_2)_2$	(1) Состав, вес. %				(2) Общее содержание азота, вес. %	(3) Общее давление паров мм рт. ст.				(5) Влажность при 20°C, см.кв.	(6) Плотность при 20°C, г/см ³	(7) Температура выпадения твердой фазы, °C
	NH_4NO_3	NH_3	CO_2	H_2O		(4) при 10°C	(4) при 20°C	(4) при 30°C	(4) при 40°C			
	—	19.94	12.51	15.04		52.51	17.28	220	234			
—	29.20	10.94	12.63	47.23	19.23	200	218	241	271	2.57	1.121	-19.7
22.75	—	10.22	12.12	54.91	19.06	136	154	172	191	—	1.15	-15.2
24.04	—	9.18	10.74	56.04	18.77	144	156	173	194	2.58	1.142	-15.4
19.90	—	11.61	11.38	57.11	18.84	139	157	185	223	2.55	1.127	-24.5

Key:

1. Composition, weight. %
2. Total content of nitrogen, weight. %
3. Total vapor pressure, mm Hg
4. At
5. Viscosity at 20°C, cP
6. Density at 20°C, g/cm³
7. Temperature of precipitation of solid phase, °C

TABLE II-76. SOLUBILITY OF AMMONIUM CARBONATE IN WATER

(1) Температура, °C	(2) Состав насыщенного раствора, вес. %		(3) Твердая фаза
	NH ₃	CO ₂	
0	18.62	22.77	(NH ₄) ₂ CO ₃ + NH ₄ HCO ₃
10	19.93	23.77	
20	20.24	24.81	
30	20.41	25.77	

Key:

1. Temperature, °C
2. Composition of saturated solution, weight. %
3. Solid phase

TABLE II-77. JOINT SOLUBILITY IN SYSTEM¹⁰⁹ CO(NH₂)₂-NH₃-CO₂-H₂O AT 0°C

(1) Состав насыщенного раствора, вес. %				(2) Общее содержание азота, вес. %	(3) Твердая фаза	
CO(NH ₂) ₂	NH ₃	CO ₂	H ₂ O			
(4) При 0°C						
—	18.62	22.77	58.61	15.33	(4) То же + CO(NH ₂) ₂	
9.08	18.83	20.63	53.46	18.09		
17.43	14.46	17.81	50.30	20.03		
23.74	12.59	15.35	48.32	21.45		
27.69	10.51	12.73	49.07	21.58		
29.19	9.25	11.54	50.02	20.64		
31.41	7.85	9.72	51.02	21.11		
33.45	5.25	6.52	54.78	19.93		
(4) При 10°C						
45.62	—	—	54.38	21.27		(4) То же + + (NH ₄) ₂ CO ₃ + + NH ₄ HCO ₃
40.28	4.60	5.76	49.36	22.57		
36.43	7.91	9.12	46.64	23.41		
34.29	9.83	11.86	44.02	24.08		
33.3	10.82	13.25	42.63	24.43		
27.17	15.97	18.35	38.51	25.72		
26.85	16.15	18.44	38.56	25.82		
24.86	15.21	17.80	42.13	24.10		
23.01	15.60	18.25	43.14	23.58		
20.62	15.86	19.24	44.28	22.67		
18.99	17.16	19.78	46.09	22.05		
8.3	18.77	21.93	51.0	19.33		
—	19.93	23.77	56.30	16.41		
(4) При 20°C						
—	20.24	24.31	55.45	16.6	(5) Состав не определялся	
6.20	18.88	23.50	51.42	18.39		
12.72	18.25	22.20	46.83	20.95		
19.50	16.94	20.58	42.98	23.06		
26.53	15.80	19.24	38.43	25.43		
34.28	12.48	15.38	37.86	26.35		
38.04	10.87	13.57	37.52	28.79		
43.4	6.73	8.28	41.59	25.92		

Key:

1. Composition of saturated solution, weight. %
2. Total content of nitrogen, weight. %
3. Solid phase

4. The same
5. Composition not defined
6. At

TABLE II-78. JOINT SOLUBILITY IN SYSTEM¹⁰⁹ OF
 $\text{NH}_4\text{NO}_3\text{-NH}_3\text{-CO}_2\text{-H}_2\text{O}$

(1) Состав насыщенного раствора, вес. %				(2) Общее содержание азота, вес. %	(1) Состав насыщенного раствора, вес. %				(2) Общее содержание азота, вес. %
NH_4NO_3	NH_3	CO_2	H_2O		NH_4NO_3	NH_3	CO_2	H_2O	
(3) При 0 °C					(3) При 20 °C				
—	18.62	22.77	58.61	15.27	—	20.21	24.31	55.45	16.67
11.34	16.66	20.77	51.23	17.63	4.93	19.72	23.40	51.95	17.90
19.32	15.50	19.18	46.00	19.47	11.25	19.17	22.51	47.07	19.73
28.37	14.94	17.70	38.99	22.18	18.48	17.95	21.25	42.32	21.25
35.50	11.23	13.45	39.82	21.64	24.70	16.31	19.23	36.76	22.07
38.18	9.73	12.61	39.48	21.65	34.75	12.66	15.20	37.39	22.58
43.66	6.83	8.66	40.85	20.88	41.11	11.81	14.66	32.42	24.07
					43.33	11.68	14.50	30.49	24.75
					54.18	7.75	9.58	28.49	25.32
					56.90	5.28	6.87	30.95	24.25

Key:

1. Composition of saturated solution, weight. %
2. Total content of nitrogen, weight. %
3. At

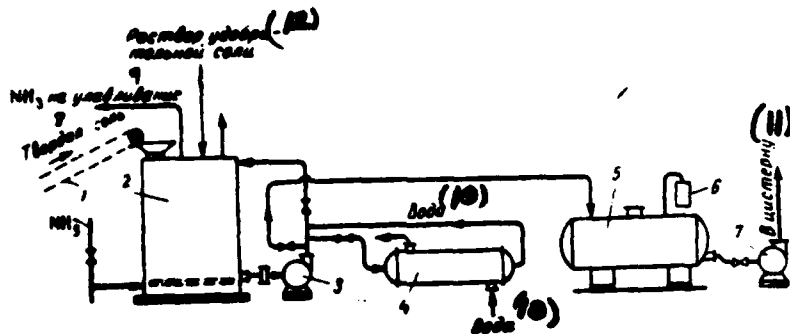


Figure II-93. Flowsheet for Production of Ammoniates

Key:

1. Conveyer
2. Tank for preparation of ammoniate
- 3, 7. Pumps
4. Water cooler
5. Storage tank of ammoniate
6. Hydraulic gate
8. Solid salt
9. To recovery
10. Water
11. To tank car
12. Solution of fertilizer salt

water reaches 10-15%, hot 75-82% solution of ammonium nitrate is fed into the tank (from the ITN units) ^{R.P. 136} The process of ammoniate formation during the interaction of a solution of ammonium nitrate and ammonia is accompanied by the release of heat. The removal of this heat is done when the solution circulates between tank 2 and water cooler 4. The temperature of the circulating solution is maintained in limits of 20-25°C. The unreacted ammonia is sent to a scrubber for recovery.

When the composition of the circulating solution corresponds to the required composition of the finished ammoniate, it is pumped into storage tank 5, from which it is sent by pump into the truck tank cars and then shipped to the distribution points.

If ammoniate is produced from a mixture of ammonium and potassium nitrate, then an appropriate quantity of potassium nitrate is simultaneously loaded into tank 2 with the ammonium nitrate in the form of a dry salt or 75-80% solution.

All the equipment that is used to produce ammoniates on the basis of ammonium nitrate is made of aluminum or stainless steel.

In studying the properties of ammoniates of varying composition it was established that ammoniates based on ammonium nitrate cause more intensive corrosion of steel than ammoniates which contain, in addition to ammonium nitrate, potassium nitrate. It is therefore expedient to use ammoniates of roughly the following composition (in %):

NH ₃	20	Ca(NO ₃) ₂	27.7
NH ₄ NO ₃	30	H ₂ O	22.3

Ammoniate of this composition contains 31.9% nitrogen. The density at 20°C equals 1.25 g/cm³. The vapor pressure at 20-30°C is roughly 1 atm.

Ammoniates are more concentrated liquid nitrogen fertilizers than ammonia water. They are especially necessary for ammoniation of superphosphates and fertilizer mixtures which makes it possible to improve their physical properties and agrochemical effectiveness.

TABLE II-79. AMMONIATES BASED ON AMMONIUM NITRATE AND CARBAMIDE¹⁰⁹

Состав, вес. % (1)				Содержание азота % (2)		Температура выпадения твердой фазы °C (5)	Плотность г/см ³ (7)
NH ₄ NO ₃	CO(NH ₂) ₂	NH ₃	H ₂ O	общее (3)	амидного (4)		
45.1	15.2	20.1	19.6	39.4	7.1	-32.1	} От 1.07 до 1.12
40.1	15.1	22.6	22.2	39.68	7.04	-36.2	
40.3	20.0	20.1	19.6	40.0	9.3	-28.6	
50.0	10.0	20.0	20.0	38.7	4.7	-28.3	

Key:

1. Composition, weight. %
2. Nitrogen content, %
3. Total
4. Amide
5. Temperature of precipitation of solid phase, °C
6. Density, g/cm³
7. From 1.07 to 1.12

TABLE II-80. AMMONIATES BASED ON AMMONIA AND POTASSIUM NITRATE²

Показатели (1)	Марки аммианатов (2)		
	A	B	C
(3) Состав, вес. %			
NH ₃	14.17	23-28	18-20
Ca(NO ₃) ₂	—	—	25-28
NH ₄ NO ₃	64-67	53-56	27-30
H ₂ O	22-18	24-18	30-22
(4) Содержание азота, вес. %	34-37.5	37.5-41	30.5-31.6
(5) Температура выпадения твердой фазы, °C	9	-25	-35
(6) Избыточное давление паров (NH ₃ +H ₂ O) при 40 °C, атм	0.1	1.1	0.1

Key:

1. Indicators
2. Brands of ammoniates
3. Composition, weight. %
4. Content of nitrogen, weight. %
5. Temperature of precipitation of solid phase, °C
6. Gage pressure of vapors (NH₃+H₂O) at 40 °C, atm.

Note: Ammoniate of brand A is intended for use at warm season of the year.

Among these ammoniates one can include ammoniates based on ammonium nitrate and carbamide (table II-79), as well as based on ammonium and potassium nitrate (table II-80).

Information regarding ammoniates used in the United States is presented in tables II-81 and II-82.

TABLE II-81. AMMONIATES BASED ON AMMONIUM NITRATE AND CARBAMIDE USED IN THE UNITED STATES^{110,111}

(1) Марки аммиакатов	(2) Состав, вес. %				(3) Содержание азота, вес. %				(8) Плотность при 15.5 °C, г/см ³	(9) Избыточное давление паров при 40 °C, атм	(10) Температура выпадения твердой фазы, °C
	NH ₄ NO ₃	CO(NH ₂) ₂	NH ₃	H ₂ O	(4) общее	(5) в нитратной форме	(6) в амидной форме	(7) в аммиачной форме			

(11)
На основе аммиачной селитры

6	60	—	34	6.0	49.0	10.50	—	38.50	1.042	3.5	-46.6
3	55.5	—	26	18.5	40.8	9.62	—	31.18	1.079	1.2	-25
2A	65.0	—	21.7	13.3	40.6	11.36	—	29.24	1.142	0.7	-5
4	66.8	—	16.6	16.6	37.0	11.65	—	25.35	1.182	0.07	+9

(12)
На основе карбамида

A	—	32.5	36.8	24.8	45.5	—	15.1	30.4	0.99	4.8	-15
B	—	43.3	30.5	17.6	45.5	—	20.2	25.3	1.06	3.8	+1
C	—	26.5	30.0	38.6	37.0	—	12.3	24.7	1.0	1.54	-14.4
D	—	35.3	25.0	32.8	37.0	—	16.4	20.6	1.05	1.26	} +1
5	—	43.1	30.6	26.3	45.3	—	20.1	25.2	1.05	1.79	
37 (13)	—	35.3	25.0	24.8	37.1	—	9.1	20.6	1.08	1.6	} +1
Жидкий аммиак	—	—	99.9	—	82.2	—	—	82.2	0.618	14.8	
Аммиачная вода (14) 30%-ная	—	—	30	70	24.6	—	—	24.6	0.895	0.77	-80

Key:

- Brands of ammoniates
- Composition, weight. %
- Nitrogen content, weight. %
- Total
- In nitrate form
- In amide form
- In ammonia form
- Density at 15.5°C, g/cm³
- Gage pressure of vapors at 40°C, atm.
- Temperature of precipitation of solid phase, °C
- Based on ammonium nitrate
- Based on carbamide
- Liquid ammonia
- Ammonia water, 30%

Note: Ammoniates based on carbamide, with the exception of brand 5 product, contain ammonium carbamates.

Liquid Complex Fertilizers¹¹²⁻¹¹⁴

In recent years a number of countries have started to manufacture liquid fertilizers that contain two or three nutrient elements (N, P, K). Often their composition includes trace elements, herbicides and insecticides. The additives that can be separated from

TABLE II-82. CERTAIN CARBAMIDE-AMMONIA LIQUID FERTILIZERS USED IN THE UNITED STATES¹¹¹

(1) Содержание азота всех. %	(2) Состав, вес. %				(3) Плотность при 15° С г. см ³	(4) Избыточное давление паров при 40° С атм	(5) Температура выпадения твердой фазы °С
	NH ₃	H ₂ O	NH ₄ NO ₃	CO(NH ₂) ₂			
45.5	36.8	23.3	—	32.5	0.90	4.5	-15
45.5	30.5	16.2	—	43.3	1.06	3.5	1.4
37.0	30.0	37.3	—	26.5	1.0	1.4	-14
37.0	25.0	32.5	—	35.3	1.05	1.1	1.1
37.1	25.0	23.3	—	35.3	1.09	1.4	1.1
45.1	36.8	30.7	—	32.5	0.93	4.0	-9
45.3	30.6	26.3	—	43.1	0.97	3.4	7.9
46.0	37.3	29.8	—	32.9	0.93	4.9	-17
46.0	31.1	25.1	—	43.8	0.97	4.2	5
44.4	24.5	9.5	56.0	10.0	1.11	1.5	-26
44.4	25.0	10.0	55.0	10.0	1.11	1.5	-29
41.0	19.0	12.0	58.0	11.0	1.16	0.7	-14
44.4	26.0	12.0	50.0	12.0	1.08	1.7	-22
49.0	33.0	8.9	45.1	13.0	1.03	3.6	-27

Key:

1. Nitrogen content, weight. %
2. Composition, weight. %₃
3. Density at 15°C, g/cm³
4. Gage pressure of vapors at 40°C, atm.
5. Temperature of precipitation of solid phase, °C

the solution while standing should be added to the solution before it is put into the soil.

Extraction or thermal phosphoric acid, anhydrous ammonia or its aqueous solution and potassium chloride are used most often as the original raw material. Sometimes instead of the acid and ammonia, mono- and diammonium phosphate are used. The concentration of nutrients (N, P₂O₅, K₂O) in these liquid fertilizers reaches 26-28% and more.

Triple fertilizers are used, for example, with ratios of N:P₂O₅:K₂O equal to 2:8:16; 5:10:10; 7:6:19; 10:10:10, etc., as well as fertilizers whose composition includes only two nutrients, for example, N:P₂O₅:K₂O=8:24:0; 10:15:0; 13:20:0; 0:10:10; 0:12:12, etc.

With a content of nutrient substances over 30%, a precipitate is released from the liquid fertilizers which impairs their putting into the soil. However, the addition to the solution of stabilizing additives, for example, hydrophilic colloid substances, prevents

the formation of these precipitates. In this case, the total content of nutrients in the liquid fertilizer may be brought to 40% and higher.

The temperature of crystallization of liquid complex fertilizers, depending on their composition can fluctuate in limits from -29 to +11°C. A significant factor which influences crystallization of salts is the degree of neutralization of phosphoric acid. Preservation of all the fertilizer salts in the dissolved state when they are mixed is possible in a relatively narrow interval of concentrations and ratios of $\text{NH}_3:\text{P}_2\text{O}_5$. The maximum solubility corresponds to the region of conversion of monoammonium phosphate into diammonium phosphate, i.e., with molar ratio of $\text{NH}_3:\text{H}_3\text{PO}_4=1.56$ at 0°C and 1.53 at 25°C.

The process of preparation of liquid complex fertilizers is relatively simple.^{71, 112-114} Phosphoric acid is neutralized by ammonia. The heat of the neutralization process is used for partial evaporation of water from the solution. Then carbamide or ammonium nitrate and potassium chloride are added to the reactor and it is thoroughly mixed until a transparent solution is obtained.

In order to reduce the cost of the liquid complex fertilizers, extraction phosphoric acid that was obtained by nitric acid breakdown of the phosphates is often used. The extraction acid is less expensive than the thermal phosphoric acid, however, the extraction acid is not always suitable for the described process because of the presence in it of a number of admixtures. Their removal may significantly increase the net cost of the final products, the fertilizers.

The capital investments for units to produce complex liquid fertilizers are significantly lower than the capital outlays needed to produce an equivalent quantity of solid fertilizers. However, storage of the liquid complex fertilizers is associated with considerable expenditures. Consequently, the total economic effect of using these fertilizers is still low.

Liquid complex fertilizers generally have a low pH, therefore their storage and shipping require containers made of stainless steel

of different brands.

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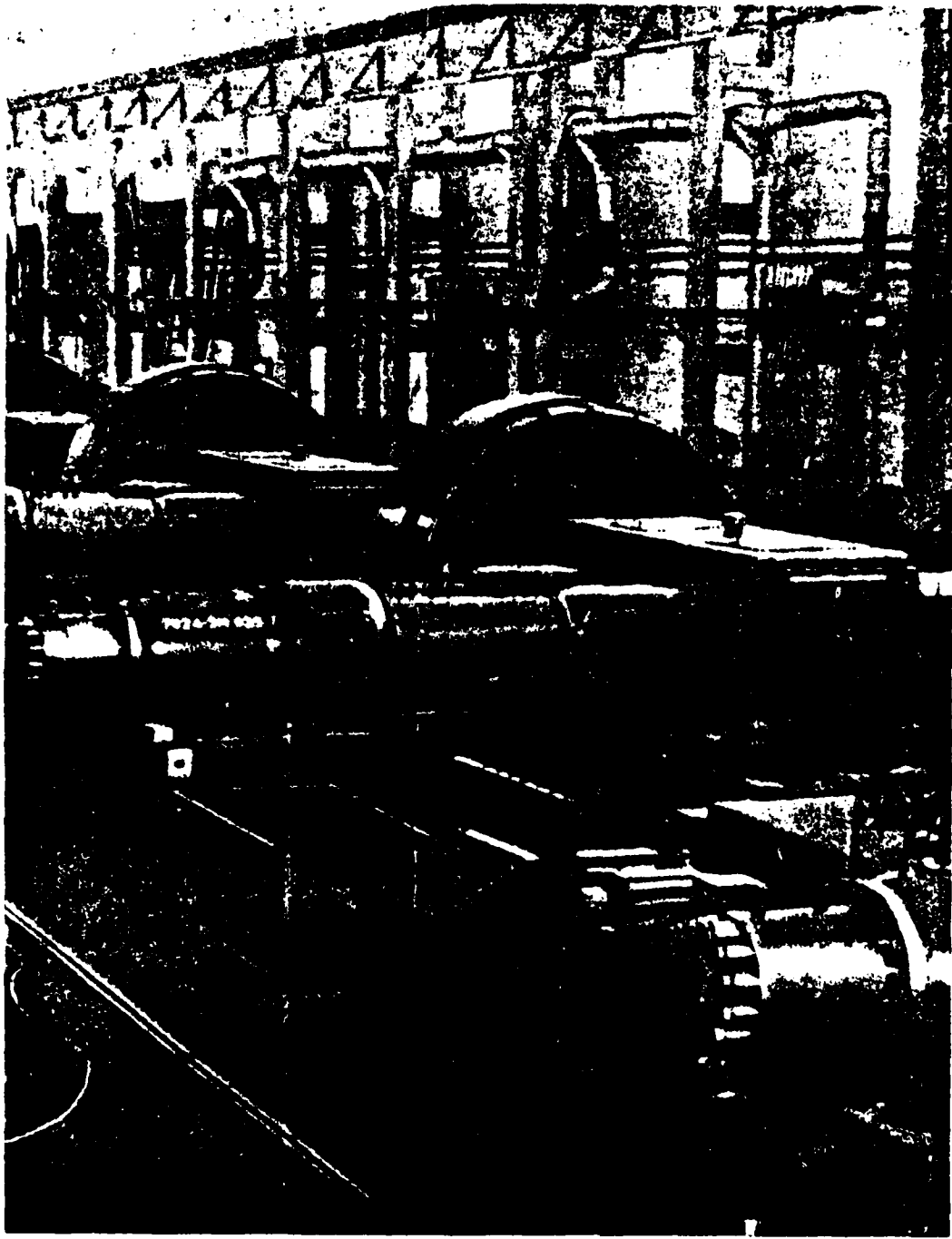
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III. Materials and Main Specialized Equipment

Editor-in-chief of the section S. A. Tveretskiy

1. Metals and Alloys

General Section

TABLE III-1. PHYSICAL PROPERTIES OF CERTAIN ELEMENTS WHICH ARE COMPONENTS OF DIFFERENT STEELS AND ALLOYS

(1) Элемент	(2) Плотность в твердом состоянии г/см ³	(3) Температура плавления, °C	(4) Коэффициент линейного расширения α · 10 ⁶ , град ⁻¹	(5) Удельная теплоемкость в твердом состоянии кал/(г · град)	(6) Теплота плавления кал/г	(7) Теплопроводность кал/(см · сек · град)	(8) Модуль упругости E · 10 ⁻³ , мм ² /мм ²
(9) Алюминий	2.7	658	24	0.247	93	0.52	7.2
(10) Ванадий	5.88	1710	—	0.1153	—	—	—
(11) Вольфрам	18.0—19.3	3370	4	0.034	44	0.476	42
(12) Кобальт	8.9	1490	12.08	0.0989	58.38	0.165	20
(13) Кремний	2.4	1427	6.95	0.1762	—	0.20	11.2
(14) Марганец	7.44	1244	23	0.107	64.8	—	—
(15) Молибден	10.2	2620	5.49	0.06447	—	0.35	35
(16) Никель	8.9	1452	13.7	0.112	73.8	0.14	21
(17) Хром	7.14	1550	8.1	0.12	31.75	0.165	—
(18) Железо	7.87	1530	11.9	0.1075	65	0.19	21
(19) Углерод	2.22	—	1.2	0.165	—	0.057	0.49
(20) Титан	4.5	1813	7.14	0.142	—	—	—
(21) Тантал	16.6	2850	6.5	0.0356	—	0.13	18.9
(22) Ниобий	8.57	1950	7.2	0.071	—	—	—
(23) Олово	7.3	232	22.4	0.054	14.4	0.157	4.9
(24) Медь	8.94	1083	16.42	—	50.6	0.923	11.2
(25) Цинк	7.14	419.4	32.6	0.094	2.4	0.268	13
(26) Цирконий	6.14	1700	—	0.066	6.2	—	—
(27) Свинец	11.34	327.3	29.5	0.031	6.26	0.083	1.8

Key:

1. Element
2. Density in solid state, g/cm³
3. Temperature of melting, °C
4. Coefficient of linear expansion, α x 10⁶, deg⁻¹
5. Specific heat capacity in solid state, cal/(g x deg)
6. Heat of melting, cal/g
7. Heat productivity, cal/(cm x s x deg)
8. Modulus of elasticity, E x 10⁻³, kg-f/mm²
9. Aluminum
10. Vanadium
11. Tungsten
12. Cobalt
13. Silicon
14. Manganese
15. Molybdenum
16. Nickel
17. Chrome
18. Iron
19. Carbon
20. Titanium
21. Tantalum
22. Niobium
23. Tin
24. Copper
25. Zinc
26. Zirconium
27. Lead

The nitrogen industry has characteristic processes which occur at high pressures and in working media that contain hydrogen, a mixture of hydrogen and carbon dioxide, and ammonia. Therefore in selecting the metal for the equipment and pipelines, one should take into consideration in many cases the possibility of hydrogen and carbonyl corrosion, and when there is ammonia in the gas at temperatures above 350°C, also the possibility of the formation of a brittle nitrated layer (fig. III-3 and III-4).



Figure III-1. Change in Mechanical Properties of Construction Steels with Addition to Them of 0.1% Alloying Elements

Key:

1. Reduction in δ and ψ , %
2. Increase in σ and α , kg-f/mm²
3. Ultimate strength
4. Yield limit
5. Constriction of cross section
6. Elongation

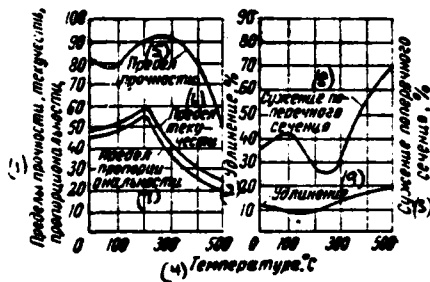


Figure III-2. Change in Mechanical Properties of Carbon Steel Depending on Temperature

Key:

1. Ultimate strength, yield limit, limit of proportionality
2. Elongation, %
3. Constriction of cross section, %
4. Temperature, °C
5. Ultimate strength
6. Yield limit
7. Limit of proportionality
8. Constriction of cross section
9. Elongation

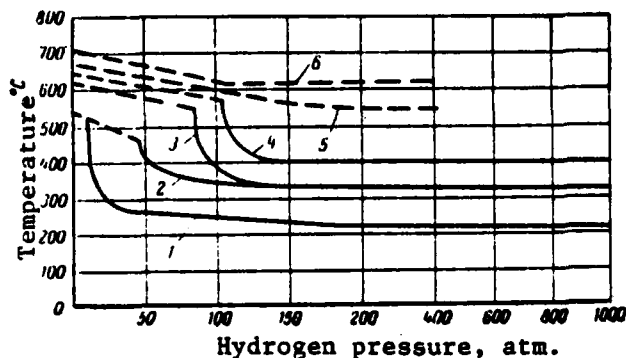


Figure III-3. Boundaries of Water Resistance of Carbon and Certain Alloyed Steels at High Temperatures and Pressure (according to Nelson)³

Key:

- Hydrogen corrosion
- - - - Surface decarbonization
1. Low-carbon steel
 2. 0.5% Mo
 3. 1.0% Cr, 0.5% Mo
 4. 2% Cr, 0.5% Mo
 5. 3% Cr, 0.5% Mo
 6. 6.0% Cr, 0.5% Mo

TABLE III-2. EFFECT OF ALLOYING ELEMENTS ON PROPERTIES OF STEEL (according to Bevnu)¹

Element	Solubility, %		Carbide-forming capacity	Effect on steel hardenability	Effect on ferrite	Basic purpose
	In γ -iron	In α -iron				
Aluminum	1.1 (increases with rise in carbon quantity)	30	Less than iron	Weak	Considerably increases hardness	Active deoxidizing agent Graphitizer Inhibits growth of grain as a consequence of formation of dispersed oxides and nitrides Basic alloying component in nitrided steels Increases scale resistance of steel
Vanadium	1-2 (to 4% with 0.2% C content)	Unlimited	Very strong but less than titanium and niobium Strong	Considerable	When present in solid solution, moderately increases hardness	Increases fine-graininess, hardenability, resistance to creep (less than molybdenum)
Tungsten	~6 (to 11% with 0.25% C content)	~32	Strong	Considerably increases, especially with low content	-	Increases heat resistance Basic alloying component in fast-cutting steels (because of formation of strong and solid carbides)
Cobalt	Unlimited	~80	The same as iron	Hardenability reduced	Considerably increases strength	Austenite-forming component in special alloys for high temperatures
Silicon	~2% (to 8% with 0.3% C content)	18.5	Less than iron	Weak	Increases strength (Mn < Si < P)	Basic deoxidizing agent Graphitizer Basic alloying element for dynamic and magnetic steels
Manganese	Unlimited	15-18	More than iron, but less than chrome	Moderate (Ni < Mn < Cr)	Noticeably increases strength, but reduces plasticity	Increases heat resistance Deoxidizing agent and desulfurizer Austenite-forming elements Increases hardenability of steel

Molybdenum	~3(to 8% with 0.3% C content)	~32(decreases with drop in temperature)	Strong (more than chrome)	More (Mo>Cr)	When present in solid solution increases strength	Increases heat-resistance Considerably improves creep resistance Increases hardenability Improves corrosion resistance of austenite steels
Nickel	Unlimited	~25	Less than iron	Weak	Increases strength and viscosity	Basic austenite-forming element in chrome-nickel steels Graphitizer Increases strength of untempered steel Increases impact viscosity, especially at low temps. Reduces formation of martensite in chrome steels Stabilizes structure of austenite steels Inhibits grain growth
Titanium	0.75(1% with 0.25% C content)	6(drops with decline in temperature)	Maximum(2% Ti makes steel with 0.5% C non-hardenable)	Stable and not easily soluble carbides reduce hardenability	-	Increases corrosion resistance Improves mechanical workability of soft steel Increases corrosion resistance and oxidation resistance Increases hardenability Somewhat increases heat-resistance
Phosphorus	0.5%	2.5%(regardless of carbon content)	Not formed	-	Considerably increases hardness	Increases corrosion resistance Improves mechanical workability of soft steel Increases corrosion resistance and oxidation resistance Increases hardenability Somewhat increases heat-resistance
Chrome	12% (20% with 0.5% C content)	Unlimited	More than manganese, but less than tungsten	Moderate (but more effective than Mn)	Slightly increases hardness	Increases corrosion resistance and oxidation resistance Increases hardenability Somewhat increases heat-resistance

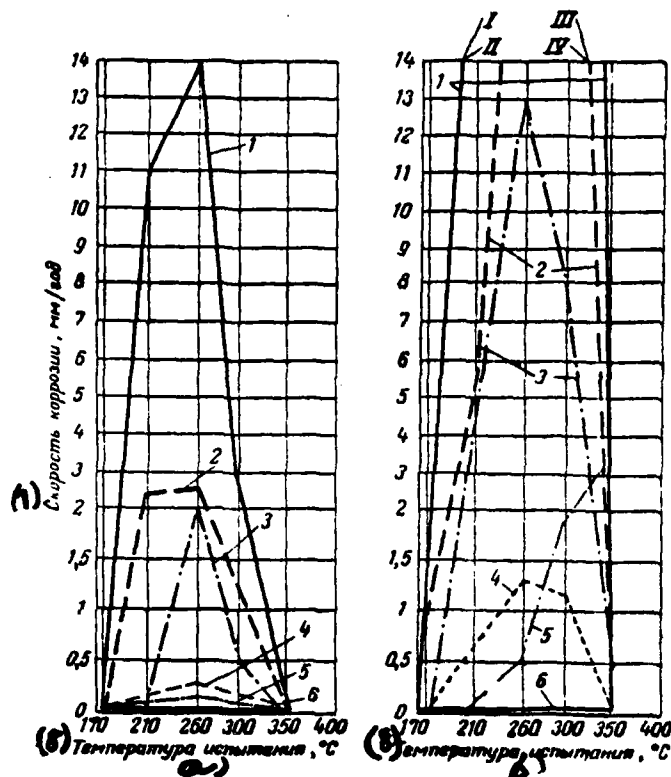


Figure III.4. Resistance of Different Structural Materials to Carbonyl Corrosion in Gas Mixture with Ratio of Components $\text{CO}:\text{H}_2 = 1:1$ at High Temperatures and Pressure (according to Nelson)³

Key:

- a. at 250 atm.
- b. at 700 atm.

- 1. Carbon steel
- 2. Chrome-molybdenum steel
- 3. The same
- 4. Carbon steel, protected by galvanic coating (zinc-plated)
- 5. Chrome-nickel austenite steel
- 6. Manganese copper

Composition, %

C	Mn	Cr	Ni	Mo	Ti	Cu
0.09	—	—	—	—	—	—
0.12	0.75	9.98	0.08	0.30	—	—
0.008	0.38	13.7	0.37	0.34	—	—
—	—	17.2	8.22	—	0.88	—
—	8.1	—	—	—	—	94.1

- I. 23.9 mm/year (at 210°C)
- II. 136.8 (at 260°C)
- III. 43.4 (at 300°C)
- IV. 21.2 (at 260°C)
- 7. Rate of corrosion, mm/year
- 8. Testing temperature, °C

In selecting the material for making the equipment, it is necessary to be guided by the regulations of the State Scientific and Technical Mining Inspection. According to these regulations, tables III-5-III-9 indicate the areas of application of steels without consideration for the adverse effect of hydrogen and other

aggressive media.⁴

TABLE III-2a. RESISTANCE OF CERTAIN STEELS TO NITRIDING²

(1) Химический состав стали, %							(3) Толщина азотированного слоя, мм
C	Mo	Ni	Cr	Ti	W	прочие ²⁾ элементы	(5)
0.038	—	—	—	—	—	0.03% S	Отсутствует
0.15	—	—	—	—	—	—	»
0.12	0.91	0.11	0.46	—	—	—	»
0.24	0.37	—	3.01	—	0.57	0.77% V	2
(4) 0.15	0.35	—	4.00—6.00	—	—	—	2.75
Не более 0.15	—	—	11.5—14.5	—	—	—	1.5
» 0.15	—	—	15.5—18.5	—	—	—	1.0
» 0.20	—	Не более 2.0	23.0—27.0	—	—	—	0.75
» 0.12	—	8.0—11.0	17—20.0	0.50	—	—	0.30
0.12	—	12.0	13.0	0.70	1.25	—	0.25
(4) 0.08	—	9.0	18.0	—	—	0.3% Nb	0.20
Не более 0.25	—	17.0—21.0	22—26.0	—	—	—	0.45
0.06	—	—	—	0.16	—	—	0.1
0.05	—	0.30	0.10	0.35	—	—	0.75
0.0035	—	3.68	—	0.61	—	—	1.5
0.05	—	0.14	—	0.54	2.97	—	3.0

Key:

1. Chemical composition of steel, %
2. Other elements
3. Thickness of nitrided layer, mm
4. Not more than
5. Lacking

Note: The data were obtained as a result of tests on samples of metals in an ammonia synthesis column at 325 atm. and 450-500°C; ammonia content 11-16%; duration of testing 4380 h.

TABLE III-3. MATERIALS TO MAKE PARTS OF PIPELINES WHICH CONTACT WORKING MEDIA CONTAINING HYDROGEN
(From standards of Irkutsk branch of State Scientific Research and Planning Institute of Oil Machine Construction)
Coefficient of conversion into SI system: pressure atm. x 98066.6 = n/m², or atm. x 0.980665 = bar.

Working pressure	320 atm.			700 atm.		
	I	II	III	I	II	III
Temperature degree	I	II	III	I	II	III
Temperature of working medium °C	from -50 to +200	200-400	400-510	from -50 to +200	200-400	400-510
Conventional openings mm	6-200	6-200	6-32 40-200	6-15 25-150	6-150	6-150
Name of parts	Brands of steels and alloys					
pipes	20	18Kh3MV	18Kh3MV 20Kh3MVF	30KhMA 40Kh	18Kh3MV	20Kh2MVF
Shaped parts	20, 25, 35, 15G	18Kh3MV	18Kh3MV 20Kh3MVF	20KhG, 30Kh	18Kh3MV	20Kh3MVF
Flanges, blind and connecting	20, 25, 30, 35, 15G	18Kh3MV	18Kh3MV 20Kh3MVF	20KhG, 40, 30Kh	18Kh3MV	20Kh3MVF
Threaded flanges	35, 40, 30G	38KhA, 40Kh	25Kh2MFA 18Kh3MV	35, 40, 30G, 30Kh	38KhA, 40Kh	25Kh2MFA 20Kh3MVF
Dowels	35KhG2, 38KhA, 30Kh, 40Kh	40KhFA 30KhMA, 38KhA	25Kh2MFA	35KhG2, 38KhA, 40KhFA 30KhMA, 40Kh 30KhMA	40KhFA 30KhMA	25Kh2MFA
Nuts	30Kh, 35, 30G	30Kh, 20KhG	30KhMA	30Kh, 20KhG	30Kh, 20KhG	30KhMA
Lenses	20	18Kh3MV	20Kh3MVF	20 20KhG 40Kh 30KhMA	18Kh3MV	20Kh3MVF

- Note: 1. Brands 18Kh3MV and 20Kh3MVF correspond to the old brands EI578 and EI579.
2. Here and further the pressure is absolute
3. If ammonia is transported on the pipelines (or gas mixtures which contain ammonia) at temperatures above 350°C, the pipe material is selected with regard for its resistance to nitriding (see table III-2a).

TABLE III-4. RECOMMENDATIONS FOR USE OF CARBON AND CERTAIN ALLOYED STEELS FOR WORKING MEDIA CONTAINING HYDROGEN AT DIFFERENT TEMPERATURES IN PRESSURE INTERVAL FROM 1 TO 100 ATM.

Partial pressure of hydrogen, atm.	Maximum temperature of use, °C			
	200	450	500	540
1-1.7	Carbon			12KhM
1.7-11	Carbon			18Kh3MV, 20Kh3MVF, 1Kh18N9T
11-70	Carbon	12KhM	18Kh3MV, 20Kh3MVF, 1Kh18N9T	20Kh3MV, 1Kh18N9T

7C-100

Carbon

18Kh3MV, 20Kh3MV
1Kh18N9T

20Kh3MVF

1Kh18N9T

- Note: 1. If it is impossible during operation to guarantee constant partial pressure of hydrogen and temperature of the working medium, then when the table data are used one should introduce the appropriate corrections.
2. When carbon steels are used for welded apparatus and pipelines, as well as if their parts are exposed to deformation (bent arms, stamped bottoms, etc.) under temperature conditions over 200°C, the partial pressures of hydrogen must not exceed 7 atm.
3. Brands 18Kh3MV and 20Kh3MV correspond to old brands EI578 and EI579.

TABLE III-5. AREA OF APPLICATION OF SHEET STEEL

Materials	GOST or TU	Area of application		Types of tests
		working temperature of wall, °C	working pressure of medium, atm. no more	
St.2, St.3. St.4, rimming	380-60 (group A)	from -15 to +200	16	Testing from batch of sheets for stretching and bending
St.3, St.4 rimming		from -30 to +200		Testing from batch of sheets for stretching, bending and impact viscosity
St.3, St.4 killed The same	380-60 (group A)	from -30 to +400 from -40 to +425	50	Testing of each sheet for stretching, bending and impact visc.
15K, 20K, 25K	5520-62	from -40 to +475	Not limited	According to GOST
10, 15, 20 killed 10G2T	1050-60 TU	from -40 to +450 from -70 to +450	the same "	According to TU The same
12MKh	TU	from -40 to +540	"	"
1Kh18N9T	7350-55 and TU	from -196 to +600	"	According to GOST and TU
Kh18N12M2T	5632-61 7350-55	from -196 to +700	"	According to TU

- Notes: 1. At temperatures lower than those indicated in tables III-5-III-9, the use of steels that are presented in these tables is only permitted with mandatory testing of the base metal and welded seam of the vessel for impact viscosity at working temperature; impact viscosity in this case must be no less than 2 kg-f x m/cm².
2. The rimming carbon steel must be used to make vessels only with thickness of the sheet no more than 26 mm.

TABLE III-6. AREA OF APPLICATION OF STEEL PIPES IN MAKING IMPORTANT CONTAINERS AND THEIR ELEMENTS

Coefficient of conversion into SI system: pressure--atm. x 98066.5 = n/m², or atm x 0.980665=bar

Brand of steel	GOST or TU	Area of application		Types of tests
		working temperature of wall, °C	working pressure of medium, atm. no more	
St. 5, St. 6	8731-66 8732-58 8733-66 8734-58	from -30 to +120	220	According to GOST
MSt. 2, MSt. 3	10704-63	from -15 to +200	16	The same
St. 2, St. 4	8731-66 8732-58 8733-66 8734-58	from -15 to +300	16	"
MSt. 3, killed	10704-63	from -30 to +350	50	Checking mechanical properties of welded seam of every 10th pipe according to regulations of State Sci. and Techn. Mining Inspection X-raying of 15% longitudinal seam of every pipe Hydraulic test of every pipe or container housing under pressure, 1.5-fold greater than working
10, 20	10705-63 and TU	from 0 to +300	13	According to GOST and TU
10, 20, killed	8731-66	from -40 to +400	50	According to GOST
10, 20	8732-58	from -40 to +450	60	The same
	8733-66	from -40 to +450	160	
	8734-58	from -40 to +475	160	Testing of each pipe according to GOST
30KhMA	4543-61 and TU	from 0 to +500	Not limited	According to TU
12MKh and 12MKhF Kh5M	TU	from -40 to +500	The same	The same
	TU	from -40 to +550	"	"
12KhM (15KhM) 12KhMF	TU	from -40 to +560	"	"

1Kh18N9T	9940-62	from -196 to +600	"	According to GOST
Kh18N12M2T	9941-62	from -196 to +700	"	The same

TABLE III-7. AREA OF APPLICATION OF LARGE STEEL FORGED PIECES FOR MANUFACTURE OF CONTAINERS

Steel brand	GOST or TU	Area of application	
		temperature of wall, °C, no more	pressure, atm
15, 20, 25, 22K	GOST 8479-57	from -40 to +450	Not limited
12Mkh (12MKhF)	TU	from -40 to +540	The same
12Mkh (15KhM), 12MKhF	"	from -40 to +560	"
1Kh18N9T	"	from -40 to +600	"

TABLE III-8. AREA OF APPLICATION OF STEEL SHEET FOR CONTAINERS AND THEIR COMPONENTS

Steel brand and casting group	GOST or TU	Area of application	
		wall temperature, °C	pressure, atm. no more
15L, 20L, 25L, 30L (group I)	977-58	from -15 to +400	50
15L, 20L, 25L, 30L (group II)	the same	from -40 to +450	Not limited
Kh17	according to TU	from 0 to +450	the same
30KhMAL	the same	from 0 to +480	"
18KhML	"	from -40 to +540	"
1Kh18N9T	"	from -196 to +600	"
Kh5ML	"	from -40 to +550	"
1Kh18N9TL	"	from -40 to +500	"
20KhMFL	"	from -40 to +570	"
20KhML	7832	from -40 to +540	"

- Note: 1. The casting is used in a thermally-treated state depending on the chemical composition and mechanical properties (σ_B, δ); for castings of the II and III groups with pressure over 50 atm. and temperature above 400°C the impact viscosity is also determined.
2. For castings made of alloyed steel, a study is also made of the macro- and microstructure in a thermally-treated state, and if necessary, the tendency towards intercrystalline corrosion.

TABLE III-9. AREA OF APPLICATION OF STEELS FOR MANUFACTURE OF BOLTS, DOWELS AND NUTS

Steel brand	GOST	Area of application		Purpose
		temperature, °C	Pressure, atm. no more	
St. 3, St. 4, St. 5	380-60	From -30 to +350	50	Bolts, dowels, nuts
25, 30, 35 , 40	1050-60	From -30 to +435	Not limited	The same
35Kh, 38KhA, 40Kh	4543-61	From -40 to +435	The same	Dowels, bolts
35Kh, 38KhA, 40Kh	4543-61	From -40 to +480	"	Nuts

3CKhMA	4543-61	From -40 to +480	"	Dowels, bolts
20KhMA	4543-61	From -40 to +510	"	Nuts
25Kh2MFA	4543-61	From -40 to +550	"	The same
4Kh12N14V2M EI69)	5632-61 and TU	To +600	"	Bolts, dowels, nuts
IKh18N9T	5632-61 and TU	From -196 to +600	"	The same

Carbon Structural Steels

TABLE III-10. CHEMICAL COMPOSITION (in %) OF CARBON STRUCTURAL STEELS

(1) Марка стали	C	Si	Mn	P	S	Cr	Ni
					(2) не более		

(3) Сталь углеродистая конструкционная
(ГОСТ 1050-60)

10	0.07-0.14	0.17-0.37	0.35-0.65	0.35	0.04	0.15	0.25
20	0.17-0.24	0.17-0.37	0.35-0.65	0.040	0.04	0.25	0.25
25	0.22-0.30	0.17-0.37	0.50-0.80	0.040	0.04	0.25	0.25
30	0.27-0.35	0.17-0.37	0.50-0.80	0.040	0.04	0.25	0.25
35	0.32-0.40	0.17-0.37	0.50-0.80	0.040	0.04	0.25	0.25
40	0.37-0.45	0.17-0.37	0.50-0.80	0.040	0.04	0.25	0.25

(4) Сталь углеродистая с повышенным содержанием марганца
(ГОСТ 1050-60)

15Г	0.12-0.19	0.17-0.37	0.7-1.0	0.04	0.04	0.25	0.25
20Г	0.17-0.24	0.17-0.37	0.7-1.0	0.04	0.04	0.25	0.25
30Г	0.27-0.35	0.17-0.37	0.7-1.0	0.04	0.04	0.25	0.25

(5) Сталь углеродистая листовая для котлостроения
(ГОСТ 5520-62)

15K	0.12-0.20	0.15-0.30	0.35-0.65	0.04	0.045	-	-
20K	0.16-0.24	0.15-0.30	0.35-0.65	0.04	0.045	-	-

Key:

1. Brand of steel
2. Not more
3. Carbon structural steel (GOST 1050-60)
4. Carbon steel with increased manganese content (GOST 1050-60)
5. Carbon sheet steel for boiler construction (GOST 5520-62)

TABLE III-11. CERTAIN PHYSICAL PROPERTIES OF CARBON STEELS⁵

(1) Марка стали	(2) Плотность г/см ³	(3) Коэффициент линейного расширения * $\alpha \cdot 10^6$, град ⁻¹		(5) Коэффициент теплопроводности кал/(см·сек·град)		(6) Удельная теплоемкость (кал/г·град)	
		(4) при 20-100 °C	(4) при 20-200 °C	(4) при 100 °C	(4) при 200 °C	(4) при 100 °C	(4) при 200 °C
10	7.830	11.6	12.6	0.193	0.165	0.111	0.114
20	7.820	11.1	12.1	0.186	0.159	0.112	0.115
25	7.830	11.1	12.3	0.180	0.154	0.112	0.115
30	7.817	11.1	—	0.180	0.154	0.112	0.115
35	7.817	11.09	11.9	0.180	0.154	0.112	0.115
40	7.815	12.4	12.6	0.141	0.127	0.112	0.115
15.G	7.810	12.3	—	0.185	—	—	—
20.G	7.814	12.3	—	0.186	—	—	—
30.G	7.812	12.6	—	0.180	—	—	—
St.3	(1) Как у стали 20	(2) То же					
15K	(7) То же						
20K	(7) Как у стали 25						
25K							

Key:

1. Brand of steel
2. Density, g/cm³
3. Coefficient of linear expansion*, $\alpha \times 10^6$, deg⁻¹
4. at
5. Coefficient of heat conductivity, cal/(cm x s x deg)
6. Specific heat capacity (cal/g x deg)
7. As in steel
8. The same

*Average values for indicated temperature intervals.

TABLE III-12. MODULUS OF ELASTICITY OF CERTAIN CARBON STEELS^{5,6} AT DIFFERENT TEMPERATURES ($E \times 10^{-4}$, kg-f/mm²)

(1) Температура °C	(2) Марка стали						
	10	15	20	25	30	35	40
20	(3) 1.98 (при -15 °C)	2.05	2.0	2.02	2.02	2.1	2.13
100	2.12 (при -40 °C)	1.96	—	2.00	2.00	2.01	2.10
200	(3) 2.10 (при -100 °C)	1.88	—	—	1.95	1.90	—
300	(3) 2.12 (при -180 °C)	1.75	—	1.89	1.85	1.79	1.98
400	—	1.61	—	—	1.67	1.71	—
450	—	—	—	1.52	1.52	1.57	—

Key:

1. Temperature, °C
2. Brand of steel
3. at

TABLE III-13. MECHANICAL PROPERTIES OF CARBON STRUCTURAL STEEL (GOST 1080-60)

(1) Марка стали	(2) Предел текучести σ_T кгс/мм ²	(3) Предел прочности σ_B кгс/мм ²	(4) Относительное удлинение δ %	(5) Относительное сужение ψ %	(6) Ударная вязкость кгс·м/см ²
	не менее (7)				
10	21	34	31	55	—
20	25	42	25	55	—
25	28	46	23	50	9
30	30	50	21	50	8
35	32	54	20	45	7
40	34	58	19	45	6
15 G	25	42	26	55	—
20 G	28	46	24	50	—
30 G	32	55	20	45	8

Key:

1. Brand of steel
2. Yield limit, σ_T , kg-f/mm²
3. Ultimate strength, σ_B , kg-f/mm²
4. Relative elongation, δ , %
5. Relative constriction ψ , %
6. Impact viscosity, kg-f x m/cm²
7. No less

- Note:
1. The tabular data cover hot-rolled forged sectional steel of size (diameter or thickness) to 250 mm.
 2. The mechanical properties of steel indicated in table III-13 are defined on samples made of normalized blanks. The impact viscosity is defined on thermally treated samples (tempering temperature about 600°C).
 3. Here and further σ_B --ultimate strength during stretching.

TABLE III-14. MECHANICAL PROPERTIES OF BOILER STEEL (GOST 5520-62)

(1) Марка стали	(2) Предел прочности, кгс/мм ²	(3) Предел текучести, кгс/мм ² для групп толщин *			(4) Относительное удлинение при разрывном пределе прочности			(5) Ударная вязкость при 20 °С (6) для групп толщин *			(7) Загиб ** в холодном состоянии на 180° при толщине листа	
		I	II	III	δ_5 %	δ_{10} %	I	II	III	до 30 мм (8)	свыше 30 мм (9)	
												кгс/мм ² (7)
15K	38	23	22	21	38—40	27	23	8.0	7.5	7.0	d=0,5a	d=1,5a
					41—42	26	22	7.0	6.5	6.0		
					≥ 43	25	21	7.0	6.5	6.0		
20K	41	25	24	23	41—42	26	22	7.0	6.5	6.0	d=1,5a	d=2,5a
					43—44	25	21	6.0	5.5	5.0		
					45—47	24	20	6.0	5.5	5.0		
					≥ 48	23	19	6.0	5.5	5.0		

Key:

1. Brand of steel
2. Ultimate strength, kg-f/mm²

3. Yield limit, kg-f/mm² for group of thickness*
4. Relative elongation with varying ultimate strength
5. Impact viscosity at 20°C kg-f x m/cm² for group of thickness*
6. Bending** in cold state at 180° with sheet thickness
7. kg-f/mm²
8. to 30 mm
9. over 30 mm

* Depending on the yield limit, the sheets of steel are divided in thickness into three groups: I--from 4 to 20 mm; II--from 21 to 40 mm; III--from 41 to 60 mm.

** d--diameter of casting; a--thickness of sample.

Below are the mechanical properties of steel for the manufacture of high pressure pipes (according to the standards of the Irkutsk branch of the State Scientific Research and Planning Institute of Oil Machine Construction for parts of pipelines for 320 and 700 atm)⁷:

Brand of steel	20
Ultimate strength*, kg-f/mm ² , no less	40
Yield limit, kg-f/mm ² , no less	22
Relative elongation, %, no less	
δ ₅	20
δ ₁₀	17
Impact viscosity*, kg-f x m/cm ² , no less	5
Brinell hardness HB, kg-f/mm ²	111-156

* Coefficients of conversion into SI system: kg-f/mm² x 9.80665 x 10⁶ = n/m²; kg-f x m/cm² x 9.80665 = J/m²

TABLE III-15. MECHANICAL PROPERTIES OF FORGED PIECES MADE OF CARBON STEEL (GOST 8479-57)

(1) Категория прочности	(2) Предел прочности кгс/мм ²	(3) Диаметр или толщина поковки перед термической обработкой, мм												(4) Твердость по Бринеллю НВ
		№ 100				№ 150				№ 200				
		101-200	201-300	301-400	401-500	101-200	201-300	301-400	401-500	101-200	201-300	301-400	401-500	
		(5) Относительное удлинение %, не менее				(6) Относительное сужение %, не менее				(7) Ударная вязкость кгс·м/см ² , не менее				
КР18	36	28	25	22	20	55	50	45	40	6.5	6.0	5.5	5.0	101-140
КР20	40	25	22	20	18	55	50	45	38	5.5	5.0	4.5	4.0	111-156
КР22	44	22	20	18	16	53	48	40	35	5.5	4.5	4.0	3.5	128-167
КР25	50	20	18	16	14	48	42	35	30	4.0	3.5	3.0	3.0	140-179
КР28	56	18	16	14	12	40	38	32	30	4.0	3.5	3.0	3.0	156-197
КР32	62	16	14	12	11	38	35	30	30	3.5	3.0	—	—	174-217
КР35	67	14	12	11	10	35	33	30	28	—	—	—	—	187-229

Key:

1. Category of strength
2. Ultimate strength, kg-f/mm²
3. Diameter or thickness of forged pieces before thermal

- treatment, mm
4. Brinnell hardness, HB
 5. Relative elongation, %, no less
 6. Relative constriction, %, no less
 7. Impact viscosity, kg-f x m/cm², no less

Note: 1. In the column "Category of strength" the two-term number after the letters KP designates the amount of yield limit.
 2. The norms of mechanical properties for forged pieces with diameter or thickness over 800 mm are set by agreement between the manufacturer and the customer.
 3. The values of mechanical properties refer to the longitudinal cylindrical quintuple sample of diameter 10 mm and normal impact sample (according to GOST 9454-60).

TABLE III-16. CALCULATED CHARACTERISTICS FOR CERTAIN CARBON STEELS⁸

Coefficient of conversion into SI system: mechanical stress kg-f/mm² x 9.80665 x 10⁶ n/m²

(1) Марка стали	(2) Температура, °C									
	20	200	250	300	350	400	425	450	475	500
(3) Условный предел текучести σ_t , кгс/мм ²										
10	18	16.0	14.5	13.5	11.5	10.0	—	8.0	—	6.0
20	22	19.0	17.5	15.5	13.5	12.0	—	10.0	—	8.0
25	24	20.5	18.5	16.5	14.5	13.0	—	11.0	—	9.0
30	26	22.0	20.0	17.5	15.5	13.5	—	11.5	—	9.5
35	28	24.0	21.5	19.0	17.0	14.5	—	12.5	—	10.5
MSt.3	21	18.0	17.0	15.0	13.0	—	—	—	—	—
15K	20	17.5	16.0	14.5	12.5	11.0	—	9.0	—	7.0
20K	22	19.0	17.5	15.5	13.5	12.0	—	10.0	—	8.0
25K	25	21.0	19.0	17.0	15.0	13.0	—	11.0	—	9.0
(4) Условный предел ползучести σ_n , кгс/мм ²										
10	—	—	—	—	—	8.5	6.3	4.4	3.1	2.2
15	—	—	—	—	—	9.5	7.0	4.8	3.6	2.5
20	—	—	—	—	—	10.0	7.5	5.0	3.6	2.5
25	—	—	—	—	—	10.5	8.0	5.3	3.7	2.5
30	—	—	—	—	—	11.0	8.3	5.5	3.6	—
35	—	—	—	—	—	12.0	8.5	5.5	3.6	—

Key:

1. Brand of steel
2. Temperature, °C
3. Conventional yield limit, σ_t , kg-f/mm²
4. Conventional creep limit, σ_n , kg-f/mm²

Note. 1. The calculated characteristics given in table III-16 correspond to the lower limits of strength and can be used to compute the parts made of rolled metal and forgings.

2. The data for steel brand 30 and 35 correspond to steel after normalization.

3. The conventional creep limit is given for creep rate of 10⁻⁷ mm/mm x h.

TABLE III-17. MECHANICAL PROPERTIES OF METAL OF CASTINGS MADE OF CARBON STEEL IN NORMALIZED, OR NORMALIZED AND TEMPERED, OR ANNEALED STATE (GOST 977-65)

(1) Марка стали	(2) Предел текучести кгс/мм ²	(3) Предел прочности кгс/мм ²	(4) Относительное удлинение %	(5) Относительное сужение %	(6) Ударная вязкость кгс·м/см ²
	(7) не менее				
15Л	20	40	24	35	5.0
20Л	22	42	22	35	5.0
25Л	24	45	19	30	4.0
30Л	26	48	17	30	3.5
35Л	28	50	15	25	3.5
40Л	30	53	14	25	3.0

Key:

1. Brand of steel
2. Yield limit, kg-f/mm²
3. Ultimate strength, kg-f/mm²
4. Relative elongation, %
5. Relative constriction, %
6. Impact viscosity, kg-f x m/cm²
7. No less

Note: For castings with minimum thickness of the wall over 100 mm, the standards of mechanical properties are set by the specifications.

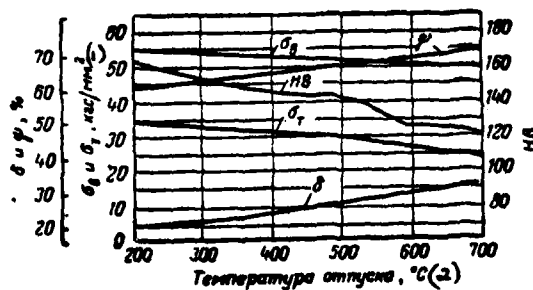


Figure III-5. Effect of Tempering Temperature on Mechanical Properties of Steel 20

Key:

1. kg-f/mm²
2. Tempering temperature, °C

Low-Alloy and Alloy Structural Steels

TABLE III-18. CHEMICAL COMPOSITION (IN %) OF LOW-ALLOY AND ALLOY STRUCTURAL STEELS (GOST 4543-61, GOST 10500-63)

Марка стали	(1)						Прочие элементы
	C	Si	Mn	Cr	Ni	Mo	
(3) Низколегированные стали							
30 Kh	0.25-0.33	0.17-0.37	0.50-0.80	0.80-1.10	—	—	—
40 Kh	0.36-0.44	0.17-0.37	0.50-0.80	0.80-1.10	—	—	—
38KhA	0.35-0.42	0.17-0.37	0.50-0.80	0.80-1.10	—	—	—
15KhF	0.12-0.18	0.17-0.37	0.40-0.70	0.80-1.10	—	—	0.1-0.2% V
40KhBA	0.37-0.44	0.17-0.37	0.50-0.80	0.80-1.10	—	—	0.1-0.2% V
15KhM	0.11-0.18	0.17-0.37	0.40-0.70	0.80-1.10	—	0.40-0.55	—
30KhMA	0.26-0.33	0.17-0.37	0.40-0.70	0.80-1.10	—	0.15-0.25	—
35KhG2	0.32-0.40	0.17-0.37	1.60-1.90	0.40-0.70	—	—	—
30KhGS	0.28-0.35	0.90-1.20	0.80-1.10	0.80-1.10	—	—	—
30KhGSA	0.28-0.34	0.90-1.20	0.80-1.10	0.80-1.10	—	—	—
38KhYu	0.35-0.43	0.17-0.37	0.20-0.50	1.50-1.80	—	—	0.5-0.8% Al
38KhMYuA	0.35-0.42	0.17-0.37	0.30-0.60	1.35-1.65	—	0.15-0.25	0.7-1.1% Al
18 KhG	0.15-0.21	0.17-0.37	0.90-1.20	0.90-1.20	—	—	—
(4) Легированные стали							
25Kh1MF	0.22-0.30	0.17-0.37	0.40-0.70	1.60-1.80	≤0.30	0.25-0.35	0.2-0.3% V
18Kh3MV	0.11-0.20	≤0.40	0.25-0.50	2.50-3.00	≤0.25	0.50-0.70	0.5-0.8% W
20Kh3MVF	0.16-0.22	≤0.40	0.25-0.50	2.5-3.0	≤0.25	0.35-0.50	0.70-0.85% W
25Kh3NM	0.20-0.30	0.26-0.32	0.60-1.0	2.8-3.2	0.9-1.5	0.35-0.50	—

Key:

1. Brand of steel
2. Other elements
3. Low-alloy steel
4. Alloy steel

Note: The content of sulfur and phosphorus in the quality steels is 0.04% each, and in the high-quality steels 0.03 and 0.035% respectively.

TABLE III-19. CERTAIN PHYSICAL PROPERTIES OF LOW-ALLOY STEELS⁶

Марка стали	(2) Плотность ρ , г/см ³	(3) Температура, °C							
		(4) Средние значения коэффициента линейного расширения $\alpha \cdot 10^6$, град ⁻¹				(5) Коэффициент теплопроводности λ , ккал / (см·сек·град)			
		20-100	20-200	20-400	20-600	100	200	400	500
30 Kh	7.82	13.4	13.3	14.8	14.8	0.110	0.104	0.092	0.0827
40 Kh	7.82	13.4	13.3	14.8	14.8	0.110	0.10	—	0.09
20KhA	7.80	12.0	12.5	13.0	13.7	—	—	—	—
40KhF	7.81	11.0	12.0 (при 25-300 °C)	14.5 (при 25-600 °C)	16.5 (при 25-500 °C)	0.125	0.116	0.108	0.10
30KM	—	—	12.5	13.9	14.4	0.102	0.097	—	—
35KM	—	—	12.5	13.9	14.4	0.099	0.097	0.094 (при 300 °C)	0.091 (при 400 °C)
30 KhGS	7.75	11.0 (при 25-100 °C)	—	—	—	0.09 (при 25-100 °C)	—	—	—
25 Kh1MF	—	11.3	11.7	13.9	14.4	—	—	—	—

Key:

1. Brand of steel
2. Density, g/cm^3
3. Temperature, $^{\circ}\text{C}$
4. Average values of coefficient of linear expansion, $\alpha \times 10^6$, deg.
5. Coefficient of heat conductivity, λ , $\text{cal}/(\text{cm} \times \text{s} \times \text{deg})$
6. at

TABLE III-20. MODULUS OF NORMAL ELASTICITY AND SHEAR MODULUS OF CERTAIN LOW-ALLOY STEELS⁶ (in kg-f/mm^2)

(1) Марка стали	(2) Предел прочности кгс/мм^2	(3) Температура, $^{\circ}\text{C}$							
		20	100	300	500	20	100	300	500
		(4) Модуль нормальной упругости				(5) Модуль сдвига			
30Kh	70	21 850	21 500	20 100	17 950	8500	8300	7600	6600
40Kh	86	20 000	—	—	—	—	—	—	—
35KhM	76	21 900	21 600	20 500	18 600	8400	8300 ⁽⁶⁾ (при 200°C)	7550	6600
30KhMA	76	21 900	21 600	20 500	18 600	8400	8300 ⁽⁶⁾ (при 200°C)	7550	6600
25Kh1MF	76	21 900	21 600	20 560	19 000	—	—	—	—

Key:

1. Brand of steel
2. Ultimate strength, kg-f/mm^2
3. Temperature, $^{\circ}\text{C}$
4. Modulus of normal elasticity
5. Shear modulus
6. At

Figure III-6 presents the curves which characterize the effect of temperature on the change in yield limit of German steel No 10 (FRG) which is similar in chemical composition to steel 20Kh3MFV (EI579).

TABLE III-21. MECHANICAL PROPERTIES OF CONSTRUCTION ALLOY STEEL (GOST 4543-61)

Coefficients of conversion into SI system: mechanical stress-- $\text{kg-f/mm}^2 \times 9.80665 \times 10^6 = \text{n/m}^2$; impact viscosity $\text{kg-f} \times \text{m/cm}^2 \times 98066.5 = \text{J/m}^2$

(1) Марка стали	(2) Условия термической обработки				(7) Механические свойства				
	закалка (3)		отпуск (4)		(8) предел проч- ности, кгс/мм ²	(9) предел текуче- сти, кгс/мм ²	(10) удлинение, %	(11) сужение, %	(12) ударная вязкость кгс·м/см ²
	(5) температура °C	(6) охлажда- ющая среда	(5) температура °C	(6) охлажда- ющая среда					
30Kh	860	Масло ⁽¹³⁾	500	Вода или масло ⁽¹⁴⁾	90	70	12	45	7
40Kh	850	"	500	То же ⁽¹⁴⁾	100	80	10	45	6
38KhA	860	"	550	"	95	80	12	50	9
15KhF	880	Вода или масло ⁽¹⁴⁾	180	Воздух ⁽¹⁷⁾	75	55	13	50	8
40KhFA	880	Масло ⁽¹³⁾	650	Вода или масло ⁽¹⁴⁾	90	75	10	50	9
30KhMA	880	"	540	То же ⁽¹⁴⁾	95	75	12	50	9
35KhG2	860	"	600	"	85	70	12	45	8
3C KhGS	880	"	540	Вода ⁽¹⁵⁾	110	85	10	45	4.5
38KhYu	930	Теплая вода ⁽¹⁵⁾	630	Вода или масло ⁽¹⁴⁾	95	75	10	45	8
38KhYuA	940	То же ⁽¹⁵⁾	640	То же ⁽¹⁴⁾	100	85	14	50	9
20KhG	880	Масло ⁽¹³⁾	180	Воздух ⁽¹⁷⁾	90	75	10	40	—

Key:

1. Brand of steel
2. Conditions of thermal treatment
3. Hardening
4. Tempering
5. Temperature, °C
6. Cooling medium
7. Mechanical properties
8. Ultimate strength, kg-f/mm^2
9. Yield limit, kg-f/mm^2
10. Elongation, %
11. Constriction, %
12. Impact viscosity, $\text{kg-f} \times \text{m/cm}^2$
13. Oil
14. Water or oil
15. Warm water
16. The same
17. Air
18. Water

Note. 1. The standards of mechanical properties given in the table cover hot-rolled sectional steel used as construction material.
 2. The indicators of mechanical properties for brands of steels not indicated in the table are set by special specifications.
 3. The standards presented in the table for mechanical properties cover steel with profile dimension to 80 mm. A reduction in the standards is permissible for profiles larger than 80 mm.

TABLE III-22. MECHANICAL PROPERTIES OF HIGH PRESSURE PIPE METAL MADE OF ALLOY STEEL^{1,7,8}

Coefficients of conversion into SI system: mechanical stress--kg-f/mm² x 9.80665 x 10⁶ = n/m²; impact viscosity--kg-f x m/cm² x 98066.5 J/m²

(1) Марка стали	(2) Предел прочности кгс/мм ²	(3) Предел текучести кгс/мм ²	(4) Относительное удлинение, %		(5) Поперечное сужение %	(6) Ударная вязкость кгс·м/см ²
			δ ₁₀	δ ₅		
15KhF	45	25	—	20	45	4.8
30KhMA	60	40	13	—	45	8
15KhM	45	25	18	19	45	6
12MKh	42	28	18	19	45	7
18Kh3MV (EI578)	65	45	—	18	—	12
20Kh3MVF (EI579)	80	50	—	14	—	6

Key:

1. Brand of steel
2. Ultimate strength, kg-f/mm²
3. Yield limit, kg-f/mm²
4. Relative elongation, %
5. Transverse constriction, %
6. Impact viscosity, kg-f x m/cm²

Note: The table indicates the minimum values of mechanical properties.

TABLE III-23. CONVENTIONAL YIELD LIMIT (0.2% OF RESIDUAL DEFORMATION) OF HIGH PRESSURE PIPE METAL MADE OF ALLOY STEEL AT INCREASED TEMPERATURES^{1,7,8} (in kg-f/mm²)

(1) Марка стали	(2) Температура, °C								
	20	200	250	300	350	400	450	500	550
15KhM	30	28	24.5	23.0	21.5	20.0	19	18	16
12MKh	28	25	22.5	22.5	21.0	19.0	17	15	13
18Kh3MV (EI578)	45	—	40	—	37	30	—	—	—
20Kh3MVF (EI579)	54	52	48	44	—	37	—	—	—

Key:

1. Brand of steel
2. Temperature, °C

Note: The conventional yield limit for steels 18Kh3MV and 20Kh3MVF is taken from the IG standards (GDR) for steels of the same chemical composition.

TABLES III-24. CONVENTIONAL CREEP LIMIT OF HIGH PRESSURE PIPE METAL MADE OF ALLOY STEEL^{1,7,8} (in kg-f/mm²)

(1) Марка стали	(2) Температура, °C							
	450	475	500	510	530	540	550	600
15KhM	12.0	9.0	6.5	5.8	4.8	4.0	3.5	2.7
12MKh	11.0	8.5	6.1	5.5	4.1	3.5	—	—
183MV (EI578)	22.0	—	11.0	—	—	—	—	—
20Kh3MV (EI579)	27.0	—	17.0	—	15 (at 520 °C)	—	11	—

Key:

1. Brand of steel
2. Temperature, °C

Note: The creep limit for steel brands 15KhM and 12MKh is given with creep rate 10^{-7} mm/mm x h, and for steel brands 18Kh3MV and 20Kh3MV--with creep rate of 10^{-6} mm/mm x h.

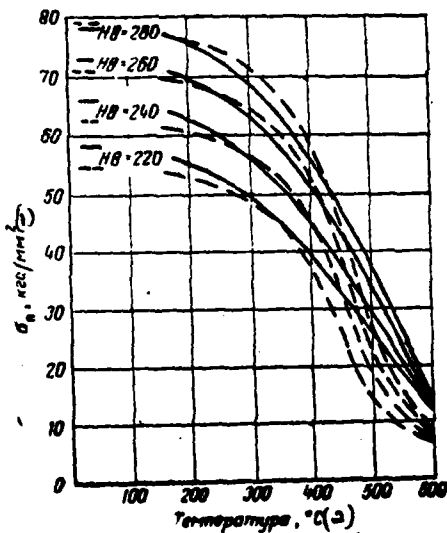


Figure III-6. Effect of Temperature on Change in Creep Limit of Steel No.10 (FRG) Which Has Passed Thermal Treatment to Varying Hardness

Key:

- hardening in air
- - - - - hardening in oil
- 1. kg-f/mm²
- 2. Temperature, °C

TABLE III-25. STRENGTH INDICATORS UNDER CONDITIONS OF CREEP FOR STEEL 20Kh3MV (EI579) (in kg-f/mm²)

(1) Температура испытания	Напряжение, вызывающее разрыв (2)		Напряжение, вызывающее (3) скорость ползучести	
	(4) за 10 000 ч	(5) за 100 000 ч	$1 \cdot 10^{-6}$ мм/мм·ч	$1 \cdot 10^{-7}$ мм/мм·ч
500	35	30	31.5	20
525	25	17.4	20.8	12
550	19	10.5	14	7
575	14.5	7.4	10	4.2
600	10.5	6	7.7	3.3

Key:

1. Testing temperature
2. Stresses causing rupture
3. Stresses causing creep rate
4. in 10,000 h
5. in 100,000 h

Note. The indicators are given for steel after normalization at 1000°C and tempering at 700°C with cooling in air (according to data of D'yakov, Giproneftemash).

Figure III-7 shows the dependence of time before rupture on the stress for steel 20Kh3MVF (according to data of Giproneftemash).

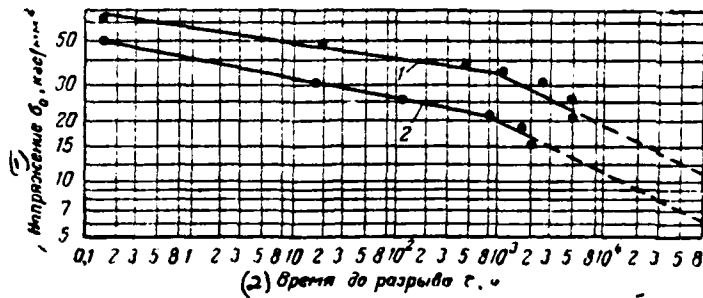


Figure III-7. Dependence of Time to Rupture on Stress for Steel 20Kh3MVF (EI579) at Temperatures 550 (curve 1) and 600°C (curve 2)

Key:

1. Stress, σ_0 , kg-f/mm²
2. Time to rupture, τ , h

TABLE III-26. MECHANICAL PROPERTIES OF STEEL 25Kh3NM (A-2 ACCORDING TO GIAP STANDARDS) FOR HOT CONTAINERS OF HIGH PRESSURE

(1) Механические свойства	(2) Температура стенки, °C				
	20	300	350	400	450
(3) Предел прочности, кгс/мм ² . . .	65-72 (65)	60-63	59-61	58-60	56-58
(4) Предел текучести, кгс/мм ² . . .	50-57 (50)	46-50 (35)	47-48	46-48	44-46
(5) Удлинение, %	15-20 (15)	12-18	11-12	10-12	12-13
(6) Сужение, %	50-63 (32)	55-60	55-60	53-58	50-52
(7) Ударная вязкость, кгс·м/см ²	10-15 (5)	15-16	14-15	13-15	11-14

Key:

1. Mechanical properties
2. Wall temperature, °C
3. Ultimate strength, kg-f/mm²
4. Yield limit, kg-f/mm²
5. Elongation, %
6. Constriction, %
7. Impact viscosity, kg-f x m/cm²

Note: In parentheses are the minimum values for the mechanical properties of the metal in large forgings that are governed by the appropriate specifications (TU).

TABLE III-27. MECHANICAL PROPERTIES OF SHEET STEEL OF BRAND 0.9G2DT (10G2T) and 30KhGSA IN SHIPMENT

Indicators	0.9G2DT(M) or 10G2T (M)							30KhGSA	
	4-10 mm	12-18	20-24	26-30	32-48	50-80	82-160	2-4	Over 4
Ultimate strength, kg-f/mm ² , no less	50	48	48	47	46	45	44	55-75	50-75
Yield limit, kg-f/mm ² , no less	35	33	32	31	30	28	24	-	-
Relative elongation, %, no less	18	18	18	18	18	18	18	18	15
GOST or TU	ChMTU TsNIICHM 157-59							GOST 2672-52	

Notes: 1. The impact viscosity of steel 0.9G2DT (10G2T) in kg-fx m/cm² at 20°C is no less than 6. At minus 40°C it is no less than 3.5. At minus 70°C it is no less than 3.
2. Samples of steel 30KhGSA which have been thermally treated (hardening at 870-890°C with cooling in oil and tempering at 510-570°C with cooling in oil) must have the following mechanical properties:

Ultimate strength, kg-f/mm ²	110
Relative elongation, σ ₅ , %	10
Impact viscosity, kg-f ⁵ x m/cm ²	5

TABLE III-28. MECHANICAL PROPERTIES OF STEELS USED TO MAKE DOWELS, BOLTS, NUTS WORKING AT HIGH TEMPERATURES^{1,10}

(i) Марка стали	(a) Температура, °C											
	20	100	200	300	350	400	425	450	475	500	525	550
	(a) Предел текучести (0,2% остаточной деформации), кгс/мм ²											
30KhA	50-49	-	-	-	49-45	47-43	-	-	-	-	-	-
40Kh	50-49	-	-	-	49-45	47-43	-	-	-	-	-	-
40KhF	85	-	-	45	-	-	-	-	-	-	-	-
30KhMA	80	-	-	-	45	40	-	35	-	30	-	-
25Kh1MF	75	-	-	68	-	60	-	55	-	45	-	35
	(d) Предел ползучести (кгс/мм ²) при скорости ползучести 0,8 · 10 ⁻⁷ мм/мм · ч											
30KhMA	-	-	-	-	-	-	13	9	8,5	4	-	-
25Kh1MF	-	-	-	-	-	-	-	20	13	8	5	3

Key:

- Brand of steel
- Temperature, °C
- Yield limit (0.2% residual deformation), kg-f/mm²
- Creep limit (kg-f/mm²) with creep rate 0.8 x 10⁻⁷ mm/mm x h

Note: The yield limit of steel brand 38KhA and 40Kh is from the laboratory No 7 of GIAP; steel 40KhF is from standards of IG (GDR)

for steels of similar composition.

TABLE III-29. MECHANICAL PROPERTIES OF PARTS OF HIGH PRESSURE PIPES MADE OF ALLOY STEELS (ACCORDING TO TU OF THE IRKUTSK BRANCH OF GIPRONEFTEMASH)

(1) Детали	(2) Марка стали	(3)	(4)	(5)	(6)	(7) Твердость НВ
		Предел прочности кгс/мм ²	Предел текучести кгс/мм ²	Относительное удлинение, %	Ударная вязкость кгс·м/см ²	
		(8) не менее				
(9) Фасонные фланцы глухие и переходные	20KhG	48	30	20	6	137-187
	18Kh3MV	65	45	18	8	197-241
	20Kh3MVF	80	60	14	6	241-285
(10) Фланцы резьбовые	38KhA	75	55	15	6	217-269
	25Kh1MFA	80	65	14	6	241-285
(11) Шпильки и гайки	38KhA	80	60	14	9	219-250
	35KhG2	75	55	15	8	207-255
	40KhA	80	65	14	8	241-285
	25Kh1MFA	85	70	13	8	255-302
	30KhMA	80	65	15	8	241-285
		70	50	15	6	241-285

Key:

1. Parts
2. Brand of steel
3. Ultimate strength, kg-f/mm²
4. Yield limit, kg-f/mm²
5. Relative elongation, %
6. Impact viscosity, kg-f x m/cm²
7. HB hardness
8. No less
9. Molded flanges, blind and connecting
10. Threaded flanges
11. Dowels and nuts

High pressure pipes (for $P_{раб} = 320$ and 700 kg-f/cm²) are made and supplied according to ChMTU UkrNITI 518-63 (specifications for steel seamless pipes for high pressure units of chemical and petrochemical industries:

(1) Условный проход, мм	(2) Номинальное рабочее давление кгс/см ²		(1) Условный проход, мм	(2) Номинальное рабочее давление кгс/см ²	
	320	700		320	700
6	12×3	15×4.5	70	102×16	127×28
10	20×4.5	25×7	90	127×18	159×36
15	25×5	35×9	100	140×20	180×40
25	45×9	50×12	125	180×28	219×48
32	50×9	68×16	150	219×32	273×60
40	68×12	83×19	200	273×38	
60	83×14	102×22			

Key:

1. Conventional passage, mm
2. Nominal working pressure, kg-f/cm²

The permissible deviations for pipe dimensions must not exceed those indicated below:

	Outer diameter, mm			Wall thickness, mm	
	to 30	30-50	over 50	to 5	over 5
For cold-drawn and cold-rolled pipes	±0.3mm	±0.4mm	±0.8mm	±10%	±8%
For hot-rolled pipes	±1%	(for all dimensions)		±15%	±15%

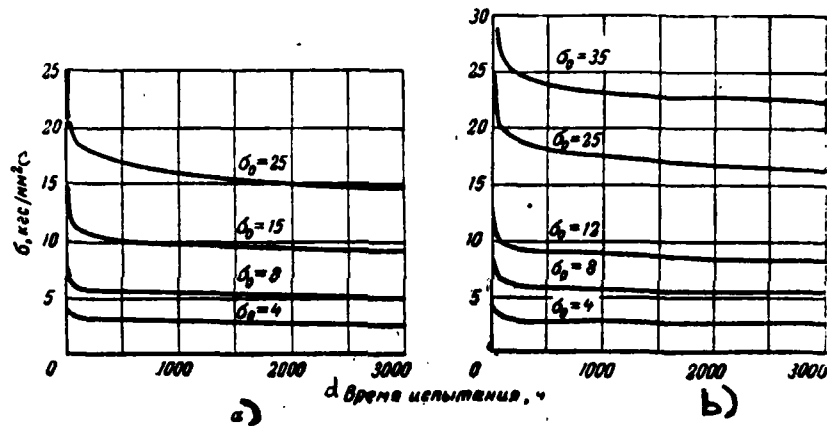
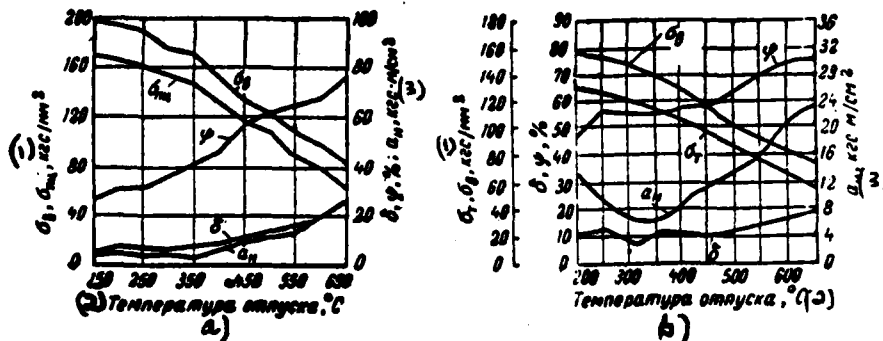


Figure III-8. Relaxation Curves for Steels Brand 30KhMA and 25Kh1MFA Which Have Passed Normalization at 1000°C and Tempering at 650°C

Key:

- a. For steel 30KhMA with testing temperature of 450°C
- b. For steel 25Kh1MFA at testing temperature 500°C (σ_0 -- initial stress)
- c. kg-f/mm²
- d. Testing time, h



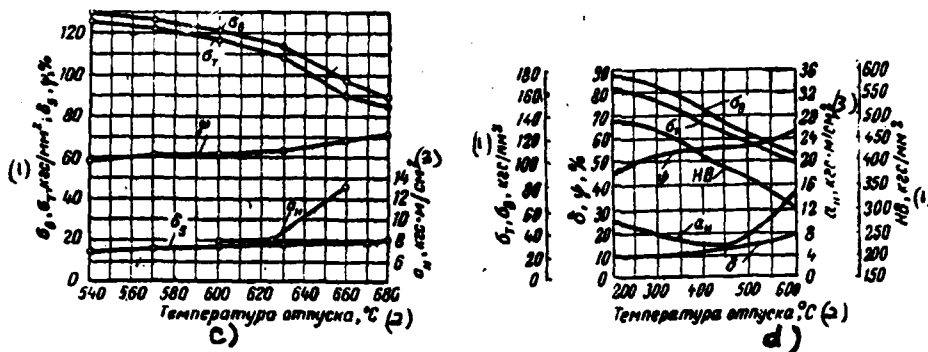


Figure III-9. Effect of Tempering Temperature on Mechanical Properties of Alloyed Steels of Different Brands

Key:

- a. 40Kh and 38KhA
- b. 30KhMA
- c. 25Kh1MFA
- d. 30KhGS (duration of tempering 50 min., cooling in water)

- σ_b $\sigma_{0.2}$ σ_T . Respectively ultimate strength, limit of proportionality and yield limit, kg-f/mm²
- HB. Brinell hardness, kg-f/mm²
- δ . Relative elongation, %
- ψ . Transverse constriction, %
- α_k . Impact viscosity
- 1. kg-f/mm²
- 2. Tempering temperature, °C
- 3. kg-f x m/cm²

High-Alloy (Scale-Resistant and High-Temperature) Steels

The temperature for the beginning of intensive oxidation in air of carbon steel approximately equals 530°C, and of low-alloy steels (for example, steel 30KhMA) about 560°C. The strength indicators of the carbon and low-alloy steels in the temperature interval of 500-600°C drastically drop even in the most thermally-stable low-alloy steels (fig. III-6, III-7). At high temperatures, therefore, special high-alloy scale-resistant and high-temperature steels are used.

Scale-resistant steels are resistant to chemical destruction of the surface in gas media at 600°C and higher in an unloaded or slightly loaded condition.

High-temperature steels maintain sufficient scale-resistance and mechanical strength at high temperatures.

TABLE III-30. CHEMICAL COMPOSITION (%) OF CERTAIN SCALE-RESISTANT STEELS (GOST 5632-61)

(1) Марка стали	C	Si	Mn	Cr	Ti	Al	NI	S	P
							(2) не более		
Kh5	0.15	0.30—0.60	0.50	4.50—6.00	—	—	0.50	0.025	0.035
Kh5SYu	0.15	1.20—1.80	0.50	5.50—7.00	≤0.20	0.70—1.10	0.30	0.025	0.035
lKh13	0.09—0.15	0.60	0.60	12.0—14.0	—	—	0.60	0.025	0.035
Kh17T	0.10	0.80	0.70	16.0—18.0	5C+0.60	—	0.60	0.025	0.035
Kh18SYu	0.15	1.00—1.50	0.50	17.0—20.0	—	0.70—1.20	0.50	0.025	0.035
Kh25T	0.15	1.00	0.80	24.0—27.0	5C+0.80	—	0.60	0.025	0.035

Key:

1. Brand of Steel
2. no more than

TABLE III-31. PHYSICAL PROPERTIES OF CERTAIN SCALE-RESISTANT STEELS¹¹

(1) Марка стали	(2) Плот- ность г/см ³	(3) Температура, °C							
		20—100	20—400	20—600	20—800	100	400	600	800
		(4) Средние значения коэффициента линейного расширения $\alpha \cdot 10^6, \text{град}^{-1}$				(5) Коэффициент теплопро- водности $\lambda \text{ ккал}/(\text{м} \cdot \text{ч} \cdot \text{град})$			
lKh13	7.74	10.1	11.4	12.25	—	23.76	23.76	22.7	—
Kh17T	7.70	10.4	11.2	11.60	12.1	—	—	—	—
Kh25T	7.65	—	10.8	11.20	11.7	—	20.00	22.2	24.0

Key:

1. Brand of steel
2. Density, g/cm³
3. Temperature, °C
4. Average values of coefficient of linear expansion, $\alpha \times 10^6, \text{deg}^{-1}$
5. Coefficient of heat conductivity $\lambda \text{ kcal}/(\text{m} \times \text{h} \times \text{deg})$

Note: For steels Kh17T and Kh25T, data are presented which correspond to steels Kh17 and Kh25.

Below are the values for the elasticity modulus E for certain

chrome steels at 20°C:

Steel	E, kg-f/mm ²
lKh13	21,000
Kh17T	21,000
Kh25T	20,000

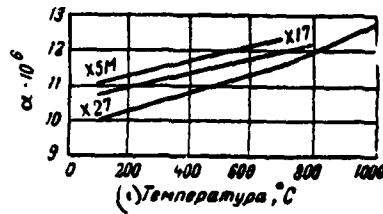


Figure III-10. Dependence of Coefficient of Linear Expansion of Chrome Steels on Temperature

Key:

1. Temperature

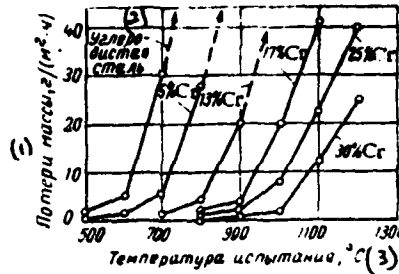


Figure III-11. Losses of Mass of Certain Chrome Steels Depending on Temperature of Oxidation in Air with Testing Duration 200 h.

Key:

1. Losses of mass, g/(m² x h)
2. Carbon steel
3. Testing temperature, °C

TABLE III-32. CONDITIONS OF USING SCALE-RESISTANT STEELS

Brand of steel	Ultimate working temp. of medium, °C	Purpose of steel	Resistance in gas media, containing			
			SO ₂	H ₂ S	N ₂ with small quantity of O ₂	carbonizing components
Kh5	600-650	Pipes of apparatus	Average	-	-	-
Kh6S10	800	Pipes, parts of boiler units	High	Average	Low	Average
lKh13	700	Pipes, parts of boilers	High	Average	Low	Average
Kh17T	900	Pipes of heat-exchangers	Average	-	-	-
Kh18S10	1050	Pipes of pyrolysis units	High	Average	Low	Average
Kh25T	1050	The same	Average	-	Low	Average

Note: At temperature to 500°C, steel of brand lKh13 is scale-resistant and heat-resistant.

TABLE III-33. MECHANICAL PROPERTIES OF SCALE-RESISTANT STEELS (GOST-5949-61)

(1) Марка стали	(2) Условия термической обработки				(7) Предел прочности кгс/мм ²	(8) Предел текучести кгс/мм ²	(9) Относительное удлинение, %	(10) Поперечное сужение, %	(11) Ударная вязкость кгс·м/см ²	(12) Твердость HB не более
	отжиг (3)		отпуск (4)							
	(5) температура °C	(6) охлаждающая среда	(5) температура °C	(6) охлаждающая среда						
Kh5	860	Воздух ⁽¹⁴⁾	—	—	40	17	24	50	10	4.6
Kh6SYu	750—800	Воздух или масло ⁽¹⁵⁾	—	—	45	25	20	40	12	4.2
1Kh13	1000—1050 (закалка) (16)	То же ⁽¹⁴⁾	700—790	Воздух или масло ⁽¹⁵⁾	60	42	20	60	9	4.6
Kh17T	760—780	Воздух ⁽¹⁴⁾	—	—	50	—	18	—	—	—
Kh18SYu	800—850	Воздух или вода ⁽¹⁴⁾	—	—	50	30	20	50	—	4.8
Kh25T	750	Воздух ⁽¹⁴⁾	—	—	45	30	20	45	—	5.0

Key:

1. Brand of steel
2. Conditions of thermal treatment
3. Annealing
4. Tempering
5. Temperature, °C
6. Cooling medium
7. Ultimate strength, kg-f/mm²
8. Yield limit, kg-f/mm²
9. Relative elongation, %
10. Transverse constriction, %
11. Impact viscosity, kg-f x m/cm²
12. Brinell hardness HB, no more
13. No less
14. Air
15. Air or oil
16. The same
17. Air or water
18. Hardening

TABLE III-34. CREEP LIMIT OF CERTAIN SCALE-RESISTANT STEELS^{1,11} (IN kg-f/mm²)

(1) Марка стали	(2) Скорость ползучести	(3) Температура, °C							
		550	600	650	700	800	875	900	1000
1Kh13	1% за 10 000 ч	7.6	3.2	1.5	—	—	—	—	—
	1% за 100 000 ч	6.1	3.0	1.2	—	—	—	—	—
Kh17T	1% за 10 000 ч	—	2.8	1.0	0.20	—	—	—	—
	1% за 10 000 ч	—	—	—	0.80	—	0.17	—	0.008
Kh25T	1% за 10 000 ч	—	—	—	0.90	—	0.20	—	0.012
	2% за 10 000 ч	—	—	—	—	—	—	—	—

Key:

1. Brand of steel
2. Creep rate
3. Temperature, °C

TABLE III-35. COMPOSITION (IN %) OF CERTAIN SCALE-RESISTANT AND HIGH-TEMPERATURE STEELS (GOST 5632-61)

Марка стали (1)	C	Si	Mn	Cr	Ni	Ti	Mo	S P	
								(2) не более	
Kh6M	0.50	1.50-2.00	0.7	5.0-6.0	—	—	0.45-0.60	0.030	0.035
Kh18N9T	0.12	0.08	1.0-2.0	17.0-19.0	9.0-11.0	(C-0.02) 5	—	0.020	0.035
Kh23N18	0.20	1.00	2.0	22.0-25.0	18.0-20.0	—	—	0.020	0.035
Kh18N12M2T	0.12	0.80	2.0	16.0-19.0	11.0-14.0	0.30-0.60	2.00-3.00	0.030	0.035
Kh25N20S2	0.20	1.20-2.00	0.2-0.7	24.0-27.0	18.0-21.0	—	—	0.020	0.035
Kh14N3T (EI711)	0.10	0.80	13.0-15.0	13.0-15.0	2.5-3.5	(C-0.02) 5	—	0.020	0.035

Key:

1. Brand of steel
2. No more than

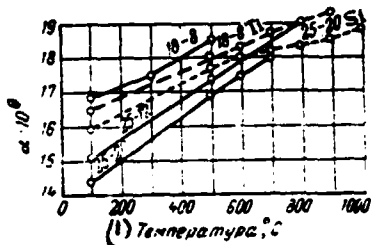


Figure III-12. Dependence of Coefficient of Linear Expansion of Certain Austenite Steels on Temperature

1. Temperature, °C

Figure III-13. Change in Mass of Certain Austenite Steels Depending on Temperature of Oxidation in Air with Duration of Testing 200 h

Key:

1. Testing temperature, °C
2. Loss of mass, g/(m² x h)
3. 10 g/(m² x h) at 1200°C
4. Nichrome

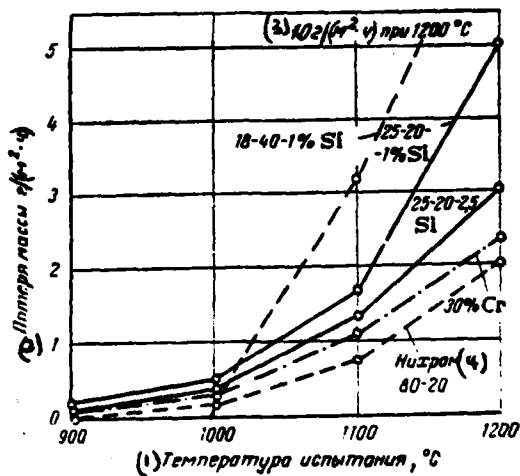


TABLE III-36 PHYSICAL PROPERTIES OF CERTAIN HEAT-RESISTANT AND SCALE-RESISTANT STEELS
 Coefficient of conversion into SI system: heat conductivity--kcal/(m x h x deg) x 1.163 = W/(m x deg)

(1) Марка стали	(2) Температура, °C							(3) Коэффициент теплопроводности λ, ккал/(м х h х deg)							
	0-100	0-100	0-500	0-700	0-800	0-900	0-1000	100	200	300	400	500	600	800	900
Kh6SM	11.0	12.0	12.20	12.35	—	—	—	—	—	—	—	28.0	—	25.0	—
Kh25N20S2	16.1	—	17.80	17.80	18.10	18.5	18.8	12.0	—	—	—	18.8	20.2	23.2	24.3
Kh14N18T	16.6	17.0	18.20	18.60	18.90	19.3	—	13.9	—	—	—	19.0	20.4	23.2	—
Kh23N18	15.4	17.42	19.2	21.23	22.02	22.4	—	13.3	14.4	16.20	17.6	19.1	20.5	23.8	—
	(при 20-100 °C)	(сред.)	(сред.)	(сред.)	(сред.)	(сред.)	(сред.)								
Kh14G14N3T (EI711)	10.1	18.20	19.04	19.74	20.02	20.7	21.1	16.5	15.5	15.55	—	17.3	18.4	20.2	—
	(при 100 °C)	(при 200 °C)	(при 400 °C)	(при 500 °C)	(при 600 °C)	(при 700 °C)	(при 800 °C)								

- Key:
1. Brand of steel
 2. Temperature, °C
 3. Average coefficient of linear expansion $\alpha \times 10^6$, deg⁻¹
 4. Coefficient of heat conductivity λ , kcal/(m x h x deg)
 5. At

TABLE III-37. PURPOSE AND CONDITIONS OF OPERATION OF CERTAIN HIGH-TEMPERATURE AND SCALE-RESISTANT STEELS

Brand of steel	Purpose	Ultimate working temperature °C	Operating life	Temperature for beginning of intensive oxidation in air, °C
Kh6SM	Pipes, parts of pumps, bolts plungers	660	Long	700
1Kh18N9T	Pipes, adapters of ammonia and methanol synthesis columns, heat exchangers, parts of furnace fittings, muffles, sleeves and collectors of exhaust systems	600	Very long	800-850
Kh23N18	Parts of units in chemical and oil sectors of industry, gas pipelines, pipes of pyrolysis furnaces	1000	Long	1050
Kh25N20S2	Suspensions and supports of boilers, pipes of furnaces of pyrolysis and conversion	1000-1100	The same	1150-1200
Kh18N12-M2T	Parts of units in chemical industry, pipes of pyrolysis furnaces	700	"	800-850
Kh14G14-N3T	Substitute of steel 1Kh18N9T under conditions indicated for this steel	600	"	800-850

- Note: 1. In low pressure units, steels Kh18N9^T, Kh18N12M2T and Kh14G14N3T can be used at higher temperatures than indicated in the table. In this case, one should take into consideration the temperature for the beginning of oxidation indicated in the table.
2. In the temperature interval 600-800°C, steels Kh23N18 and Kh25N20S2 are prone to embrittlement (formation of σ-phase).

TABLE III-38. MECHANICAL PROPERTIES OF STEEL DEFINED ON THERMALLY-TREATED SAMPLES (GOST 5949-61)
Coefficient of conversion into SI system: mechanical stress--kg-f/mm² x 9.80665 x 10⁶ = n/m²

Brand of steel	Conditions of thermal treatment of blanks or samples		Ultimate strength kg-f/mm ²	Yield limit kg-f/mm ²	Relative elongation %	Relative constriction %
	Hardening temp. °C	Cooling medium				
1Kh18N9T	1050-1100	Water, air or oil	55	20	40	55
Kh23N18	1100-1150	Water or air	50	20	35	50
Kh25N20S2	1100-1150	The same	60	30	35	50
Kh18N12M2T	1050-1100	"	52	22	40	55
Kh14G14N3T	1000-1080	"	65	25	35	50

TABLE III-39. YIELD LIMIT AND MODULUS OF NORMAL ELASTICITY OF STEELS AT HIGH TEMPERATURES^{1,11}
(in kg-f/mm²)

(1) Марка стали	(2) Температура, °C										
	500	600	700	800	900	1000	20	100	300	500	700
	(3) Предел текучести						(4) Модуль нормальной упругости E · 10 ⁴				
Kh6SM	20.0	13.0	7.0	3.0	—	—	—	—	—	—	—
1Kh18N9T	14.0	13.0	12.0	8.0	5.0	3.5	2.05	—	1.82 (при 400 °C)	1.62	1.34 (при 600 °C)
Kh23N18	21.5	20.5	20.3	16.6	—	—	2.04	—	1.84	1.73	1.53
Kh25N20S2	16.0	16.0	15.0	12.0	7.0	5.0	—	—	—	—	—
Kh14G14N3T	11.0	9.3	8.0	—	—	—	2.31	2.073	1.88	1.65	1.47
Kh18N12M2T	13.0 (при 550 °C)	12.5	12.0 (при 650 °C)	—	—	—	—	—	—	—	—

Key:

1. Brand of steel
2. Temperature, °C
3. Yield limit
4. Modulus of normal elasticity, E x 10⁴
5. At

Note: For steel Kh23N18, the yield limit is given after aging at 800°C for 4 h.

TABLE III-40. CREEP LIMIT σ_n OF HIGH-TEMPERATURE AND SCALE-RESISTANT STEELS (in kg-f/mm²)
Coefficient of conversion into SI system: mechanical stress kg-f/mm² x 9.80665 x 10⁶ = n/m²

(1) Марка стали	(2) Скорость ползучести за 10 000 ч %	(3) Температура, °C								
		600	650	700	750	800	875	1000	1100	
Kh6SM	1	3.5	2.2	1.2	0.70	0.20	—	—	—	
1Kh18N9T	1	10.0	—	1.5	0.60	—	—	—	—	
	2	10.5	—	1.9	0.75	—	—	—	—	
Kh23N18	1	—	—	4.5	—	1.30	0.7	0.14	—	
	2	—	—	5.0	—	1.60	0.8	0.17	—	
Kh25N20S2	1	—	—	—	—	—	0.6	0.13	0.02	
	2	—	—	—	—	—	0.6	—	0.03	
Kh18N12M2T	1	7.0	5.0	—	—	—	—	—	—	
Kh14G14N3T	1	10.0	—	3.0	—	0.92	—	—	—	

Key:

1. Brand of steel
2. Creep rate in 10,000 h, %
3. Temperature, °C

Note: For the presented brands of steel (except Kh6SM), it is recommended that the coefficient of reduction in working stress 0.7 be used.

2. The creep limits for steel Kh18N12M2T are given with creep rate of 1% in 100,000 h.

TABLE III-41. CHEMICAL COMPOSITION (IN %) OF METAL OF CASTINGS MADE OF HIGH-ALLOY STEEL (GOST 2176-57)

Марка стали ⁽¹⁾	C не более ⁽²⁾	Si	Mn	Cr	Ni	Mo	Ti	S P	
								не более ⁽³⁾	не более
1Kh13L	0.15	He 60- лее 0.7	He 60- лее 0.6	12-14	He 60- лее 0.6	—	—	0.03	0.035
Kh25TL	0.20	> 1.2	> 0.8	23-27	> 0.6	—	0.4-0.8 От(3)	0.03	0.035
1Kh18N9TL	0.14	> 1.0	1.0-2.0	17-20	8-11	—	5 (C-0.03) до 0.8	0.03	0.035
Kh18N12M3TL	0.12	> 1.0	1.0-2.0	16-19	11-13	3-4	0.3-0.6	0.03	0.035
Kh25N15S2L	0.20	2.0-3.0	He 60- лее 1.5	23-27	18-20	—	—	0.03	0.035
Kh6S2ML	0.15	1.5-2.0	> 0.7	5-6.5	He 60- лее 0.6	0.45-0.60	—	0.03	0.035

Key:

1. Brand of steel
2. No more than
3. From 5 (C--0.03) to 0.8

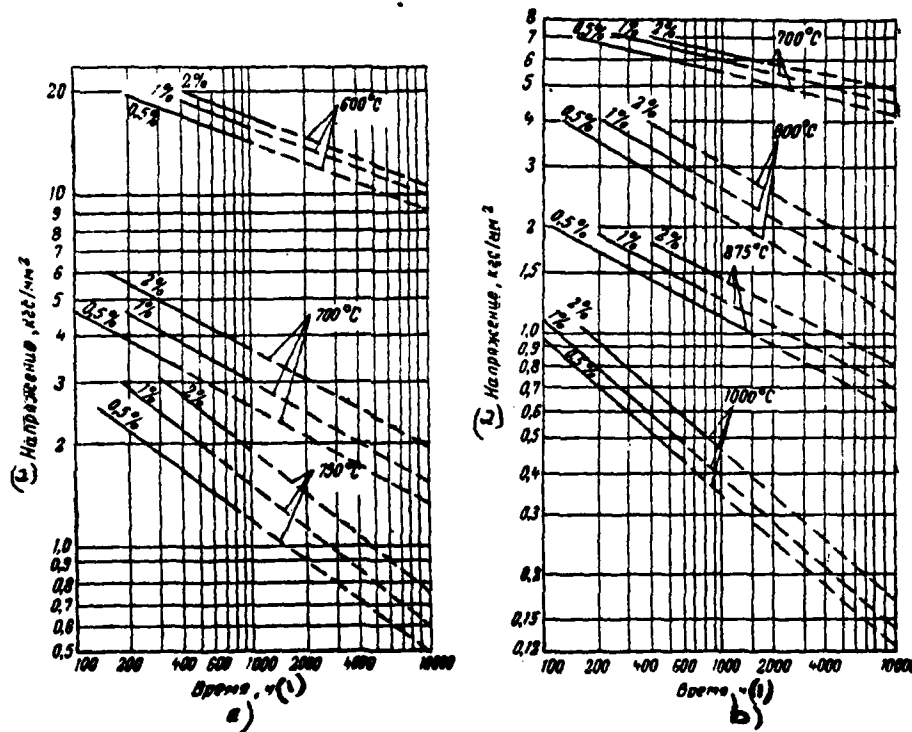


Figure III-14. Creep Limit of Steels of Different Brands at High Temperatures (for creep rate 0.5-2%)

Key:

- a. steels 1Kh18N9T at 600, 700 and 750°C
- b. steels Kh23N18 at 700, 800, 875 and 1000 °C
- c. steels Kh25N20S2 at 875, 1000 and 1100°C
1. Time, h
2. Stress, kg-f/mm²

Continuation of Fig. III-14

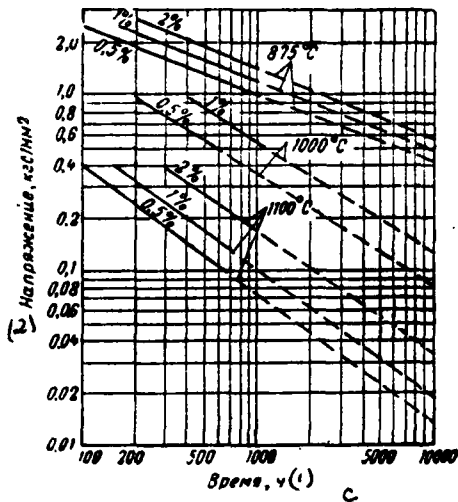


TABLE III-42. MECHANICAL PROPERTIES OF METAL OF CASTINGS

Brand of steel	Conditions of thermal treatment		Yield limit kg-f/mm ²	Ultimate strength kg-f/mm ²	Relative elongation, %	Relative constriction, %	Impact viscosity kg ₂ -f x m/cm ²
	Hardening temp. °C	Cooling medium					
	No less than						
1Kh13L*	1050	Water	40	56	20	50	8
Kh25TL	Without thermal treatment		28	45	-	-	-
1Kh18N9TL	1100	Water	20	45	25	32	10
Kh18N12M3-TL	1150	"	22	50	30	30	10
Kh25N19S2L	1100	"	25	50	25	28	-
Kn6S2ML	780	"	40	56	20	50	-

* Tempering temperature 500-750°C (depending on condition of application).

TABLE III-43. SAMPLE PURPOSE OF CASTINGS MADE OF HIGH-ALLOY STEELS

Brand of steel	Basic properties	Sample purpose
1Kh13L	High resistance to atmospheric corrosion. Scale-resistant to 700°C, heat-resistant to 500°C	Parts with increased plasticity in impact loads; fittings of cracking units
Kh25TL	Scale-resistant to 1100°C, acid-resistant	Parts of chemical equipment, furnace fittings with very small loads
1Kh18N9TL	Heat-resistant to 600°C, acid-resistant, scale-resistant in different gas media	Different parts of chemical equipment
Kh18N12M3TL	Heat-resistant to 800°C, acid-resistant	The same
Kh25N19S2L	Scale-resistant to 1100°C, acid-resistant	Pipes of conversion furnaces, furnace fittings,

Kh6S2ML Scale-resistant to 750°C, heat-resistant

and other parts at high temperatures and moderate loads
Parts operating under load at temperature to 750°C

It is difficult to fabricate rolled pipes made of steel 25/20, therefore pipes made of this steel, made by the method of centrifugal casting have been used. An increase in the carbon content in the metal of cast pipes to 0.3-0.5% promotes an increase in the strength under conditions of creep. Figure III-15 gives the curves of permissible stresses for cast and hammered steel brand 25/20 as applied to pipes.¹³

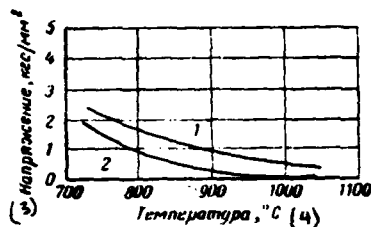


Figure III-15. Recommended Permissible Stresses with Different Temperatures for Cast and Hammered (or Rolled) Steel 25/20

Key:

1. Steel 25/20, cast with increased carbon content
2. Steel 25/20, hammered (or rolled), common
3. Stress, kg-f/mm²
4. Temperature, °C

Below is an example of foreign high-temperature steels and alloys are certain data on the so-called thermolloys which can be used in casting parts in American and English industry.

TABLE III-44. CHEMICAL COMPOSITION OF THERMOLLOYS (IN %)

(1) Марка термоллоя	(2) Обозначения по ASTM (США)	C	Mn	Si	P	S	Cr	Ni
			(3) не более					
T.30	HF	0.2-0.4	2	2.0	0.04	0.04	18-23	8-12
T.38E	HE	0.2-0.5	2	2.0	0.04	0.04	26-30	8-12
T.40B	HH	0.2-0.5	2	2.0	0.04	0.04	24-28	11-14
T.47	HK	0.2-0.5	2	3.0	0.04	0.04	24-28	18-22
T.50	HT	0.4-0.7	2	2.5	0.04	0.04	13-17	33-37
T.58	HV	0.4-0.7	2	2.5	0.04	0.04	17-21	37-41
T.72	HW	0.4-0.7	2	2.5	0.04	0.04	10-14	58-62
T.85	HX	0.4-0.7	2	2.5	0.04	0.04	16-20	65-69

Key:

1. Brand of thermolloy
2. Designations according to ASTM (United States)
3. No more than

TABLE III-45. PERMISSIBLE TEMPERATURES OF THE USE OF THERMOLLOYS IN DIFFERENT MEDIA (IN °C)

(1) Марка термоллоя	(2) Воздух	(3) Окислительная среда		(4) Восстановительная среда	
		(5) с низким содержанием S	(6) с высоким содержанием S	(5) с низким содержанием S	(6) с высоким содержанием S
T.30	930	930	930	980	930
T.38E	1180	1180	1150	1180	1120
T.40B	1120	1120	1090	1120	1040
T.47	1180	1180	1120	1180	1040
T.50	1070	1070	980	1070	950
T.58	1120	1120	1070	1090	980
T.72	1070	1070	930	1070	870
T.85	1180	1180	1040	1180	1010

Key:

1. Brand of thermolloy
2. Air
3. Oxidizing medium
4. Reduction medium
5. With low S content
6. With high S content

Note. 1. With indicated permissible working temperatures, the amount of losses from oxidation does not exceed 1-1.2 mm/year.
 2. The adopted low sulfur content is $\sim 9 \text{ g/m}^3$, the high content is about 200 g/m^3 .

TABLE III-46. CREEP LIMIT OF THERMOLLOYS WITH CREEP RATE 1% IN 10,000 h (in kg-f/mm²)

Марка термоллоя ⁽¹⁾	(2) Температура, °C				Марка термоллоя ⁽¹⁾	(2) Температура, °C			
	760	871	982	1093		760	871	982	1093
T.30	4.20	2.24	—	—	T.50	5.60	3.15	1.40	0.35
T.38E	2.45	1.40	0.70	—	T.58	5.95	3.50	1.54	0.42
T.40B	2.10	1.19	0.77	0.21	T.72	4.20	2.10	0.98	—
	4.90	2.80	1.47	0.56	T.85	4.48	2.24	1.12	0.42
T.47	4.76	2.94	1.88	0.70					

Key:

1. Brand of thermolloy
2. Temperature, °C

Note: 1. The values for the creep limits are given for operating regimes with constant temperature; with cyclically changing temperatures, they must be reduced.
 2. For thermolloy T.40B, two values are given for the creep limit: the first corresponds to partially ferrite structure, the second to completely austenite.

A casting made of high-temperature steels and alloys usually possesses higher heat-resistance properties than rolled and forged

pieces. This is primarily explained by the structural feature of cast metal and the increased content of carbon. More heat-resistant parts are obtained with centrifugal casting, therefore, for example, pipes for tube furnaces of pressure conversion are made of thermolloy T.47 by centrifugal casting. The advantages of cast metal in the ~~area~~^{area} of heat-resistance are characterized by the curves in fig. III-15.

Special (High-chrome and High-silicon) Alloys

Castings made of high-chrome steels have high corrosion resistance and heat-resistance at a temperature to 1100-1150°C. They are used in the nitrogen industry for casting housings of acid pumps, bubbling pipes, etc.

TABLE III-47. COMPOSITION AND PHYSICAL-MECHANICAL PROPERTIES OF CASTINGS MADE OF HIGH-CHROME STEELS (GOST 2176-67)

Indicators	Brand	
	Kh28L	Kh34L
Composition, %		
C	0.5-1.0	1.5-2.2
Si	0.5-1.3	1.3-1.7
Mn	0.5-0.8	0.5-0.8
Cr	26-30	32-36
S, no more	0.08	0.10
P, no more	0.10	0.10
Density, g/cm ³	7.3-7.4	7.3-7.4
Melting point, °C	1350-1450	1350-1450
Coefficient of linear expansion in temperature interval 0-200°C, deg. ⁻¹	(9.4-10) x 10 ⁻⁶	(9.4-10) x 10 ⁻⁶
Modulus of elasticity, kg-f/mm ²	18,000-22,000	18,000-22,000
	No less than	
Brinell hardness	220-270	250-320
Ultimate strength, kg-f/mm ²		
in rupture	35	40
in bending	55	60
in stretching		
at 800°C	15-18	20-22
at 900°C	9-12	12-15
at 1000°C	5-7	10-12
at 1100°C	3-4	6-8
Deflection with distance between supports 600 mm, mm	6	5

The nitrogen industry in the shops of concentrated nitric (and sulfuric) acid uses different parts made of high-silicon pig iron

(ferrosilide): pipes, molded parts, valves, column parts. Parts made of ferrosilide are also used in the sulfuric acid production.

TABLE III-48. COMPOSITION AND PHYSICAL-MECHANICAL PROPERTIES OF CASTINGS MADE OF HIGH-SILICON ALLOYS (FERROSILIDES) (GOST 2233-43)

Indicators	Brand of alloy	
	S15	S17
Composition, %		
C	0.5-0.8	0.3-0.5
Si	14.5-16.0	16.0-18.0
Mn	0.3-0.8	0.3-0.8
P, no more	0.10	0.10
S, no more	0.07	0.07
Physical properties		
density, g/cm ³	6.9	6.9
melting point, °C	1200	1200
average coefficient of linear expansion in temperature interval 0-200°C, deg ⁻¹	4.7 x 10 ⁻⁶	4.7 x 10 ⁻⁶
coefficient of heat conductivity λ, cal/(cm x s x deg)	0.125	0.125
electrical resistance, ρ Ohm x mm ² /m	0.63	0.63
Mechanical properties		
ultimate strength in bending, kg-f/mm ²	17	14
deflection with distance between supports 600 mm, mm	2	1.5
Brinell hardness HB, kg-f/mm ²	300-400	400-600

Since the mechanical properties of the castings deteriorate with an increase in the silicon content, pig iron of brand S17 is only used in those cases where a casting of increased chemical stability is required.

Solid Alloys

In certain cases, when making throttle devices for operation in media that cause considerable erosion, valves, valve seatings, diaphragms and other parts made of the solid alloys indicated below are used.

The composition and properties of the solid alloys (according to GOST 4872-65):

Brand of alloy
Composition, %

VK3	VK6	VK8

W_2C	97	94	92
$C\delta$	3	6	8
Density, g/cm^3	14.9	14.6	14.4
Rockwell hardness R_A	89.0	88.5	88.0
Ultimate strength in bending, $kg-f/mm^2$	100	130	140

Consultation on designing parts made of solid alloys can be obtained from the design office of the Moscow Plant of Solid Alloys.

Nonferrous Metals and Their Alloys

Copper

TABLE III-49. COMPOSITION AND PROPERTIES OF COPPER OF DIFFERENT BRANDS (GOST 859-66)

Показатели ⁽¹⁾	Марки меди ⁽²⁾				
	М0	М1	М2	М3	М4
⁽³⁾ Состав, %					
Cu, не менее ⁽⁴⁾	99.95	99.90	99.70	99.50	99.00
⁽⁵⁾ примеси, не более	0.05	0.10	0.30	0.50	1.00
⁽⁶⁾ в том числе					
Bi	0.002	0.002	0.002	0.003	0.005
Sb	0.002	0.002	0.005	0.050	0.200
As	0.002	0.002	0.010	0.050	0.200
Fe	0.005	0.005	0.050	0.050	0.100
Ni	0.002	0.002	0.200	0.200	—
Pb	0.005	0.005	0.010	0.050	0.300
Sn	0.002	0.002	0.050	0.050	—
Zn	0.005	0.005	—	—	—
S	0.005	0.005	0.010	0.010	0.020
O ⁽⁷⁾	0.020	0.080	0.100	0.100	0.150
Физические свойства					
⁽⁸⁾ плотность, g/cm^3	8.9	8.9	—	8.89	8.89
⁽⁹⁾ коэффициент линейного расширения при $20^\circ C$, $\alpha \cdot 10^6 \text{ град}^{-1}$	17.7	17.7	—	17.4	17.3
⁽¹⁰⁾ теплопроводность, $кал/(см \cdot сек \cdot град)$	0.96	0.95	—	0.43	—
⁽¹¹⁾ Модуль нормальной упругости, $кас/мм^2$	11 200	11 200	—	11 200	11 200

Key:

1. Indicators
2. Brand of copper
3. Composition
4. Cu, no less
5. Admixtures, no more
6. Including
7. Physical properties
8. Density, g/cm^3
9. Coefficient of linear expansion at $20^\circ C$, $\alpha \times 10^6 \text{ deg}^{-1}$
10. Heat conductivity, $кал/(см \times s \times \text{deg})_2$
11. Modulus of normal elasticity, $кг-ф/мм^2$

TABLE III-50. MECHANICAL PROPERTIES OF COPPER AT DIFFERENT TEMPERATURES¹⁴

Механические свойства (1)	(2) Температура, °C						
	-253	-196	17	100	200	300	500
3) Предел прочности, кгс/мм ² . . .	46	38	24	22	18	15	8.4
4) Относительное удлинение, % . . .	48	41	—	48	46	32	18
5) Относительное сужение, % . . .	74	72	—	—	—	—	—
6) Ударная вязкость, кгс·м/см ² . . .	—	—	—	5	4.9	4.8	4.8

Key:

1. Mechanical properties
2. Temperature, °C
3. Ultimate strength, kg-f/mm²
4. Relative elongation, %
5. Relative constriction, %
6. Impact viscosity, kg-f x m/cm²

Below are the mechanical properties of sheet copper (GOST 495-50) and copper pipes (GOST 617-64):

Grades	σ_B	δ_{10}	Grades	σ_B	δ_{10}
	kg-f/mm ²	%		kg-f/mm ²	%
	no less			no less	
Sheets, cold-rolled soft	20	30	Pipes drawn, soft	21	35
the same, hard	30	3	pressed	19	35
hot-rolled	20	30			

The strength properties of copper depend on the degree of its deformation (fig. III-16).

Solid, cold-hardened copper as a result of deformation can be made into a soft state by annealing at a temperature of 500-700°C.

Copper of brands M0 and M1 are used to fabricate current conductors, alloys of high purity and high-quality special bronzes. The rolled products, sheets and pipes, are usually made of copper brands M2 and M3.

According to the norms of the State Mining Inspection, the use of sheets and pipes made of copper of brands M2 and M3 to make containers operating under pressure is only permitted in limits of temperatures from -196 to +250°C. One should take into consideration that at high temperatures in a gas medium, the reduction gases

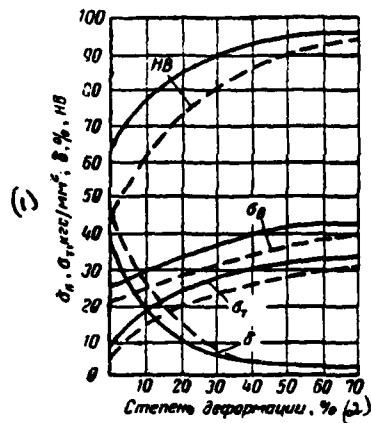


Figure III-16. Change in Mechanical Properties of MO Copper Depending on Degree of Deformation and Grain Size

Key:

- material with grain 0.015 mm
- material with grain 0.040 mm
- 1. kg-f/mm²
- 2. Degree of deformation, %

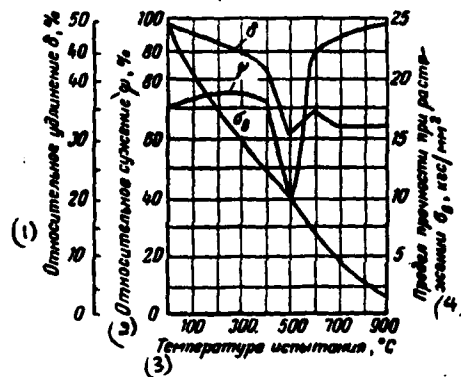


Figure III-17. Mechanical Properties of M1 Copper at High Temperatures

Key:

- 1. Relative elongation
- 2. Relative constriction
- 3. Testing temperature
- 4. Ultimate strength in stretching, σ_B , kg-f/mm²

(such as hydrogen, carbon monoxide and hydrocarbons) cause embrittlement of the oxidized copper. The latter can occur, for example, when copper is influenced by alternating reducing and oxidizing media.

Aluminum

Aluminum has relatively low density, high plasticity, electrical conductivity, heat conductivity, cold-resistance and corrosion resistance in a number of media. The nitrogen industry uses it in the fabrication of equipment and pipelines in the shops of concentrated nitric acid, in the deep cold units, as a packing material in packing flange compounds of high pressure, etc.

Below are certain physical properties of aluminum:

Density, g/cm ³	2.7
Coefficient of linear expansion, α , deg ⁻¹	23.8 x 10 ⁻⁶

Coefficient of heat conductivity*

λ , cal/(cm x s x deg)

0.52

Specific resistance* ρ , Ohm x mm²/m

0.026

*Coefficients of conversion into SI system: cal/(cm x s x deg) x 418.68 = W/(m s deg)
 Ohm x mm²/m x 10⁻⁶ = Ohm x m

TABLE III-51. CHEMICAL COMPOSITION OF ALUMINUM (IN %) OF DIFFERENT BRANDS (GOST 11069-64)

Brand	Al no less	Admixtures, no more					Sample purpose
		Fe	Si	Fe+Si	Cu	total	
AV0000	99.996	0.0015	0.0015	—	0.0010	0.004	For chemical apparatus of special purpose, electrical apparatus, electrical equipment
AV000	99.99	0.0030	0.0025	—	0.0050	0.010	
AV00	99.97	0.015	0.015	—	0.0050	0.03	
AV0	99.93	0.04	0.04	—	0.01	0.07	Cable, chemical apparatus, aluminum alloys, aluminum alloys, vessels, consumer goods
A000	99.80	0.12	0.10	0.18	0.01	0.20	
A00	99.70	0.16	0.16	0.26	0.01	0.30	
A0	99.6	0.25	0.20	0.36	0.01	0.40	
A1	99.5	0.30	0.30	0.45	0.015	0.50	
A2	99.0	0.50	0.50	0.90	0.02	1.0	
A3	98.0	1.1	1.0	1.80	0.05	2.0	

TABLE III-52. MECHANICAL PROPERTIES OF SHEET ALUMINUM (GOST 7869-56)

Condition during shipping	Sheet thickness, mm	Ultimate strength, kg-f/mm ²	Relative elongation δ_{10} , % no less
Annealed (soft)	To 0.5	Not more than 11	20
	0.5-0.9		25
	Over 0.9		28
Cold-hardened	To 4	No less than 15	4
	Over 4	No less than 13	5
Hot-rolled	Over 4	No less than 7	15

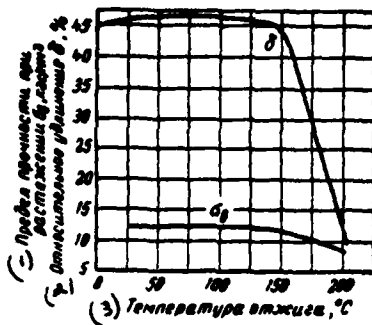


Figure III-18. Dependence of Mechanical Properties of Aluminum on Degree of Deformation and Temperature of Annealing

Key:

1. Ultimate strength in stretching, σ_B , kg-f/mm²
2. Relative elongation, δ , %
3. Annealing temperature, °C

The mechanical properties of aluminum are presented more completely below:¹⁴

Properties	Aluminum	
	soft	hard
Ultimate strength, kg-f/mm ²	8-10	15-25
Yield limit, kg-f/mm ²	5-8	12-24
Relative elongation, %	32-40	4-8
Relative constriction, %	70-90	50-60
HB hardness, kg-f/mm ²	15-25	40-55
Modulus of elasticity, E, kg-f/mm ²	6000-7000	-

The mechanical properties of aluminum at low temperatures:

	Temperature, °C		
	-185 (cold-hardened, deformation 93%)	-196 (bar, d=10 mm)	-253
Ultimate strength, kg-f/mm ²	443	21	35
Relative elongation, %	26	42	45
Relative constriction, %	28	75	66

2. Corrosion-Resistant Materials

Stainless Corrosion-Resistant Steels

According to GOST 5272-50, a 10-point scale is stipulated for evaluating the corrosion resistance of metals (table III-53).

TABLE III-53. SCALE OF CORROSION RESISTANCE OF METALS

Group of stability	Rate of corrosion mm/year	Point
I. Completely stable	Less than 0.001	1
II. Very stable	Over 0.001 to 0.005	2
	Over 0.005 to 0.01	3
III. Stable	Over 0.01 to 0.05	4
	Over 0.05 to 0.1	5
IV. Reduced stability	Over 0.1 to 0.5	6
	Over 0.5 to 1.0	7
V. Low stability	Over 1.0 to 5.0	8
	Over 5.0 to 10.0	9
VI. Unstable	Over 10.0	10

The chemical composition and mechanical properties of stainless (corrosion-resistant steels) is presented in tables III-54.

Below is a sample purpose of the brands of corrosion-resistant steels¹⁵⁻¹⁹ indicated in table III-54.

TABLE III-54. CHEMICAL COMPOSITION AND MECHANICAL PROPERTIES OF STAINLESS ACID-RESISTANT STEELS

(1) Марка стали или сплава	(2) Состав, %					(3) Механические свойства								
	C	Si	S	P	не более (4)	Mn	Cr	Ni	Ti	Mo	(5) Предел прочности кг/мм ²	(6) Предел теку- щей прочности кг/мм ²	(7) Относительное удлинение %,	(8) Относительное сужение %
(a) Сталь ферритного класса														
OKh13 (EI496)	0.08	0.60	0.025	0.030	не более 0.60(4)	11.0-13.0	-	-	-	-	40	-	20	-
Kh17 (EZh-17)	0.12	0.80	0.025	0.035	не более 0.70(4)	16.0-18.0	-	-	-	-	40	25	20	50
OKh17T (EI645)	0.08	0.80	0.025	0.035	не более 0.70(4)	16.0-18.0	-	-	5-C-0.80	-	По согласованию с заказчиком			
Kh25T (EI439)	0.15	1.00	0.025	0.035	не более 0.80(4)	24.0-27.0	-	-	5-C-0.80	-	45	30	20	45
Kh28 (EZh27, EI349)	0.15	1.00	0.025	0.035	не более 0.80(4)	27.0-30.0	-	-	-	-	54	-	17	-
(a) Сталь аустенитно-ферритного класса														
OKh21N5T (EP53)	0.08	0.80	0.025	0.035	не более 0.80(4)	20.0-22.0	4.80-5.80	0.30-0.60	-	-	55	35	25	40
1Kh21N5T (EI811)	0.08- 0.14	0.80	0.025	0.035	не более 0.80(4)	20.0-22.0	4.80-5.80	(C-0.02) 5- 0.80	-	-	60	35	20	40
OKh21N6M2T (EP54)	0.08	0.80	0.025	0.035	не более 0.80(4)	20.0-22.0	5.50-6.50	0.20-0.40	1.80-2.50	-	65	35	20	40
Kh28AN (EI657)	0.15	1.0	0.025	0.035	не более 1.30(4)	25.0-28.0	1.00-1.70	-	-	-	54	-	17	-
(a) Сталь аустенитного класса														
Kh14G14N (EP212)	0.12	0.80	0.020	0.035	13.0-15.0	13.0-15.0	1.00-1.50	-	-	-	87-90	-	70	-
Kh14G14N3T (EI711)	0.10	0.80	0.020	0.035	13.0-15.0	13.0-15.0	2.50-3.50	(C-0.02) 5- 0.80	-	-	70	-	35	-
Kh17G9AN4 (EI878)	0.12	0.80	0.020	0.035	8.0-10.5	16.0-18.0	3.50-4.50	-	-	-	70	-	40	-
Kh17N13M2T (Kh18N12M2T) EI448	0.10	0.80	0.020	0.035	1.00-2.00	16.0-18.0	12.0-14.0	0.30-0.60	1.80-2.50	-	52	22	40	55

Key:

1. Brand of steel or alloy
2. Composition, %
3. Mechanical properties
4. no more
5. Ultimate strength, kg-f/mm²
6. Yield limit, kg-f/mm²

(continuation of table)

Kh17N13M3T (E1432)	0.10	0.80	0.020	0.035	1.00-2.00	16.0-18.0	12.0-14.0	0.30-0.60	3.00-4.00	51	-	35	-
Kh18N12M3T OKh17N16M3T (E1380)	0.08	0.80	0.020	0.035	1.00-2.00	16.0-18.0	15.0-17.0	0.30-0.60	2.00-3.50	50	20	35	45
Kh17AG14 (E1413)	0.15	0.80	0.020	0.035	13.5-15.5	16.0-18.0	Не более 0.80	-	-	70	-	35	-
OKh18N10 (E1842)	0.04	0.80	0.020	0.035	1.00-2.00	17.0-19.0	9.0-11.0	-	-	45	16	40	20
OKh18N10 (OKh18N9, EYa0)	0.08	0.80	0.020	0.035	1.00-2.00	17.0-19.0	9.0-11.0	-	-	52	-	45	-
Kh18N9 (Kh18N9, EYa1)	0.12	0.80	0.020	0.035	1.0-2.0	17.0-19.0	8.0-10.0	-	-	55	-	35	-
2Kh18N9(EYa2)	0.13- 0.21	0.80	0.020	0.035	1.0-2.0	17.0-19.0	8.0-10.0	-	-	60	-	35	-
Kh18N10E (E1455)	0.12	0.80	0.020	0.035	1.0-2.0	17.0-19.0	9.0-11.0	-	-	-	-	-	-
OKh18N10T (E1914)	0.08	0.80	0.020	0.035	1.0-2.0	17.0-19.0	9.0-11.0	5C-0.60	-	50	20	40	55
Kh18N10T (Kh18N9T, EYa1T)	0.12	0.80	0.020	0.035	1.0-2.0	17.0-19.0	9.0-11.0	(C-0.02) 5- 0.70	-	52	20	40	55
Kh18N9T (Kh18N9T, EYa1T)	0.12	0.80	0.020	0.035	1.0-2.0	17.0-19.0	8.0-9.5	(C-0.02) 5- 0.70	-	52	-	35	-
OKh18N11 (E1684)	0.06	0.80	0.020	0.035	1.0-2.0	17.0-19.0	10.0-12.0	-	-	52	-	35	-
OKh18N12T	0.08	0.80	0.020	0.035	1.0-2.0	17.0-19.0	11.0-13.0	5C-0.60	-	55	20	40	55
Kh18N12T	0.12	0.80	0.020	0.035	1.0-2.0	17.0-19.0	11.0-13.0	(C-0.02) 5- 0.70	-	55	-	35	-
OKh18N12B (Kh18N12, E1402)	0.08	0.80	0.020	0.035	1.0-2.0	17.0-19.0	11.0-13.0	-	-	50	18	40	55
OKh23N28M2T (E1628)	0.06	0.80	0.020	0.035	Не более 0.80	22.0-25.0	26.0-29.0	0.40-0.70	18-25	По согласованию с заказчиком			
OKh23N28M3D3T (E1943)	0.06	0.80	0.020	0.035	То же 0.80	22.0-25.0	26.0-29.0	0.40-0.70	25-3.0	То же (13)			

Key:

7. Relative elongation, %
8. Relative constriction, %
9. By agreement with customer
10. Steels of ferrite class
11. Steels of austenite-ferrite class
12. Steels of austenite class
13. The same

Steel of brand OKh13 (EI496) is supplied in the form of thin (ChMTU 2117-49) and thick (ChMTU TsNIChM 225-59) sheets.

It is recommended for the fabrication of items that operate at room temperature in air, in river and tap water, moist steam, aqueous solutions of salts of organic acids, as well as for the fabrication of household objects. In order to increase the corrosion resistance, it is recommended that the steel be exposed to hardening at 950-1000°C in oil or in air, and tempering at 680-720°C.

Steel of brand Kh17 is used in the annealed state. It is supplied in the form of thin (GOST 5582-50) and thick (GOST 7350-55) sheets, sectional steel (GOST 5949-61) and pipes of small dimensions (GOST 8941-59).

It is used to make equipment of nitric acid plants and enterprises of the food and meat and dairy industry; to fabricate different types of items that operate in media of average aggressiveness. It is not recommended for welded designs: the welded connections made of steel Kh17 have decreased resistance to intercrystalline and general corrosion in the zone of thermal influence.

Steel of brand OKh17T is supplied in the form of thin (MPTU 3210-52) and thick (GOST 7350-55) sheets.

It is recommended as a substitute for steel brand Kh18N10T to fabricate welded designs that are not exposed to the effect of impact loads, with operating temperatures no lower than -10°C. It has satisfactory weldability. The welded connections of this steel have satisfactory resistance to intercrystalline and general corrosion and do not differ in these properties from the base metal. The welded connections have very low impact viscosity (less than 1 kg-f x m/cm²), therefore it is impossible to deform them at room temperature. Steel OKh17T has good corrosion resistance in the following media:

Medium	Concentration, %	Temperature, °C, no higher
Acid	Any	50-60
nitric	10	50
phosphoric	Less than 20	Boiling point
tartaric	Less than 85	70
citric	5	25
carbolic	5	25
acetic	Any	100
Alkalis	Less than 50	40-50
	Any	50

Steel brand Kh25T is supplied in the form of a thin sheet, thick (ChMUT 5790-57) sheet, and sectional steel and pipes.

It is recommended as a substitute for steel brand Kh18N10T for welded structures not exposed to the effect of impact loads, at operating temperatures not below -20°C. It is used for working in more aggressive media than those for which steel of brand 0Kh17T is recommended.

It is used to fabricate apparatus for solutions of sodium hypochlorite, nitric or phosphoric acids of varying concentration; pipes for heat-exchange equipment that operates in aggressive media. The weldability of steel Kh25T is satisfactory. It is recommended that steel Kh25N13 be used as an additive with coatings of KB3M and E3B, as well as steel of austenite-ferrite class of brands Kh28N4A or Kh25N5B with coatings of ENTU-3 or F-1. The impact viscosity of steel Kh25T in welded connections is $\leq 1 \text{ kg-f} \times \text{m/cm}^2$.

Steel of brand Kh28 is used for the same purposes as steel Kh25T, as well as for working in media that contain acetic acid. The welded connections are prone to intercrystalline corrosion.

Steel of brand Kh28AN is used for the same purposes as steel Kh28. The welded connections have higher impact viscosity as compared to steel Kh28.

Steel of brand 0Kh21N5T (EP-53) is supplied in the form of thin (ChMTU TsNIICHM 136-59) and thick sheets (4-60 mm thick according to ChMTU TsNIICHM 62-58, 5-11 mm thick according to

ChMTU TsNIICHM 474-61), sectional steel (ChMTU TsNIICHM 485-61), wire (ChMTU TsNIICHM 493-61) and band (ChMTU TsNIICHM 494-61).

It is recommended as a substitute for steel brand Kh18N10T to make welded apparatus in the chemical, food and other sectors of industry at operating temperatures no higher than 300°C (at a temperature above 350°C, it is prone to become brittle). It possesses satisfactory corrosion resistance under conditions of producing diluted nitric acid and ammonium nitrate.

Steel 0Kh21N5T is characterized by satisfactory weldability and increased resistance to intercrystalline corrosion and corrosion cracking.

Steel brand 1Kh21N5T (EI811) is supplied in the form of thin (ChMTU TsNIICHM 290-60) and thick (ChMTU TsNIICHM 62-58) sheets, wire (ChMTU TsNIICHM 289-60), sectional steel (ChMTU TsNIICHM 291-60), pipes (ChMTU UkrNITI 142-59), and bands (ChMTU TsNIICHM 398-60).

It is used for the same purposes as steel brand 0Kh21N5T (according to GOST 5632-61). According to the data of GIAP, steel of brand 1Kh21N5T is more prone to intercrystalline corrosion, has higher strength and can be used in less aggressive media than steel of brand 0Kh21N5T.

Steel of brand Kh17N13M2T and Kh17N13M3T is recommended for manufacturing parts and constructions that operate under conditions of the effect of formic, lactic, acetic acids; oxalic acid (concentration below 5%); phosphoric acid (to 32% P₂O₅) containing fluorine compounds; boric acid with admixture of sulfuric (to 1% H₂SO₄), as well as fluosilic acid (concentration to 10%).

Steel of brand 0Kh21N6M2T (EP54) is supplied in the form of a thin (ChMTU TsNIICHM 136-59) and thick (4-16 mm, ChMTU TsNIICHM 474-61) sheet, sectional steel (ChMTU TsNIICHM 485-61), wire (ChMTU TsNIICHM 493-61), and bands (ChMTU TsNIICHM 494-61).

It is recommended as a substitute for steel Kh17N13M2T for the manufacture of parts and welded designs operating in media of increased aggressiveness: phosphoric, formic, lactic, acetic and other acids.

Steel brand 0Kh17N16M3T is used for the same purposes as steel brand Kh17N13M2T, and is also recommended for the fabrication of linings for carbamide synthesis columns. It practically does not contain a ferrite phase. It has higher resistance to general corrosion than steel Kh17N13M2T

Steel of brand Kh18N10T and Kh18N9T are used to make welded apparatus in different sectors of industry. Steel of brand Kh18N9T is supplied in the form of sectional metal and hot-rolled sheets that are not made on continuous rolling mills. It is recommended for operation in media of average aggressiveness, in nitric, organic (excluding acetic, formic, lactic, oxalic) acids, the majority of solutions of salts of organic and inorganic acids at different temperatures and concentrations.

It has satisfactory resistance to intercrystalline corrosion.

Steel of brand 0Kh18N10T has increased resistance to intercrystalline corrosion. It is recommended for the fabrication of welded items that work in highly aggressive media, in which steels of brands Kh18N10T and Kh18N12T do not have considerable resistance to intercrystalline corrosion.

Steel of brand 00Kh18N10 is used for the same purposes as steel 0Kh18N10T. It has high resistance to intercrystalline and "knife" corrosion.

Steel of brand 0Kh18N12T is used for the same purposes as steel 0Kh18N10T. It essentially does not contain an α -phase.

Steel of brand Kh18N12T is used for the same purposes as steel Kh18N10T. It contains a lower quantity of α -phase than steel

Kh18N10T, and possesses higher resistance to intercrystalline corrosion.

Steel of brand 0Kh18N12B is fairly resistant to intercrystalline corrosion and is recommended for items that operate in highly aggressive media, in which steel Kh18N10T does not possess sufficiently high resistance to intercrystalline and "knife" corrosion. It is used as an additive for welding chrome-nickel steel.

Steel of brand 0Kh23N28M2T has increased resistance to intercrystalline corrosion. It is used to make welded designs and assemblies that operate under conditions of the effect of hot phosphoric acid with an admixture of fluorides, as well as sulfuric acid of low concentrations (to 20%) at temperatures lower than 60°C.

Steel of brand 0Kh23N28M3D3T is used to make apparatus that operates under conditions of sulfuric acid of any concentration at a temperature below 80°C; phosphoric acid (32-50% P₂O₅) containing fluorides; fluosilic acid of increased concentrations (to 25%) at operating temperature below 70°C. It has increased resistance to intercrystalline corrosion.

Low-Carbon Stainless Steels

Stainless steels of brands 000Kh18N11 and 000Kh17N13M3 with low carbon content ($\leq 0.03\%$ C) have become popular in recent years outside the Soviet Union. These steels have a purely austenite structure, are welded well and are plastic in forming in the cold state.

Welded connections of steels with low content of carbon differ are distinguished by a high resistance to intercrystalline and "knife" corrosion.

Steel brand 000Kh18N11 has higher corrosion resistance in very oxidizing media as compared to steel that is stabilized with titanium. Thus, the corrosion stability of steel 000Kh18N11 in

boiling 65% nitric acid is roughly 10-fold higher than of steel Kh18N10T.

The Scientific Research Institute of Chemical Machine Construction, State Scientific Research and Planning Institute of the Nitrogen Industry and Products of Organic Synthesis, Central Scientific Research Institute of Ferrous Metallurgy and other organizations are investigating the corrosion resistance, mechanical properties and weldability of steels with low carbon content. The Scientific Research Institute of Chemical Machine Construction has compiled temporary specifications for low-carbon steel of brand 000Kh18N11 (ChMTU 1-3-66 V-33).

Below are the composition and properties of steel 000Kh18N11 according to ChMTU 1-3-66 V-33:

Composition, %

C	.003	S	.0002
Si	.04	P	.0035
Mn	.2	Cr	.17-18
		Ni	.105-12

Yield limit, kg-f/mm ²	>20
Ultimate strength, kg-f/mm ²	>52
Relative elongation, %	45
Rate of intercrystalline corrosion,* mm/year	0.5

* Determined according to method D with inducing annealing at 650°C for 2 hours (GOST 6032-58).

Two-Layer Corrosion-Resistant Sheet Steel

Two-layer corrosion-resistant sheet steel consists of the following layers: base, thicker, made of carbon steel or steel of increased strength (low-alloy), and plating, thinner, made of corrosion-resistant steel or pure nickel.

The two-layer sheet metal can be a substitute in many cases for one-layer corrosion-resistant materials. In this case, the saving of alloying components averages about 70%.

TABLE III-55. ACTIVE SPECIFICATIONS FOR TWO-LAYER SHEET STEEL

Specifications	Manufacturing plant	Sector of Industry Customer	Brands of steel comprising layers		Total thickness of sheet mm
			base	plating	
ChMTU TsNIICHM 3258-52	Kuznetsk Metallurgical Kombinat	Oil refining	St. 3.15K, 20K, 12MKh, 16GT	OKh13	8-40
ChMTU TsNIICHM 211-59	The same	Chemical and oil refining	St. 3,10,20K 16GT	1Kh18N9T Kh18N12M2T	8-60
ChMTU TsNIICHM 390-60	Kommunarsk Metallurgical Plant	Oil refining	St. 3.15K, 20K	OKh13, 1Kh18N9T, Kh18N12M2T	8-50
ChMTU TsNIICHM 344-60	Kuznetsk Metallurgical Kombinat	Ship-building and chemical	3S, 4S, 09G2, SKhL4, SkhL45	1Kh18N12M2T 1Kh28N9T	5-35
ChMTU TsNIICHM 773-62	Kommunarsk Metallurgical Plant	The same	St. 3, 09G2, 1OKhSND (SKhL4)	OKh13, Kh14G14N3T, Kh18N9T, Kh18N10T, OKh18N10T, OKh17N3M2T	5-30

Two-layer steel combines the strength of the base and the corrosion resistance of the plating layers. In a number of cases, this creates conditions for designing equipment that is light-weight because thinner sheets are used.

The heat conductivity of the sheets that are plated with corrosion-resistant steel is twice as high in limits of 20-300°C than the heat conductivity of monosheets. This is very important for the fabrication of heat-exchangers.

Welding of equipment made of two-layer steels has been developed by the Volgograd Scientific Research Institute of Machine Construction Technology jointly with the Ye. O. Paton Institute of Electric Arc Welding.²⁰

Table III-55 presents a list of the active specifications for two-layer sheet steel.

New Structural Metals²¹⁻²⁴

The new structural corrosion-resistant metals that have valuable physical and mechanical properties include titanium, zirconium, niobium, tantalum, as well as their alloys with other metals.

Because of the high strength indicators, these metals are subject to all types of machining: stamping, forging, rolling, cutting, and welding. Because of intensive interaction of the heated metal with gases, these metals are welded in a protective medium or in a vacuum. Argon-arc welding is usually used for these metals. The welded seams can be exposed to cold treatment. In chemical machine construction, these metals can be used as independent construction material and as lining material.

Table III-56 presents the physical and mechanical properties of technically pure titanium, zirconium, niobium and tantalum, while tables III-57-III-60 present the corrosion resistance of these metals in different aggressive media.

TABLE III-56. PHYSICAL-MECHANICAL PROPERTIES OF NEW STRUCTURAL METALS

Indicators	Titanium	Zirconium	Niobium	Tantalum
Density at 20°C, g/cm ³	4.4	6.45	8.7	16.6
Melting point, °C	1668±4	1852±10	2468±10	2996
Heat conductivity at 20°C cal/(cm x s x deg)	0.036	0.042	0.125	0.13
Coefficient of linear expansion in temperature interval 20-100°C, 10 ⁶ deg ⁻¹	9.0	6.58	7.1	6.58
Specific heat capacity in tem- perature interval 0-100°C, cal/(g x deg)	0.14	0.067	0.064	0.034
Modulus of elasticity, kg-f/mm ²	11,200	9700	16,000	19,200
Ultimate strength in stretching (annealed), kg-f/mm ²	56	30-50	29.7	35-52
Yield limit (annealed), kg-f/mm ²	50.4	21-28	21	25-40
Relative extension (annealed) %	16-25	15-30	10	25-40

Depending on the depth (rate) of corrosion, three degrees of corrosion resistance are distinguished:

Degree of corrosion resistance	Rate of corrosion, mm/year
A	Less than 0.127
B	From 0.127 to 1.27
C	Over 1.27

Titanium is used as a material for making distillation unit equipment, tanks, various types of heat exchangers, and equipment for carbamide production. The corrosion resistance of titanium can be improved by alloying it with other elements. It has been established, for example, that an alloy of titanium with 0.2% palladium is more stable in hydrochloric acid than pure titanium. An alloy of titanium with 30% molybdenum has the greatest corrosion resistance in nonoxidizing media.

Niobium is used as construction material in units for the use of radioactive wastes, and in the manufacture of equipment to obtain hydrochloric and nitric acids, bromine and hydrogen peroxide. It is used as a sheet and seamless pipes.

Tantalum is used in chemical machine construction as an independent construction material for the fabrication of heat-exchange equipment (condensers, heat-exchangers, rectification units), as well as to line the equipment. It is known that tantalum is used

TABLE III-57. CORROSION RESISTANCE OF TITANIUM

Medium	Concentration weight. %	Temperature, °C	Degree of corrosion resistance
Acid			
formic, aerated	10,25,50,90	100	A
formic, nonaerated	25,50,90	Boiling point	C
acetic, aerated	5,25,50,75	The same	A
acetic, nonaerated	99.5	The same	A
phosphoric	5,10,20,30, 35-85	35 35	A B
	5	100	B
	10	80	C
nitric	5,10,30,40,50	100	A
	40	200	B
	65	175	A
	70	270	B
	Fuming, saturated with nitric oxides	20,50,70	Not recommended for use
hydrochloric, aerated	1	60	A
	3	100	C
	15	35	C
hydrochloric, nonaerated	3.5	70	B
	10	70	C
mixture of hydrochloric and nitric (HCl:HNO ₃ =1:3)	-	Room	A
sulfuric	1,3,5	35	A
	10	35	B
	20-50	35	C
	60-70	35	B
	1,5	Boiling point	C
	10	50	C
Alkali			
potassium hydroxide	10	Boiling point	A
sodium hydroxide	10	The same	A
	40	80	A
Anhydrous ammonia	100	40	A
Ammonia water	28	20,60	A
Sodium chloride	Saturated solution	20	A
Calcium chloride	5,10,25	100	A
Ammonium chloride	1,10	100	A
Hydrogen peroxide	3,6	20	A
Carbon tetrachloride (1% H ₂ O)	-	Boiling point	A
Dichloroethylene	100	The same	A

to make coils working under pressure of 60-70 atm, autoclaves and other equipment.

Figure III-19 illustrates the diagrams for corrosion resistance of titanium, niobium and tantalum in mineral acid solutions.

TABLE III-58. CORROSION RESISTANCE OF NIOBIUM IN DIFFERENT MEDIA

Medium	Concentration weight. %	Temperature °C	Degree of corrosion resistance
Acid			
nitric	Concentrated	100	A
	20	20	A
hydrochloric	Concentrated	20	A
	The same	100	A (becomes brittle)
sulfuric	25% by vol.	20	A
	Concentrated	50	A
	The same	100	B
	The same	150	C
phosphoric	85	20	A
	85	100	A (becomes brittle)
acetic, glacial	-	25	A
Alkali			
potassium hydroxide	5	20	B
	5	100	C
sodium hydroxide	5	31	A
	5	100	C
Aqueous solution of ammonia	25	150	A

TABLE III-59. CORROSION RESISTANCE OF TANTALUM IN DIFFERENT MEDIA

Medium	Concentration weight. %	Temperature °C	Degree of corrosion resistance
Acid			
formic	-	80	A
acetic	Any	20-390	A
hydrochloric	20	0-100	A
	Concentrated	0-100	A
nitric	10	20-100	A
	Concentrated	86	A
mixture of hydrochloric and nitric (aqua regia)	-	20-60	A
sulfuric	20	20-300	A
	Concentrated	150	A
	Concentrated	200	A
	Concentrated	0.25	B
phosphoric	85	145	A
Alkali			
potassium hydroxide	5	110	A
sodium hydroxide	5	100	A
	40	100	B
Chlorine, saturated with water vapors	-	20	A

Zirconium is used to make equipment that operates in contact with hydrochloric acid and organic acids. Titanium has exceptional corrosion resistance in acetic, formic and citric acids. It does

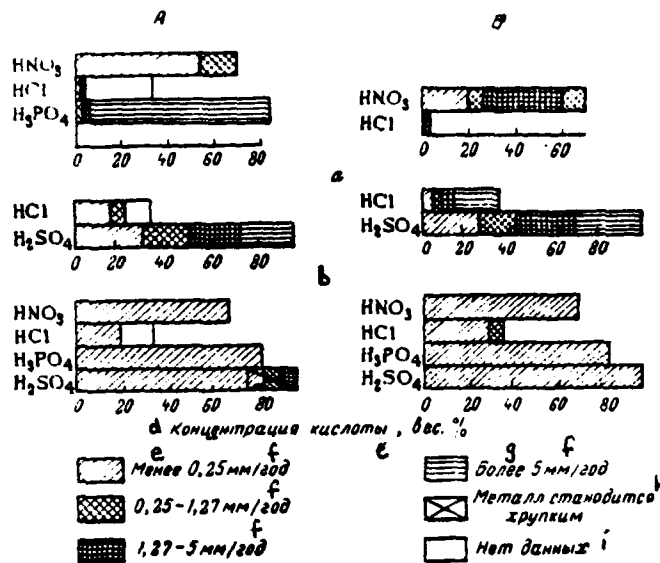


Figure III-19. Diagrams of Corrosion Resistance of Ti, Nb, Ta in Mineral Acids

Key:

- A. At boiling point of acids
- B. At 190°C
- a. For Ti
- б. For Nb
- в. For Ta
- d. Acid concentration, weight. %
- e. Less than
- f. mm/year
- g. More than
- h. Metal becomes brittle
- i. No data

not break down at all under the influence of these acids at the boiling point. It is used to make laboratory equipment: crucibles (by the extrusion method), containers for aggressive solutions (lining with sheets of zirconium).

Figure III-20 presents the diagrams for corrosion resistance of zirconium in solutions of basic mineral acids.

TABLE III-60. CORROSION RESISTANCE OF ZIRCONIUM IN DIFFERENT MEDIA

Medium	Concentration weight. %	Temperature °C	Degree of corrosion resistance
Acid			
formic	90	20; boil.pt.	A
acetic	5,99	60,100	A
hydrochloric	Diluted	Any	A
	Concentrated	20	A
	The same	Boiling pt.	C
nitric	10	20-100	A
mixture of hydrochloric and nitric	-	18-60	C
sulfuric	10	20-100	A
	96	100	C
phosphoric	20-85	20-100	A, B
Alkali			
sodium hydroxide	10-50	20-100	A
potassium hydroxide	10,20,30,40	20-100	A
Carbon tetrachloride	100	20-49	A
Hydrogen peroxide	10	49	A

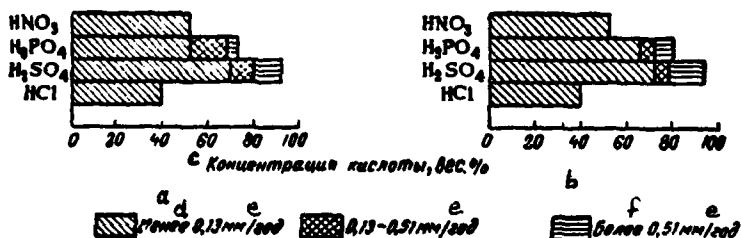


Figure III-20. Diagram of Corrosion Resistance of Zirconium in Mineral Acids

Key:

- a. At boiling point of acids
- b. At 80°C
- c. Acid concentration, weight. %
- d. Less than
- e. mm/year
- f. More than

Nonmetal Chemically Stable Materials^{24,25}

Natural Acid-Resistant Materials

These include rocks containing less than 55% SiO₂ (andesite, beschtsaunite, granite, quartzite, basalt) that have high chemical

stability and mechanical strength. The acid-resistance in nitric and sulfuric acids is 95-99%. They are used as independent construction materials for absorbing towers, concentrators, electric filters, as well as as lining materials for collectors, settling tanks, coolers and other units in the production of sulfuric, hydrochloric, nitric acids and their salts. They are used as fillers in acid-resistant concretes.

Acid-Resistant Ceramic

It is resistant to all mineral and organic acids, except fluoric (acid resistance is 96-98%), but is not resistant to alkalis. The water absorption of ceramic is from 3 to 12%.

It is used to make acid-resistant brick (GOST 474-41), acid-resistant and thermo-acid-resistant slabs (GOST 961-57) to line apparatus and to face construction designs; acid-resistant Raschig rings (GOST 748-41) used as inserts; acid-resistant pipes (GOST 585-45) with diameter from 25 to 300 mm, of length from 300 to 1000 mm for transporting aggressive liquids; acid-resistant sheet-steel cylinders (towers) (GOST 732-41) of diameter from 300 to 1200 mm and height 500-1000 mm for equipment operating in acid media.

Melted Nonmetal Materials

Stone casting is distinguished by an exceptionally dense structure. The water absorption is no more than 0.16%. The resistance to sulfuric acid is 99.8%, and to hydrochloric 99.3%. The casting is stable in all acids (except fluoric) and in alkali solutions (at low temperatures). Items made of stone casting have high mechanical strength and are abrasive-resistant, but have low impact strength.

Stone casting is used for manufacture of lining slabs (STU 36-13-718-61), wedge brick (STU 36-13-756-61), bushings and troughs for lining pipelines (VTU-2-63), and different shaped items.

Quartz glass contains 98-99% SiO_2 . It possesses high thermal

resistance, and can be used at temperatures up to 1000 °C. It is resistant to mineral and organic acids of any concentrations (except fluoric and phosphoric acids), but is not resistant to alkalis. It does not break down with a drastic change in temperature. It is used to make different parts of chemical equipment (small vessels, evaporator dishes), straight quartz tubes (GOST 8680-58) and molded ones (GOST 10239-62).

Silica glass is resistant to mineral and organic acids, but is destroyed by alkali solutions. It is used to make chemical equipment and parts for it, pipes, as well as laboratory instruments and vessels. Pipes made of silica glass (GOST 8894-58) are used²⁶ for transporting hot and cold aggressive liquids (with the exception of fluoric acid and concentrated alkalis) at a temperature from -30 to 120°C. The shaped parts for glass pipelines are manufactured according to GOST 11192-65.

The Pervoural'sk Old-Pipe Plant has mastered production of steel pipes that are lined with glass and have the same high resistance as glass pipes. The operating temperature of the line pipes is from -70 to +200°C. The temperature gradient is to 420°C.

Enameled items²⁷ are resistant to the effect of mineral and organic acids (with the exception of fluoric, fluosilic and technical-grade phosphoric acid), to solutions of salts and alkali solutions with concentration to 3%. They are not resistant to concentrated solutions and alkali melts. The operating conditions of enameled apparatus: temperature from -30 to +200°C, pressure 3-6 kg-f/cm². Industry manufactures enameled apparatus with capacity from 30 to 6300 l. Production of enameled pipes and steel enameled connecting parts has been developed at the Smelyansk Machine Construction (standards NE-10-00-11, 1963) and the Pervouralsk Old-Pipe Plants.

Devitrified glass and slag-devitrified glass are new glass-crystal chemically stable construction materials that have high heat-resistance, resistance to a drastic drop in temperature, high mechanical strength and wear-resistance, and are easily machined. The devitrified glass exceeds the slag-devitrified glass in qualities,

but is considerably higher in cost.

Industrial production of slag-devitrified glass has been set up at the Konstantinovskiy plant "Avtosteklo." Faced slabs of different sizes are manufactured. Production of pipes for working pressures of 4-8 kg-f/cm³ and temperatures from -30 to +250°C has been developed.

Composites Based on Liquid Glass

Acid-resistant composites (putty, mortar, concrete) are used as a binding agent in lining chemical equipment, installation of acid-resistant-floors and facing structures, as well as as an independent construction material for floors and foundations under equipment. They are resistant to acids of any concentrations (except fluoric acid), but are not at all resistant to alkalis and are destroyed under the lengthy effect of water. The composites are made at the site of performing the work. They are used at a temperature no lower than 10°C.

The composite composition includes: liquid glass (GOST 962-41) of modulus 2.56-2.8, with density no lower than 1.4 g/cm³; sodium fluosilicate (GOST 87-66) and acid-resistant fillers, gravel, quartz sand and ground filler.

The gravel must have acid-resistance not below 97% (according to GOST 473-64) and meet the requirements of GOST 8237-64 for granulometry. The quartz sand must contain no less than 97% SiO₂ and meet the requirements of GOST 8736-62 for granulometry. Fine-ground acid-resistant rocks, quartz sand or powder No. 2 made of stone casting (STU-36-13-717-61) are used as the ground filler. The acid-resistance of the filler is not less than 97%, and moisture content no more than 1%.

A sample composition of the composites on a liquid glass base is presented below.

Table III.61. Composition and field of employment of materials on the bases of black binders.

(1) Композиция	(2) Состав, вес. %							(14) Область применения
	битум марки BN-IV (ГОСТ 6617-56)	каменноуголь- ный пек (ГОСТ 1038-65)	каменноуголь- ная смола (ГОСТ 4492-65)	молотый кис- лотостойкий наполнитель	кварцевый песок	кислотоупор- ный щебень	асбест 6-7-го сортов (ГОСТ 7-60)	
Мастика (12) (13) битумная (14) пековая	30 —	— 30	— 10	53 45	— —	— —	17 15	(17) Для укладки штуч- ных кислотоупор- ных материалов; устройства гидро- изоляционных слоев в конструк- циях полов; защиты фундаментов и дру- гих строительных конструкций
Раствор (13) (14) битумный (15) пеково-смо- ляной	18 —	— 15	— 4	20 11	55 62	— —	7 8	(18) В конструкциях кис- лотостойких полов и фундаментов, ра- ботающих в агрес- сивных средах; для устройства кисло- тостойких отмосток
Бетон (16) (17) битумный (18) пековый	7 —	— 8-12	— 2-3	3 5-10	30 40-35	60 45-40	— —	(19) Для устройства осно- ваний полов пер- вого этажа при за- кисленном грунте; защиты фундамен- тов и устройства кислотостойких отмосток

(20)
Примечание. Композиция на основе каменноугольного пека следует применять только для закрытых конструкций, не подвергающихся воздействию солнечных лучей.

Key: (1) Materials; (2) Composition, weight %; (3) Bituman mark BN-IV (GOST 6617-56); (4) Coal-tar pitch (GOST 1038-65); (5) Coal-tar resin (GOST 4492-65); (6) Ground acid-resistant filler; (7) Quartz sand; (8) Acid-resistant gravel; (9) Asbestos 6-7th grades (GOST 7-60); (10) Mastic; (11) Bituminous; (12) Pitch; (13) Solution; (14) Field of employment; (15) Pitch - coal-tar; (16) Concrete; (17) For laying single acid-resistant materials; structures of water-proofing layers in the construction of floors; protection of foundations and other construction elements; (18) In the construction of acid - resistant floors and foundations which function in aggressive media; for structures of acid-resistant fluid areas; (19) For structures of substructures of floors of first story with overacid ground; protection of foundations and structures of acid-resistant fluid areas; (20) Note. Materials based on coal-tar pitch should be employed only with closed construction not subjected to the influence of the Sun's rays.

Composite	Composition				
	Liquid glass	Sodium fluoro-silicate	Ground acid-resistant filler	Quartz sand	Acid-resistant gravel
Putty	350-420	60	1000	-	-
Mortar	400-500	60-70	400-500	900-1200	-
Concrete	250-400	40-60	300-400	500-700	700-1000

Composites Based on Ferrous Binding Materials

Composites based on bitumen and coal pitch are made by adding fillers to diluted binding agents. They are resistant to diluted solutions of acids, acid waters, and solutions of salts at temperatures to 40-50°C. They are not resistant to hot concentrated acids, oxidizers and organic solvents.

The compositions and area of application of the composites are given in table III-61.

Polymer Materials²⁸⁻³²

They are widely used in technology to protect from corrosion. The physical-chemical properties and chemical resistance of these materials are presented in tables III-62 and III-63.

Polyvinyl chloride plastic possesses high mechanical strength and chemical stability for nonoxidizing aggressive media. It swells in the majority of organic solvents. It is inflammable. It is easily machined, decays in the heated state, and is welded by hot air.

It is manufactured in the form of sheets (GOST 9139-61), and rods (TU MKhP 4251-54). It is used most often to make vessels, ventilation systems, and different parts.

Polyvinyl chloride plastic pipes³³ of length 1-3 m and diameter 6-240 mm and shaped polyvinyl plastic chloride parts for pipelines

for transporting aggressive liquids are manufactured by the Vladimir and Okhtinskiy Plastic Plants for conventional pressure of 2.5-6 kg-f/cm² and temperature of 20-60°C (according to TU MKhP 4251-54 and plant standards).

Polyvinyl chloride plastic through-way valves of the type "Kosva" (MRTU 6-05-983-66) are used on pipelines for transporting aggressive liquids and gases at a temperature to +50°C and pressure to 25 atm.

The Dnepropetrovsk Pipe-Rolling and Pervoural'sk Oil-Pipe Plants have developed the manufacture of steel pipes which are lined with polyvinyl chloride plastic³⁴ for transporting aggressive media. In this case, there is an increase in the interval of working temperatures (from -10 to +80°C) and working pressure (to 16 atm.).

Polyethylene^{35,36} has good frost resistance, but low heat resistance. It is resistant to solutions of acids, alkalis and salts, but is not resistant to oxidizers and the effect of ultraviolet rays, especially during heating. It swells at normal temperature in the majority of organic solvents. It has high dielectric properties and is incombustible. It is easily machined. It is welded well by nitrogen at a temperature of 200-220°C.

Polyethylene of low density (high pressure) is manufactured according to MRTU 6-05-889-65 and high density (low pressure) according to MRTU 6-05-890-65 which is distinguished in its physical and mechanical properties. It is mainly used as construction material for the manufacture of container equipment. Pipes have been developed and are being manufactured made of high density polyethylene (MRTU-6-05-917-63) and low density (MRTU 6-05-918-63) with diameter of 6-300 mm, length of 6-12 m. They are designed to operate with conventional pressure from 2.5 to 10 kg-f/cm² and temperature of 20-60°C.

Polypropylene (STU 36-13-126-65) possesses better mechanical properties and thermal-resistance than polyethylene, and is less prone to oxidation destruction.³⁷ The chemical stability of polypropylene is the same as polyethylene. Parts made of polypropylene are easily welded.

TABLE III-62. PHYSICAL-MECHANICAL PROPERTIES OF POLYMER MATERIALS

Material	Density g/cm ³	Water absorption in 24 h g/m ²	Ultimate strength kg-f/cm ²			Heat conductivity kcal m-h-deg	Brinell hardness kg-f/mm ²	Martens heat stability °C	Temperature limits of application °C
			in compression	in stretching	in bending				
Polyvinyl chloride plastic	1.38-1.4	0.02	800-1000	450-550	200-1100	0.13	13	65	from 0 to +60
Polyethylene low density (PEP)	0.92	0.01	125	100	120-170	-	1.4-2.5	50-60	from -66 to +60
high density (PVP)	0.95-0.96	0.01	-	200-350	200-300	-	4.5-5.8	75	from -66 to +60
Polypropylene	0.9	-	-	300-350	600-700	-	-	100-110	from +60 to +100
Polychlorotrifluoroethylene	2.10-2.16	0.01	500-600	350-450*	600	0.2	10-13	130	from -195 to +125
Polychlorotrifluoroethylene-N	2.02	0.01	500-600	250-300	350-400	-	7-8	-	To +180
Polytetrafluoroethylene	2.13-2.22	0.01	-	170-250*	200-315	0.04-0.08	3-4	-	from -269 to +250
Polyformaldehyde	1.42	0.4%	-	700	900	0.308	-	100	from -40 to +130
Asbestos vinyl	1.4-1.5	1.1%	200-350	150-215	130-300	0.11	18-25	150	from -50 to +120
Faolite	1.4-1.7	0.3-0.5%	700-800	200	600	0.3-0.6	15-25	100	from +120 to +230
Antheinite ATM-1	1.8	-	1000-1200	100-220	400-500	0.2-0.35	-	170	to +180
Graphite, impregnated with phenol-formaldehyde resin	2.03-2.07	-	781-1850	121-178	-	-	-	-	-

*The numerator presents the strength of unhardened material, and the denominator presents the hardened material.

TABLE III-63. CHEMICAL STABILITY OF POLYMER MATERIALS IN DIFFERENT MEDIA

(Y--stable, OY--relatively stable, H--unstable)

Material	(1) Азотная кислота			(2) Серная кислота		(3) Соляная кислота	(4) Уксусная кислота		(5) Муравьиная кислота до 20%	(6) Фтористоводородная кислота	(7) Раствор NaOH	
	до 10%	до 25%	концентрированная	до 50%	концентрированная		до 50%	ледяная			до 20%	до 20%
At 20 °C												
Polyvinyl chloride plastic	Y	Y	H	Y	H	Y	Y	OY	Y	Y	Y	H
Faolite	OY	H	H	Y	H	Y	Y	Y	Y	Y	Y	H
Anthegmite (ATM-1)	Y	H	H	Y	H	Y	Y	Y	Y	Y	Y	H
Graphite impregnated with phenol-formaldehyde resin	Y	H	H	Y	H	Y	Y	Y	Y	Y	Y	H
Polyethylene	Y	Y	H	Y	H	Y	OY	H	Y	Y	Y	Y
Polychlorotrifluoroethylene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Polytetrafluoroethylene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Asbestos-vinyl	Y	OY	H	Y	H	Y	Y	Y	Y	H	Y	H
At 60 °C												
Polyvinyl chloride plastic	Y	OY	H	OY	H	OY	OY	H	OY	OY	OY	H
Faolite	H	H	H	Y	H	Y	Y	Y	Y	Y	Y	H
Anthegmite (ATM-1)	—	H	H	Y	H	Y	Y	Y	Y	Y	Y	H
Graphite impregnated with phenol-formaldehyde resin	—	H	H	Y	H	Y	Y	Y	Y	Y	Y	H
Polyethylene	Y	OY	H	—	H	Y	H	H	OY	H	H	H
Polychlorotrifluoroethylene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Polytetrafluoroethylene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Asbestos-vinyl	—	H	H	Y	H	Y	—	—	—	H	Y	—

Key:

1. Nitric acid
2. Sulfuric acid
3. Hydrochloric acid
4. Acetic acid
5. Formic acid to 20%
6. Hydrofluoric acid
7. NaOH solution
8. to
9. Concentrated
10. Glacial

* Faolite of brand T.

Production of pipes made of polypropylene with diameter of 8-219 mm for nominal pressure of 2.5-16 kg-f/cm² has been developed. The operating temperature of the polypropylene pipes is from -10 to +100°C.

Fluoroplastics.³⁸ Polytetrafluoroethylene (GOST 10007-62) has exceptionally high anti-corrosion and dielectric properties, heat

resistance and frost-resistance. It is resistant to the effect of all acids (include aqua regia), oxidizers and alkalis. It does not swell and is not dissolved in solvents. It is not wetted by water and does not swell in it. It is incombustible. It only breaks down under the influence of melted alkali metals, elementary fluorine and chlorine trifluoride.

Fluoroplastic is cold-flow, as a consequence of which the items made of it cannot operate under a load exceeding 30 kg-f/cm^3 , even at room temperature.

It is used to make different packing parts and chemically-stable items, gaskets (for closed flanges), gland packing, rings, valve seats, bellows, bushings, valves, faucets, diaphragms, pipes and other parts. The pipes made out of polytetrafluoroethylene (VTU UKhP 277-60) are manufactured in diameter of 20-430 mm for operation under pressure to 10 kg-f/cm^2 at a temperature from -100 to $+250^\circ\text{C}$. They are connected by insertion flanges.

Fluoroplastic-4D (MRTU-6-05-942-64) is not inferior in mechanical and dielectric properties, chemical stability and heat-resistance to fluoroplastic-4 (polytetrafluoroethylene). It is the raw material for the fabrication of special lubricants and packing materials FUM (MRTU 6-M-870-62).

Polychlorotrifluoroethylene (fluoroplastic-3) (MRTU-6-05-946-65) is somewhat inferior in chemical stability and heat-resistance to fluoroplastic-4. It is resistant to the effect of sulfuric, nitric, hydrochloric acids of all concentrations, aqua regia, solutions of alkalis and salts. It is broken down under the influence of melts of alkali metals and caustic alkalis, chlorosulfonic acid, elementary fluorine and high-percentage oleum. It is dissolved and swells in certain organic substances. It is not wetted by water and does not swell in it.

Polychlorotrifluoroethylene is essentially not prone to cold flow. It is easily machined. It is used to make packing, chemically stable parts. Suspensions of polychlorotrifluoroethylene are used

to apply anti-corrosion coatings on the metals.

Fluoroplastic-3M (MRTU 6-05-905-63) is somewhat softer and less elastic than fluoroplastic-3, and is similar to it in the remaining properties.

Fluoroplastic-32L (TU P-74-61) and fluoroplastic-42 (VTU 208-62) are soluble in certain organic solvents. They are used to make anti-corrosion lacquers.

Polyformaldehyde (STU 36-13-8-64) is a new plastic³⁷ that has a high degree of hardness and impact-resistance. It is not cold flow at temperatures to 100°C. It is resistant to atmospheric effects, frost-resistant, water-resistant and resistant to oils and gasoline. It is insoluble in organic solvents at temperatures to 100°C. It is not resistant to acids and alkalis. The temperature limits of application are from -40 to +130°C.

Polycarbonate ITU P-262-63) possesses very high mechanical strength and impact-resistance (to temperature of -100°C).

Water absorption of polycarbonate is 0.3-0.6%. It is resistant to the effect of oils and gasoline at 125°C, and is resistant to hydrocarbons, alcohols, nitric and hydrofluoric acids, and organic acids.³⁷ It is not resistant to alkalis, ammonia, chlorinated hydrocarbons and pyridine bases. The temperature limit of application is from -100 to +140°C.

Asbestos vinyl (VTU MKhP 3109-53) is supplied in the form of a mass ready for use.³⁹ It is used as a lining composite for protection of metal and concrete from destruction in acid and alkali media. It is applied by a spatula in several layers of total thickness 10-12 mm. It is resistant to the effect of acetone, gasoline, benzene, chlorobenzyl, ethyl and methyl alcohols.

Faolite. It is resistant to nonoxidizing acid media and to the majority of organic solvents, but is not resistant to the effect of alkalis.

Untreated (TU MKhP 322-45) and strengthened sheets made of faolite (TU GKhp 35-44) are manufactured; pipes (TU MKhP 321-51) for transporting aggressive liquids; and fittings and parts for connecting pipelines.

Items and parts made of faolite are connected by faolite putty (TU GKhp 34-44) and arзамite putty.

Textolite is somewhat inferior in chemical resistance to faolite, but significantly exceeds it in mechanical strength. It is easily machined. It is manufactured in the form of sheets and slabs (GOST 5-52) used to make different parts (for example, piston rings) and pipes (TU MKhP 1471-47) for transporting aggressive liquids at a temperature to 80°C and pressure to 3 atm.

Fiber glass is material that consists of a fiberglass filler and binding agents (different thermoreactive and thermoplastic resins).

Binding agents based on polyester, epoxy, phenol-formaldehyde resins (or their composites) have become the most widespread.

Good mechanical and physical-chemical properties determine the broader usage of fiber glass.

The chemical stability of fiber glass is determined by the chemical resistance of the binding agent. Fiber glass based on epoxy and phenol-formaldehyde resins has the greatest chemical stability. Industry manufactures sheets and pipes made of fiber glass and fiber glass molding material.

Anthegmite is a chemically stable antifriction heat-conducting material. It is resistant to the effect of solutions of salts and acids, and is not resistant to the oxidizers and alkalis. It is resistant to the majority of organic solvents. Items made of anthegmite are easily machined.

It is designed for the manufacture by the hot extrusion method of heat-exchange chemical equipment, pumps and parts of apparatus

operating in aggressive media, as well as to replace bronze and lead in bearings.

Industry manufactures anthegmite of brands ATM-1, ATM-10, and ATM-1G which are distinguished in heat-resistance and physical-mechanical properties. Anthegmite ATM-1 is manufactured in the form of lining slabs (TU 35KhP-710-64) and pipes (TU 35KhP-723-64).

Impregnated graphite.⁴⁰ Graphite is a material which combines high chemical resistance and heat conductivity with good mechanical properties. A shortcoming of it as a design material is its high porosity (30-35%). When graphite is impregnated with different chemically stable resins, its open porosity is reduced to zero. Phenol-formaldehyde resin is the most suitable for impregnation. The impregnated graphite is resistant to the majority of organic solvents. It is used to make heat-exchange apparatus that operates in aggressive media.

Arzamite (putty)⁴¹ is self-hardening, rapid-setting material. It is used as a binding agent in lining apparatus with inlaid materials, for gluing parts made of impregnated graphite, anthegmite and faolite.

The arzamite putties are impermeable for liquids at pressure to 3-5 atm., are not broken down by water, and have high mechanical strength and chemical resistance. They are supplied in the form of two components, putty powder and a solution which can be mixed before use in a ratio of 1:(0.3-0.6). It is recommended that the putty be prepared in a quantity that is needed for working for no more than 1-1.5 h, since at room temperature the arzamite putties set in several hours and harden in the space of a day.

Table III-64 presents the chemical resistance of putties of different brands manufactured by industry.

Arzamite putties of brands I-V during hardening shrink considerably. The maximum working temperature of their use is equal to

TABLE III-64. CHEMICAL STABILITY OF ARZAMITE PUTTIES IN DIFFERENT MEDIA (Y--stable; P--breaks down)

Medium	Putties				
	Arzamite I (TU M-522-50)	Arzamite		Arzamite IV (TU M-543-58)	Arzamite V (TU 58-088-59)
		I	II		
		(by special order)			
Acid	P	P	P	P	P
nitric to 35%	Y	Y	Y	Y	Y
sulfuric to 70%	Y	Y	Y	Y	Y
hydrochloric	Y	Y	Y	Y	Y
phosphoric to 70%	Y	Y	Y	Y	Y
acetic	P	P	Y	Y	Y
formic	P	Y	Y	P	Y
hydrofluoric	P	Y	Y	Y	Y
Sodium hydroxide to 50%	P	P	P	P	P
Soda solutions	Y	Y	Y	Y	Y
Acetone	Y	Y	Y	Y	Y
Gasoline					
Benzene	P	Y	Y	P	Y
Alcohol	P	Y	Y	P	Y
ethyl	P	Y	Y	P	Y
methyl	P	Y	Y	P	Y
butyl	Y	Y	Y	Y	Y
Toluene	Y	Y	Y	Y	Y
Trichloroethylene	Y	Y	Y	Y	Y
Chlorobenzol	Y	Y	Y	Y	Y
Carbon tetrachloride					

150-160°C. The arzamite putties of brands IV and V are heat-conducting.

Putties of new brands have been developed. Thermally stable putty of brand VI is resistant to the effect of phosphoric and hydrochloric acids of any concentrations and to their mixtures, to 70% acetic and to phenyl acetic acids, to 20% sulfuric acid at temperatures to 250°C. Nonshrinking arzamite-VII putty is resistant to the effect of acid and alkali aggressive media, gasoline, benzene, toluene, xylol, but is not resistant to the effect of oxidizers, acetone, ethyl acetate and amyl acetate.

Paint and Varnish Materials⁴²⁻⁴⁴

Paint and varnish coatings are the most accessible and inexpensive type of protection of metal from corrosion. They are widely used for protection from atmospheric corrosion and from corrosion in aqueous media. Complex multilayer coatings based on chemically stable paint and varnish materials are used in the

chemical industry for protection of metal. The characteristics of the paint and varnish materials used in the nitrogen industry are presented in table III-68.

TABLE III-65. CHEMICAL STABILITY OF POLYISOBUTYLENE

Medium	Temperature, °C		
	20	40	50
Acid			
hydrochloric to 35%	Stable	Stable	Stable
sulfuric to 70%	"	"	"
sulfuric to 80%	Fairly stable	Unstable	Unstable
sulfuric to 85%	Unstable	"	"
nitric from 5 to 25%	Stable	Stable	Stable
nitric 40%	"	"	Insuffi-
nitric 50%	"	Insuf. stable	ciently stab. Unstable
nitric 60%	Unstable	Unstable	Unstable
hydrofluoric 40%	Stable	Insuf. stable	Insuf. stable
acetic 25-60%	"	Stable	Stable
glacial acetic	"	"	"
formic to 10%	"	-	-
Water	Stable	Stable	Stable
Acetone	"	"	"
Gasoline	Unstable	-	Unstable
Benzene	"	-	-
Oils and fats	"	-	Unstable
Alcohol			
butyl	Stable	-	"
methyl	"	Unstable	Unstable
Carbon tetrachloride	Unstable	-	-
Solutions of alkalis of any concentration	Stable	-	-

Note: The table presents the chemical stability of polyisobutylene of brand TsBSG (TU MKhP 1655-54r).

Roll and Sheet Anticorrosion Materials

Ruberoid (GOST 10923-64) is used as roofing material, waterproofing sublayer of linings, in designs of acid-resistant floors, for the protection of foundations. It is resistant in relation to diluted solutions of acids, acid waters, and salt solutions.

Hydroisol (waterproofing material) (GOST 7415-55) is used to install waterproofing layers and protective coatings of metal pipelines. It is resistant in the same aggressive media as ruberoid.

TABLE III-66. PHYSICAL-MECHANICAL PROPERTIES OF CERTAIN BRANDS OF RUBBER AND EBONITE

Brand	Ultimate strength kg-f/cm ²		Heat-resistance °C	Density g/cm ³	Area of application
	in stretching	in bending			
Soft rubber					
829	200			1.07	For rubberizing exposed vulcanization in boiling water
1976	52	-	-	1.12	For rubberizing apparatus with sublayer made of ebonite No. 1814, as well as for lining pipes. Vulcanization under pressure and by open method
2566	160	-	-	1.07	For lining apparatus; vulcanization by open method in boiling solution of calcium chloride
4476 4477 4478 4479	-	-	-	-	For rubberizing apparatus; vulcanization under pressure and by open method
Ebonite					
1751	274	628.0	43	1.32	For rubberizing metal apparatus, pipes, mixers, centrifuges; vulcanization under pressure
1814	364	713.0	62.2	1.33	As a sublayer under soft rubber of brand 1976 and 4476-79
2109	320	577.0	55	1.21	For rubberizing stopper plugs; vulcanization under pressure
2169	450	890	56	1.14	For rubberizing apparatus; vulcanization by open method

TABLE III-67. CHEMICAL STABILITY OF SOFT RUBBER AND EBONITE

Medium	Permissible concentration, %		Permissible temperature of medium, °C
	for soft rubber	for ebonite	
Milk of lime	Any	Any	50
Solutions			
of potassium hydroxide	"	"	65
of sodium hydroxide	"	"	65
of ammonia	"	"	50
Acid			
nitric	To 2	To 8	25
sulfuric	To 50	To 60	65
sulfurous	Any	Any	65
hydrochloric	"	"	65
hydrofluoric	To 50	Concentrated	65
Acetone	"	"	55
Ethyl alcohol	"	"	60

TABLE III-68. CHARACTERISTICS OF PAINT AND VARNISH MATERIALS USED IN NITROGEN INDUSTRY

Paint and varnish materials	Working viscosity, s (from viscosimeter VZ-4)	Duration of drying, h	Solvents	Area of application
Phosphating primers of brands VL-02 (TU 35KhP-432-62), VL-08 (VTU UKhP-107-59) and VL-023 (STU 45KhP-2049-64)--two-layer primers consisting of a base (suspension of pigments in solution of polyvinylbutylene, modified by novolac resins, in a mixture of organic solvents) and acid diluent (water-alcohol solution of orthophosphoric acid) supplied in a set. Before the use of the base, it is mixed with a diluent in a 4:1 ratio (by weight), for brand VL-023--in a 5:1 ratio. The period of suitability of diluted primer is 8 h. It is applied in one layer	17	15-30 min	Toluene, xylol, solvent	For primer coating steel; primer VL-02 for primer coating steel and duralumin
Phosphating primer VL-022 (VTULF 71 63)--one-layer polyvinylbutylene primer, pigmented with lead chrome pigment. Perchlorovinyl enamels cannot be directly to it. Intermediate layer of enamel KhS-78 on base of copolymer A-15-0 needs to be applied	30-80 (when applied by brush) 18-22 (when applied by sprayer)	0.5 (at temperature above +10°C)	Mixture of ethyl and butyl alcohols in 3:1 ratio	Only for primer coating steel
Zinc-protective primer which is a mixture of 67 weight.% zinc dust (TsMTU 1229-45) with 33 weight.% of paint brand KhSL (GOST 7313-55). Made at site of use; applied by brush without diluting.	-	2-3 (at 18-23°C)	-	For primer coating steel surfaces working in aggressive atmosphere of chemical plants

<p>Protective primer of brand EP-057 VTU GIPI-4 1319-66 (suspension of zinc dust in solution of epoxy resin E-41 or E-33) and combined primer of brand EP-060 VTU GIPI-4 1320-66 (suspension of zinc dust and red lead in solution of epoxy resin E-41 or E-33). Supplied in set in form of base and hardener No. 3 (50% solution of polyamide resin PO-200 in xylene). Before using, the base is mixed with hardener No. 3 in a calculation of 100 weight. parts of base for 7 weight. parts of hardener. The primers are applied in two layers with a 1 h interval</p> <p>Enamels, perchlorovinyl of brand FKhV of different colors (GOST 6993-54)--solution of perchlorovinyl resin in organic solvents with addition of other resins, plasticizers and pigments</p> <p>Chemically stable primer of brand KhSG-26, enamels of brand KhSE of different colors and varnish of brand KhSL (GOST 7313-55)--solutions of perchlorovinyl resin in mixture of solvents with addition of pigments and plasticizer (varnish without pigments). Primer KhSG-26 and varnish KhSL can be used in integrated coating with perchlorovinyl enamels of other brands</p> <p>Chemically stable primer of brand KhS-010, enamel of brand KhS-710 and varnish of brand KhS-76 (GOST 9355-60)--solutions of resin SVKh-40 (copolymer of vinylidene chloride with vinyl</p>	<p>18-20 (by sprayer)</p> <p>Not more than 20</p> <p>No more than 20</p> <p>20</p>	<p>1(at 18-25°C)</p> <p>1(at 18-23°C)</p> <p>1(at 18-23°C)</p> <p>For primer--1; for enamel--2; for varnish--3</p>	<p>75% xylene 25% acetone</p> <p>R-4*</p> <p>R-4. In addition, mixture of 15% xylene, 15% acetone, 70% toluene</p> <p>R-4</p>	<p>For primer coating steel surfaces working under atmospheric conditions, water or aqueous solutions of salts</p> <p>For painting pre-primed metal surfaces, for protection from atmospheric corrosion)</p> <p>In complex multilayer coating for protection of outer surfaces of equipment and metal designs from effect of aggressive gases and weak solutions of acids, salts and alkalis at temperatures from -40 to +40°C</p> <p>In integrated multilayer coating for protection of equipment and metal designs from effect of solutions of mineral acids and alkalis at temperatures to +60°C</p>
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chloride) in mixture of organic solvents with addition of pigments (varnish--without pigments) Enamel, perchlorovinyl of brand KhV-124 and KhV-125 (GOST 10144-62)--solution of perchlorovinyl resin in mixture of organic solvents with addition of plasticizers and pigments. Enamel KhV-125 supplied in set as two components: base and pigment--aluminum fine powder PAK-3 or PAK-4 (GOST 5494-50). Before using, the base is mixed with the powder: 10 weight parts of powder are added to 100 weight parts of the base. The enamel is applied by paint sprayer only on the primer

(at 18-23°C)

1

R-4 or R-5**

For painting surface of metal for protection from atmospheric corrosion

* Composition of solvent R-4 (GOST 7827-55): 12% butyl acetate, 26% acetone and 62% toluene.

** Composition of solvent R-5 (TU MKHP 2191-50): 30% butyl acetate, 30% acetone and 40% xylene.

<p>Enamel KhS-78 (VTU KU-509-57)-- solution of resin A-15-0 (copolymer chlorovinyl with vinyl acetate) in mixture of organic solvents with addition of pigments and plasticizers. Apply on phosphating primer brand VL-02 or VL-022</p> <p>Varnish, bakelite (GOST 901-56) solution of resol resins in ethyl alcohol. For coating, varnish brands A and B are used. Coating thermally treated by special regime</p> <p>Varnish, ethinol (TU 1267-57) solution of polymers of acetylene derivatives in xylene fraction. Can be applied at temperatures to -25°C</p> <p>Paints, ethinol of brand EKA-15 (85-90% ethinol varnish, 15-10% aluminum powder), EKZHS-40 (60-65% ethinol varnish, 40-35% iron oxide), EKSS-50 (50-45% ethinol varnish, 50-55% red lead)</p> <p>Epoxy primer-spackle EP-00-10 (GOST 10277-62) consists of pigment, fillers and epoxy varnish. Supplied in form of two components: spackle mass and hardener No. 1 (50% solution of hexamethylenediamine in ethyl alcohol). Before use the components are mixed: for 100 weight parts of mass, 8.5 weight parts of hardener No. 1 are added.</p> <p>Epoxy-polyamide primer EG-4 (VTU GIPI-4 196-65)-- solution of epoxy and polyamide resin in mixture of solvents, with addition of pigments and</p>	<p>25-30</p> <p>-</p> <p>No less than 13</p> <p>No less than 10</p> <p>20-30</p> <p>-</p>	<p>1(at 19-23°C)</p> <p>24-30 (at 80-160°C)</p> <p>12(at 20°C)</p> <p>10(at 20°C)</p> <p>24(at 18-20°C)</p> <p>4-6 (at 18-22°C)</p>	<p>Toluene, xylene, solvent-naphtha or R-4</p> <p>Ethyl alcohol</p> <p>Xylene</p> <p>Xylene</p> <p>R-40* No. 646** or ethyl-cello-solves</p> <p>R-40</p>	<p>For protection of steel and duralumin from corrosion under conditions of increased moisture content, as well as in fresh and sea water at temperature to +40°C</p> <p>For anti-corrosion coatings of heat-exchange apparatus</p> <p>For water-stable anti-corrosion coatings (unresistant to effect of solar light)</p> <p>For water-stable anti-corrosion coatings (unresistant to effect of solar light)</p> <p>For priming metal under epoxy coatings; for anti-corrosion coatings, stable in water and alkali solutions</p> <p>For priming steel surface under epoxy and epoxy-polyamide coatings</p>
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<p>fillers. Produced in form of two components: paint paste EG-4G and hardener No. 2 (30% solution of polyamide resin PO-200 in solvent R-40). Before use of past it is mixed with hardener : 25 weight parts of hardener No. 2 are added to 75 weight parts of paste.</p> <p>Epoxy-polyamide enamel EP-140 (MRTU 6-10-599-66)--solution of epoxy and polyamide resins in mixture of solvents with addition of pigments and fillers. Produced in form of two components: base and hardener No. 2. Can be applied on EG-4 primer and without primer</p> <p>Enamel OEP-417-1, green (TU Yan-21-57) and OEP-4173-1, cream (TU Yan-22-57)--produced in form of two components: base (solution of epoxy resin E-41 in mixture of organic solvents with additions of pigments and fillers) and hardener No. 1. Before using, the base is mixed with hardener from calculation of 3.5 weight. part of hardener per 100 weight. part of base</p> <p>Varnishes, furyl, brand FL-1 (VTU P-35-58), FL-2 (VTU P-191-60) and F-10 (VTU P-186-60)--solutions of furyl resins in mixture of ethyl alcohol and acetone or alcohol and ethyl acetate. Can be strengthened by thermal treatment (drying in air--24 h; at 80-85°C--1 h; at 100-110°C--1 h; at</p>	<p>12-20 (from VZ-1)</p> <p>18-22 (at 20°C)</p> <p>-</p>	<p>4-6(at 18-22°C)</p> <p>2(at 120°C)</p> <p>-</p>	<p>R-40</p> <p>R-40, No 646</p> <p>Mixture of 50% acetone 50% ethyl alcohol</p>	<p>For protection of metal designs, pipelines of apparatus from atmospheric corrosion, as well as for protection of apparatus operating in aqueous solutions</p> <p>The same</p> <p>For anticorrosion coatings on metal (applied by special instructions of Institute of Plastics)</p>
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at 110-120°C--2 h; at 145-150°C
--3 h) or with help of hardener
(81% phosphoric acid), from cal-
culation of 2% acid in relation
to dry residue
Varnish, thermally-stable KO-815
(GOST 11066-64)--mixture of organo-
silicon resin F-9 and semi-
finished product FKh-02 dissolved
in toluene or xylene. Before use,
it is mixed with aluminum powder
in quantity of 6% of varnish weight

15

Drying regime: Toluene,
1-2 h at 20°C, xylene
then 1-2 h at
150°C

To cover parts working
at temperatures to
500°C

* Composition of solvent R-40 (VTU UKhP 86-59): 20% acetone, 30% ethyl cellosolve, 50%
toluene.

** Composition of solvent No. 646 (GOST 5630-51): 10% butyl acetate, 8% ethyl cellosolve, 7%
acetone, 15% butyl alcohol, 10% ethyl alcohol, 50% toluene.

Isol (GOST 10296-62) is a waterproofing and roofing roll material. It can be used to install waterproofing layers in structural acid-resistant floors. It is glued by bitumen of brand UV or bituminous pastes.

Relin (MRTU 21-10-65) is used to cover floors in order to protect them from the effect of solutions of salts, acids and alkali aggressive liquids. It is glued by pastes based on glue No. 88-N (TU UT 880-58).

(TU ShU-MKhP-79-56)

Brizol ^A is a new roll material. It is stable in diluted solutions of acids, and in salt solutions. It can be used as a waterproofing layer.

Polyvinyl chloride plastic compound. Industry manufactures sheet plastic compound (VTU MKhP 2024-49) of thickness from 1 to 5 mm. It can be used to line equipment, as waterproofing and for the fabrication of gaskets. It is inferior in chemical stability to polyvinyl chloride plastic (because of the use of plasticizers). It is resistant to diluted solutions of acids and alkalis, to salt solutions. It dissolves in dichloroethane and swells in benzene and toluene.

Polyisobutylene is resistant to solutions of acids and alkalis, but is not resistant to the majority of aromatic solvents and oils. It is broken down by oxidizers (see table III-65). The water absorption is 0-0.8%. Composites of polyisobutylene with fillers are used in anti-corrosion equipment.

Polyisobutylene is cold flow. The permissible compressing load on it does not exceed 3 kg-f/cm^2 . It is welded by hot air at 150-200°C. It is glued to metal and concrete by special glues: to metal by glue No. 88-N (MRTU 38-5-880-66) and to concrete by bitumen glue B-12.

Polyisobutylene is manufactured in the form of sheets. It is used to line equipment, and for installation of waterproofing. It can be used as an independent material at temperatures from -30 to +60°C, and as a sublayer in combined linings from -45 to +80°C.

Rubber (soft) and ebonite are widely used to rubberize equipment that is operating in aggressive media. Soft rubber is also used as a gasket material.

Rubber coatings are resistant to solutions of acids, alkalis and salts but are broken down in oxidizing media and in the majority of solvents. They have high resistance to wear, elasticity, high mechanical strength. The practical temperature limit of the use of rubbers is from -20 to +70°C.

The physical and mechanical properties and chemical stability of certain brands of rubbers and ebonites are presented in tables III-66 and III-67.

3. Refractory and Thermal-Insulating Materials

In the majority of productions of the nitrogen industry, the processes occur at high temperatures, therefore refractory and thermal-insulating materials have become popular in this area for lining and thermal insulation of the apparatus.

All the refractory items are divided into several groups (according to GOST 4385-48).

The refractory materials are divided into the following groups according to their chemical and mineralogical composition:

Chamotte (fireclay, fireclay-kaolin) made of refractory clays or kaolins with their leaning by chamotte (annealed clay or kaolin) or unplastic clay rock. It contains 30-45% Al_2O_3 .

High-alumina, made of minerals or artificial materials with high content of alumina (such as bauxite, artificial alumina, artificial and natural corundum). Depending on the Al_2O_3 content, high-alumina items of three classes are distinguished: VG-45, VG-62, VG-72 (content of Al_2O_3 in percents must be lower than the indicated numbers);

Chromium, made of chromite and burnt magnesite, often with the addition of alumina. If the charge contains over 50% chromite, the items are called chrome-magnesite. With a content of over 70% magnesite, they are called magnesite-chrome.

The correct selection and efficient use of refractory items which differ in quality, shape and dimensions guarantee an increase in the mechanical resistance and increase in the interrepair time of the thermal units, as well as the possibility of intensifying the processes occurring in them.

Below is a list of the properties of the refractory materials which define the possibility of their use.

Refractoriness is the capacity of the material to preserve its mechanical properties. It is usually characterized by the softening point of the items (in °C). Based on degree of refractoriness (in °C) the materials are divided into three groups:

Refractory	1580-1770
Highly-refractory	1770-2000
Highest refractoriness	over 2000

The ability to withstand the effect of high temperatures and compressing loads is characterized by the temperature at which the material begins to be deformed under the influence of a load of 2 kg-f/cm^2 (196133 n/m^2).

The construction strength of the refractory items is characterized by ultimate strengths during compression and is expressed in kg-f/cm^2 (n/m^2).

The seeming porosity (in %) is the ratio of the volume occupied by the pores that communicate with the atmosphere, to the total volume.

Additional linear shrinkage is an irreversible change in the linear dimensions of the items as a result of their heating to high

temperatures. A considerable change in the volume of the refractory materials can result in unsoundness of the lining, its premature destruction, etc. Therefore, shrinkage of the refractory items must be the minimum. It is expressed in percents of the initial volume and fluctuates in limits of 0-1%.

Table III-69 presents the basic properties of the refractory and thermal-insulation materials.

For correct lining of the refractory materials, it is important to take into consideration the coefficients of linear expansion of the employed materials. Below are the average values of these coefficients (in 10^6 deg^{-1}) in the temperature interval 20-1400°C for different refractory materials:

Zirconium dioxide	9.9-10.2	High-alumina light-weight	4.7
Magnesite-chromite	12	Chamotte classes A	
Chrome-magnesite	10.4	B	5.9
High-alumina refractory material		Light-weight chamotte of brand	
of class VG-72	6.5	BL-1.0	5.5-
of class VG-62	5.7		5.9
of class VG-45	5.5	Foam-chamotte	5.7-
			5.8
		Ultra light-weight	5.7

Figures III-21 and III-22 show the dependence of heat conductivity of the materials presented in table III-69 on temperature.

Tables III-70 present GOST and TU for refractory and thermal-insulation items. Their areas of application are in the nitrogen industry as well as the manufacturing enterprises of refractory materials 46-50, 54.

The described main properties of refractory and thermal-insulation materials and the requirements for the conditions of their use make it possible to select the material and to compute the necessary thickness of the equipment lining.⁵¹ However, the quality and performance capacity of the lining are determined not only by the use of the appropriate refractory materials, but also by the care-

careful making of the lining (including drying out of the lining after laying).

All the seams of the refractory lining (inner and outer) are made of refractory mortars, and when laid dry, predried refractory powder. Table III-71 presents the composition, main properties and area of application of the refractory mortars. 52, 53, 55

Depending on the required operating conditions of the equipment, the refractory lining is divided into three categories:

Category of lining	Thickness of seam, mm, no more	Volume of dry mortar, % of volume of lining
First	1	3-4
Second	2	5-6
Third	3	8-9

Designing and rating of units made of heat-resistant concrete are done according to "Instructions for Manufacture and Use of Heat-Resistant Concretes" (Gostroyizda, 1958) and "Temporary Instructions for Designing Heat-Resistant Reinforced Concrete Designs" (Gostroyizdat, 1957).

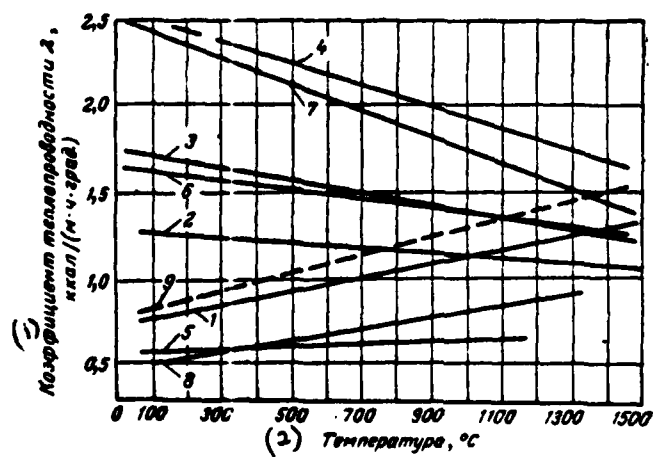


Figure III-21. Dependence of Heat Conductivity of Refractory Materials on Temperature from Data of Different Researchers:

Curve	Material	λ
1	Chamotte	$0.72+0.0005t$
2	High-alumina refractory material of class VG-45	-
3	The same of class VG-62	$1.72-0.00038t$ (for $t=200-1000^{\circ}\text{C}$)
4	The same of class VG-72	$2.56-0.0007t$ (for $t=300-1000^{\circ}\text{C}$)
5	Zirconium dioxides (with compact crock)	-
6	Chrome-magnesite	$1.61-0.0002t$
7	Magnesite-chromite	$2.51-0.00078t$
8	High-alumina light-weight	$0.564+0.000066t$
9	Zirconium dioxide (grainy structure)	-

- Key:
1. Coefficient of heat conductivity λ , kcal/(T x h x deg)
 2. Temperature, $^{\circ}\text{C}$

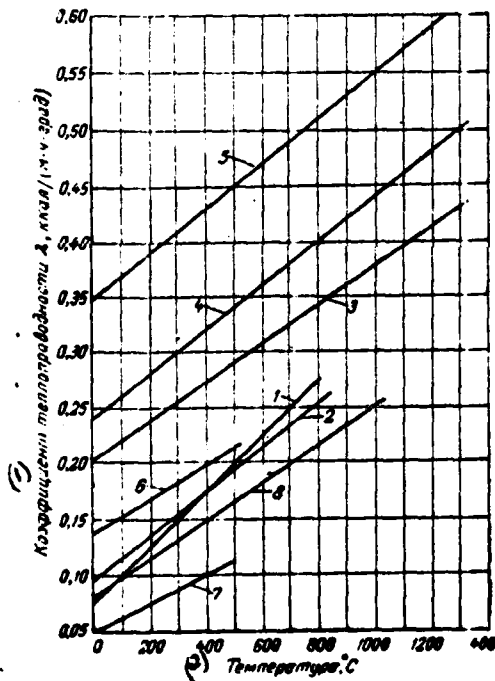


Figure III-22. Dependence of Heat-Conductivity of Thermal-Insulation Materials on Temperature from Data of Different Researchers

- Key:
1. Coefficient of heat conductivity, λ , kcal/(T x h x deg)
 2. Temperature, $^{\circ}\text{C}$

Curve	Material	λ
1	Diatomic powder	$0.078+$ $0.00024t$
2	Diatomite of brand 600	$0.095+$ $0.0002t$
3	Light-weight chamotte of brand BL-0.8	$0.20+$ $0.00018t$
4	Foam chamotte	$0.24+$ $0.0002t$
5	Light-weight chamotte of brand BL-1.0	$0.35+$ $0.0002t$
6	Asbestos cardboard	$0.135+$ $0.00016t$
7	Mineral wool	$0.05+$ $0.000125t$
8	Ultra lightweight	$0.08+$ $0.00017t$

4. Compressors⁵⁶⁻⁶⁰

General Section

Compressor machines are designed to mix and compress gases and gas mixtures. Piston and centrifugal compressors have become the

TABLE III-69. MAIN PROPERTIES OF REFRACTORY AND THERMAL-INSULATING MATERIALS

Indicators	(1)	(2)	(3)	(4) Refractory materials			(5)	(6) Thermal insulating materials			(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)									
				(a)	(b)	(c)		A	B	C										D	E	F	G	H	I	J	K	L
Density, kg/m ³	3300	2800	2900	2800	2650	2500	1400	2150	2050	1800	800	800	600	600	600	600	600	600	600									
Refractoriness, °C	2400	1900	1900	> 1810	> 1800	> 1750	1850	1730	1670	1610	1670	1670	1670	1670	1670	1670	1670	1670	1670									
Temperature for beginning of deformation (with load of 2 kg-f/cm ²), °C	-	1500	1500	1500	1450	1100	1370	1300	-	-	-	-	-	-	-	-	-	-	-									
Ultimate strength in compression, kg-f/cm ²	-	200	250	200	200	200	45-50	125	125	100	20-30	20-30	30	30	30	30	30	30	30									
Maximum permissible temperature of use, °C	1800	1650	1650	1500	1500	1300	1450	1430	1250	-	1250	1250	1150	950	1300	1100	800	600	500									
Seaming porosity, %	28	20	25	21-24	14-24	14-24	57-65	30	30	30	60	57-65	57-65	-	-	-	-	-	-									
Additional shrinkage with indicated temperature (in °C), %	-	-	-	1.0	0.4	0.5	0.5	0.7	0.7	0.7	0.7	0.5-1.2	1.0	-	-	-	-	-	-									
Insulation**	Открытая (21)			Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)	Открытая (21)									

* At 1 kg-f/cm²

- ** Insulation contacting medium in apparatus called open; noncontacting--closed.
- | | | |
|--|---|-------------------------------|
| 1. Zirconium dioxide | 8. Lightweight chamotte of brands BL-0.8 and BL-1.0 | 17. Mineral wool of brand 150 |
| 2. Magnesite-chromite | 9. Foam chamotte | 18. Refractory materials |
| 3. Chrome-magnesite | 10. Ultra-lightweight material | 19. Thermal insulation |
| 4. High-alumina refractory material of class | 11. Diatomite of brand 600 | 20. Not standardized |
| 5. VG | 12. Fill | 21. Open |
| 6. High-alumina refractory unyielding lightweight material | 13. Made of chamotte | 22. Open and closed |
| 7. Chamotte of class | 14. Made of lightweight chamotte | 23. Closed |
| | 15. Made of diatomite | 24. No less than |
| | 16. Asbestos cardboard | |

TABLE III-70. AREA OF APPLICATION OF REFRACTORY MATERIALS AND THERMAL INSULATION IN NITROGEN INDUSTRY. MANUFACTURING PLANTS OF REFRACTORY MATERIALS

Refractory and thermal-insulation materials	Use in nitrogen industry	Certain manufacturing plants	GOST or TU
Zirconium dioxide	First row of lining of converter for high-temperature conversion of methane	Experimental UNIIO plant	CHMTU 7-59
Magnesite-chromite	First row of lining of converter for high-temperature conversion of methane and heating chamber in section of methane conversion	Izhorskiy "Magnesite," Panteleymonovka	CHMTU 5129-55 and 10204-57
Chrome-magnesite	First row of lining of heating chamber in section of methane conversion	Chasov-Yar "Magnesite," Panteleymonovka	GOST 5381-50
High-alumina refractory material of classes VG-72 and VG-62**	First row of lining of converters for catalytic conversion of methane, preheaters (lower part), gas generators; second row of lining of converter for high-temperature conversion of methane	Chasov-Yar Semiluki, Podol'sk, Chasov-Yar	MRTU 14-06-03-14-62
High-alumina refractory material of class VG-45	In number of cases, substitute for high-alumina refractory materials of classes VG-72 and VG-62		
High-alumina refractory light-weight Chamotte:	Third row of lining of converter of high-temperature methane conversion	Chasov-Yar, Podol'sk, Snegirevka	MRTU 14-19-20-66
class A	First row of lining of moistener; second row of lining of heating chamber; lining of pipelines	Semiluki, Chasov-Yar plants; Borovichi kombinat	GOST 390-54 GOST 8691-58
class B	Substitute of chamotte class A for lining moistener and pipelines		
class C	Not used		
Light-weight chamotte of brands BL-0.8 and BL-1.0	Second row of lining of converters of high-temperature conversion of methane, moistener; first row of lining of heating collector	Snegirevka, Chasov-Yar	GOST 5040-58 GOST 8691-58
Foam-chamotte ultra light-weight	Substitutes of light-weight chamotte brand BL-0.8 and EL-1.0	Podol'sk, Snegirevka, Chasov-Yar	GOST 5040-58 GOST 8691-58
Diatomite brand 500	Lining of preheaters, pipelines		GOST 2694-52

Fill:			
of chamotte	In methane converters	-	-
of light-weight chamotte	Not used	-	-
of diatomite	In preheaters, moisteners	-	-
Asbestos card-board	In all lined apparatus and pipelines	-	GOST 2850-58
Mineral wool of brand 150	To insulate covers of certain apparatus and insulate pipelines of complex configuration	-	GOST 4640-66

* Only experimental batches made.

** For methane converters in new units, high-alumina refractory material is used with Al_2O_3 content no less than 98% (according to MRTU 14-06-25-63).

TABLE III-71. CHARACTERISTICS OF REFRACTORY MORTARS

Indicators	High-alumina mortars of fine grinding (GOST 6137-61)		Chamotte mortars of fine grinding (GOST 6137-61)		Chrome-magnesite mixture (ChMTU 8-59) UNIIO
	brand VT-1	brand VT-2	brand ShT-1	brand ShT-2	
Refractoriness, °C	1800	1750	1730	1690	2000
Oxide content, weight %					
Al ₂ O ₃ +TiO ₂	60	45	38	33	-
MgO	-	-	-	-	33
Cr ₂ O ₃	-	-	-	-	22
Raw composition, wgt.%					
leaning additive	80-85		80-85		-
plastic refractory clay	20-15		20-15		-
ground chromite ore	-		-		70
magnesite powder	-		-		30
Granulometric composition, weight.%					
passes through sieve					
No. 1	100		100		-
No. 05, no less	95		95		-
No. 009, no less	60		60		-
No. 009, no more	85		85		-
fraction 1-2 mm, no more	-		-		10-15
fraction 0.088 mm, no less	-		-		35-50
Approximate quantity of water for preparation of mortar, l per 1 m ³ of dry mixture	500		600		-
Use	Filling of seams of lining made of high-alumina refractory materials		made of chamotte foam chamotte, ultra light-weight, diatomite		made of chrome-magnesite and magnesite-chromite

the most popular in the nitrogen industry.

In selecting the compressor, one should take into account the presence of admixtures in the compressible gas in order to determine the permissible duration of operation of the machine. For example, with considerable (over 0.02%) content in the compressible gas of hydrogen sulfide, the valves of the piston machine rapidly malfunction or the rotary blades of the centrifugal machine. The high content of benzene (over 2 g/m³) causes a disruption in the lubrication of the piston machine (as a consequence of the thinning of the

grease); the unsaturated hydrocarbons contained in the gas when deposited on the walls of the cylinder or the moving parts of the machine may break down with ignition and explosion; the content in the gas of over 5 mg/m^3 of dust or other mechanical admixtures (carbon black, naphthalene, resins, etc.) results in rapid wear of the main machine assemblies, etc.

In order to maintain the compressors in good working condition, preventive maintenance is performed (maintenance, average repairs and major overhaul).

In maintenance, individual assemblies of the compressor are checked, interaction of the components of each part, in particular, the fastening assemblies and those exposed to the effect of sign-variable loads (crank bolts, sockets, dowels, etc.); gaps and clearances of the controllable parts (bushings of bearings, keys, tightening bushings, etc.), packings of gaskets, tightness of the fittings, valves, condition of the electrical contacts, etc.

Small rapidly worn out parts are replaced; the working surfaces are cleaned and polished; the valves are set or replaced; the gasket packings are replaced; the washers are replaced; the fastening parts are tightened; the lubricating and cooling systems are cleaned; and the accuracy and quality of assembly of the unit are checked.

In average repairs, individual large assemblies of the compressor are checked with replacement of some of the parts. In this case, the bearings are resealed; the washers are replaced, the gaskets and the fastening parts are packed; the pistons are bored out, as well as the seats and valves with subsequent setting; the piston rings are changed; the interstage apparatus is examined at set times and protective anticorrosion coatings and linings are made; the insulation is repaired, etc.

Major overhaul is restorative repair of the entire compressor unit. In this case all the basic parts of the compressor may be completely (or partially) disassembled and sent to the specialized repair base or plant. This work includes complete dismantling of the

entire unit, replacement of the parts or whole assemblies, verification of the operation of all mechanisms, and assembly of the compressor. All the worn-out parts are repaired or replaced with new ones; the coaxial alignment of the parts is checked and the working plantes are treated; the banks, crankshaft and other machine parts are checked and centered.

After major overhaul, the output of the machine must be the original and the entire unit must operate normally with a high efficiency.

Halting of the compressors for repair, runs between repairs and coefficients of machine use are normed according to the indicators which have been attained at the leading enterprises of the nitrogen industry (table III-72).

TABLE III-72. RUNNING AND IDLE TIME OF CERTAIN PISTON MULTISTAGE COMPRESSORS ACCORDING TO NORMS OF LEADING ENTERPRISES OF NITROGEN INDUSTRY FOR 1965-1966

Type and brand of compressor	Characteristics of compressor	Running time between repairs, h			Idle time for repair, h			Coef. of machine use
		major	average	maint.	major	aver.	maint.	
Gas six-stage IG-266/320 and 2ShLK-1420	Q=16,000 n=125 rpm P _k =320	25,920	4320	1440	720	120	48	0.932
Nitrogen-hydrogen four-stage 3G-83-10/320	Q=5000, P _H =10 P _k =320	25,920	4320	2160	336*	60*	16*	0.967*
		25,920	-	-	480	60	16	0.972
Nitrogen five-stage	Q=3000, P _k =200	25,920	4320	2160	432	56	16	0.969
For compression of coking gas, two-stage 3G-141/13	Q=8500 P _k =13	25,920	4320	2160	360	72	24	0.968
Gas circulation one-stage with electric drive	Q=360-630 (for suction) P _H =285, P _k =320	43,200	2880	1440	288	96	48	0.975

Notes: 1. The numbers indicated by an asterisk refer to old, better developed machines.

2. Q--output of compressor (in m³/h); P_H and P_k--respectively the beginning and final gage pressure of the gas^H (in atm.).

It should be noted that recently large compressors have been made on new, so-called opposite bases. These are horizontal piston multiple-cylinder compressors with counter movement of the pistons ("boxer" compressors). The flowsheet of these machines consists of the fact that the multiple crankshaft is placed on the crankshaft bearings of the opposite frame. Cylinders are attached to both sides of it. Thus, during rotation of the shaft, the pistons either move toward each other, or are separated from each other, at the same time almost completely balancing the developing inertia forces. These compressors are fast, compact, have lower weight and do not require construction of a cumbersome foundation. They should be given preference when selecting machines. The maximum output of the piston multiple-stage opposite high-pressure compressors with electric drive is up to 40,000-60,000 m³/h. The standards for running and the coefficients of use of these machines are set based on the accumulated experience of operation.

Piston Compressors

Working Process of Compressor

In examining the active (working) process of the piston compressor, we take into consideration all those phenomena whose influence is excluded in the theoretical process.

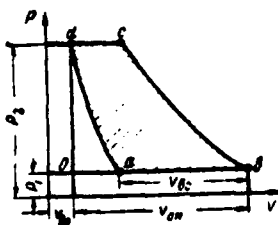


Figure III-23. Effect of Harmful Space on Output of Compressor

The presence of harmful space is inevitable in piston compressors. It is 3-12% (and sometimes even more) of the volume described by the piston.

The diagram (fig. III-23) shows the effect of harmful space. The gas remaining in the harmful space v_{bp} at pressure p_2 is

expanded when the piston reverses on line da; consequently, the fresh gas will begin to enter only from point a with suction pressure p_1 . Thus, the volume described by the piston v_{on} is not completely used, but only on line ab (quantity v_{ec}). Complete operation of the compressor is determined in this case by the area abcd.

The ratio of the volume of gas sucked in one piston stroke to the volume that is circumscribed by the piston is called the volume efficiency of the compressor λ_{06} :

$$\lambda_{06} = \frac{v_{ec}}{v_{on}}$$

The sizes of the segments v_{ec} and v_{on} can be taken from the indicator diagram which is removed from the active machine or a constructed one during the designing.

The ratio of the volume of harmful space v_{sp} to the volume that is described by the piston v_{on} is expressed by the quantity of relative harmful space ϵ :

$$\epsilon = \frac{v_{sp}}{v_{on}}$$

By knowing the initial p_1 , final p_2 pressures, the quantity of relative harmful space and the specific volumes of gases before expansion v_1 and after it v_2 , one can determine the volume efficiency of the compressor λ_{06} , depending on these quantities:

$$\lambda_{06} = 1 - \epsilon \left(\frac{p_2}{p_1} - 1 \right) \quad (III-1)$$

for isothermic compression

$$\lambda_{06} = 1 - \epsilon \left(\frac{p_2}{p_1} - 1 \right) \quad (III-2)$$

for adiabatic

$$\lambda_{06} = 1 - \epsilon \left[\left(\frac{p_2}{p_1} \right)^{1/k} - 1 \right] \quad (III-3)$$

for polytropic

$$\lambda_{06} = 1 - \epsilon \left[\left(\frac{p_2}{p_1} \right)^{1/m} - 1 \right] \quad (III-4)$$

In practice, the polytropic curve index is $m=1.2-1.4$.

It is apparent from equations (III-1)-(III-4) that the larger the harmful space and the degree of compression $\tau = \frac{p_2}{p_1}$, the lower the volume efficiency of the compressor. It is usually assumed to be no less than 0.7.

If the final pressure in the cylinder is increased, then the volume efficiency will be reduced, and a moment can occur when it becomes equal to zero. The output of the compressor in this case will also equal zero. From equation (III-4) with $\lambda_{06} = 0$ we obtain the limit quantity of the degree of compression in one stage:

$$\tau = \frac{p_2}{p_1} = \left(\frac{1}{\epsilon} + 1\right)^n \quad (\text{III-5})$$

If we assume that the volume efficiency is 0.7, then the limit degree of compression equals:

$$\tau = \left(\frac{0.3}{\epsilon} + 1\right)^n$$

The dependence of the limit degree of compression on the temperature for the end of compression is expressed by the equation:

$$\tau = \left(\frac{T_2}{T_1}\right)^{\frac{k}{k-1}} \quad (\text{III-6})$$

The final temperatures of compression must not exceed 160-170°C since at higher temperatures, the grease begins to break down with the release of volatile substances. This results in the appearance of carbon deposits, disruption in the operation of the valves and threat of formation of an explosive mixture.

Effect of resistance in the suction pipeline and compressor valves. If significant resistance to the flow of gas is created in the suction line (because of insufficient section of the suction pipeline, the presence of separating or filtering apparatus, large number of fittings, etc.), then the pressure of suction can be set lower than atmospheric, i.e., a vacuum is formed in the compressor cylinder which results in reduction in volumetric efficiency. Resistance to gas flow in the compressor valves also leads to the same results.

The effect of resistance on the output of the compressor is taken into consideration by the so-called coefficient of throttling λ_p . The quantity λ_p usually fluctuates in limits of 0.95-0.98. It can be >1 with pressurization.

Effect of gas preheating. The temperature of the suctioned gas is increased as a consequence of its mixing with the gas that remains in the harmful space of the cylinder, as well as as a result of its contact with hot parts of the cylinder. Consequently, the output of the compressor in this case will be reduced by the quantity λ_t which is called the coefficient of preheating.

The value λ_t practically fluctuates in limits of 0.98-0.99.

The effect of gas leaks is taken into consideration by the coefficient of hermetic sealing λ_r . Its quantity is adopted in the interval of 0.95-0.98.

External leaks develop as a consequence of the poor assembly of the gaskets; in the safety valves installed at each stage of the compressor; in the interstage coolers; with periodic blowing through of the oil-separators, etc.

Internal gas leaks occur in the valves, in the piston rings, etc.

Coefficient of supply and output of the compressor. The ratio of the volume of the gas that is actually fed to the pressure line (v_ϕ) to the volume described by the piston (v_{on}) is called the coefficient of supply λ :

$$\lambda = \frac{v_\phi}{v_{on}}$$

The actual output of the compressor is determined from the equation

$$v_\phi = i F s n \lambda \text{ m}^3/\text{min}$$

where i --number of sides of effect of cylinder (one or two);

F --working area of piston, m^2 ;

s --piston stroke, m ;

n --rate of rotation of shaft of compressor, rpm.

The coefficient of supply λ is smaller than the volumetric efficiency (λ_{06}) since its determination takes into consideration all the main losses of the compressor which are not reflected by the indicator diagram (and consequently, the volumetric efficiency). In order to evaluate these losses, the coefficient of effectiveness of suction ϕ_s is introduced which takes into account the effect of all the losses of the basic factors on the compressor productivity. Then the coefficient of supply

$$\lambda = \lambda_{06} \phi_s$$

The coefficient of effectiveness of suction can be expressed by the product of the coefficients:

$$\phi_s = \lambda_p \lambda_i \lambda_r$$

Thus, the coefficient of supply equals:

$$\lambda = \lambda_{06} \phi_s = \lambda_{06} \lambda_p \lambda_i \lambda_r$$

For approximate determination of the quantity ϕ_s , either graphs constructed from experimental data are used, or an empirical formula for one-stage compression:

$$\phi_s = 1.01 - 0.022\tau$$

where $\tau = p_2/p_1$ -- degree of compression.

Indicator Diagram

Using the indicator diagram taken by a special instrument (indicator) from the active compressor, one can determine the average indicator pressure from the formula:

$$P_{\text{ind}} = \frac{l}{lM} \text{ kg-f/cm}^2$$

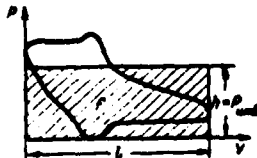


Figure III-24. Indicator Diagram of Compressor

where f --area of indicator diagram (determined, for example, with the help of a planimeter), cm^2 ;

l --length of abscissa corresponding to the piston stroke, cm ;

M --scale of pressures of spring of indicator (given in certificate of instrument).

If the indicator area f is replaced by an equally large area of a rectangle with base l , then height h in a definite scale will equal the average indicator pressure $P_{\text{вмд}}$ (fig. III-24).

The area of the indicator diagram in a certain scale is numerically equal to the work of the compressor that is completed in one rotation of the crankshaft relative to a unit of area of the piston. In the case of cylinders of double action, the computations are made for each side. The obtained quantities are added.

The indicator power for the compressor of simple (one-sided) action is determined according to the formula:

$$N_{\text{вмд}} = \frac{P_{\text{вмд}} F s n}{60 \cdot 102} \text{ kW}$$

where $P_{\text{вмд}}$ --average indicator pressure (from the diagram), kg-f/cm^2 ;

F --area of piston section, cm^2 ;

s --piston stroke, m ;

n --rotation rate of compressor crankshaft, rpm .

In designing, the rated indicator power of the compressor can be defined as follows:

$$N_{\text{вмд}} = \frac{L_{\text{ад}}}{60 \cdot 102} = 1.634 \frac{k}{k-1} P_1 V_1 \left(\tau^{\frac{k-1}{k}} - 1 \right) \text{ kW}$$

where $L_{\text{ад}}$ --work of adiabatic compression, $\text{kg-f} \times \text{m}$;

k --index of adiabatic curve;

P_1 --pressure in cylinder at end of suction, atm ;

V_1 --volume suctioned in 1 min. with pressure and temperature at end of suction, m^3 ;

τ --degree of compression.

Efficiency

The isothermic efficiency η_{is} is the ratio of the amount of work or output which is determined for the isothermic compression to their values found from the indicator diagram:

$$\eta_{is} = \frac{L_{is.}}{L_{ind.}} = \frac{N_{is.}}{N_{ind.}}$$

The isothermic efficiency is the indicator of thermal efficiency of the compressor. It does not take into consideration the losses for friction and depends on a number of different factors. The maximum value of η_{is} for the piston machines reaches 0.68.

The adiabatic efficiency η_{ad} characterizes the work of the compressors without cooling

$$\eta_{ad} = \frac{L_{ad.}}{L_{ind.}} = \frac{N_{ad.}}{N_{ind.}}$$

The quantity η_{ad} is usually 0.93-0.97.

The mechanical efficiency $\eta_{mex.}$ is the ratio of indicator power to power expended on the compressor shaft:

$$\eta_{mex.} = \frac{N_{ind.}}{N_s}$$

The power spent to overcome friction equals:

$$N_{fp.} = N_s - N_{ind.}$$

Then

$$\eta_{mex.} = \frac{N_{ind.}}{N_{ind.} + N_{fp.}} = \frac{1}{1 + \frac{N_{fp.}}{N_{ind.}}}$$

With direct drive (the engine is seated on the compressor crankshaft), the quantity $\eta_{mex.}$ is 0.8-0.96.

The total or complete isothermic efficiency equals:

$$\eta_{is.} = \eta_{ad.} \eta_{mex.}$$

The complete efficiency of the compressor with regard for the efficiency of the engine and the drive (reducer or belt textrope or other transmission) equals:

$$\eta_n = \eta_{\text{gas}} \cdot \eta_{\text{mech}} \cdot \eta_{\text{tr}} \cdot \eta_{\text{prop}}$$

The complete efficiency of modern compressors lies in broad limits:

$$\eta_n = 0.45 - 0.62$$

Multiple-Stage Compression

In order to guarantee the normal process of compression of gas to the required amount, multiple-stage compressors are used since the process in one stage is restricted by the limiting degrees of compression and the limiting temperatures [equations (III-5) and (III-6)].

Figure III-25 presents the theoretical diagram of three-stage compression. Compression in the first stage occurs according to the adiabatic curve BC to intermediate pressure P_1 . The gas is further cooled in the interstage cooler of the first stage to the initial temperature according to the isobar CB' and is compressed in the second stage according to the adiabatic curve B'C', etc. At each stage, during cooling, the point for the beginning of compression is returned to the isotherm BE. Consequently, the line is shifted towards the isotherm, i.e., passes with the greatest efficiency. Since multiple-stage compression is a set of single-stage processes, its operation is equal to the sum of operations of the single-stage cycles. The hatched area expresses the advantage in the operation with three-stage compression as compared to one-stage.

With a rise in the number of stages, the design of the compressor is complicated, therefore, in practice, for a different number of stages, the following pressures are adopted (in kg-f/cm²):

Number of stages	Pressure	Number of stages	Pressure
1	to 7	5	150-1000
2	5-30	6	200-1100
3	13-150	7	450 1100
4	35-400		

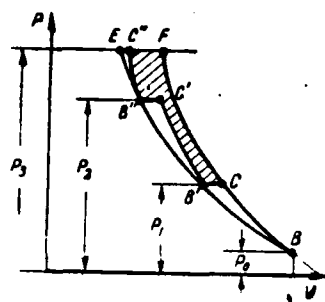


Figure III-25. Diagram of Three-stage Compression of Gas

If we assume the same degree of compression τ for each stage, with z stages of compression it equals:

$$\tau = \sqrt[z]{\frac{P_2}{P_1}}$$

where P_1 and P_2 -- initial and final pressure of gas, atm.

With the same degrees of compression in all stages and complete cooling between the stages, the theoretical operation of the compressor and the temperature at the end of compression can be computed according to the following equations:

$$L = z \frac{k}{k-1} P_1 V_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{z}} - 1 \right] \text{ kg-f x m}$$

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{z}} \text{ } ^\circ\text{K}$$

In actuality, the degrees of compression in the multistage compressor are not the same and are usually greater than the theoretical, since they take into consideration the pressures between the stages. If we designate through ψ the coefficient which takes into consideration these losses, then the actual amount of the degree of compression equals:

$$\tau = \psi \sqrt[z]{\frac{P_2}{P_1}}$$

From here the actual number of stages of compression will be:

$$z = \frac{\lg P_2 - \lg P_1}{\lg \tau - \lg \psi}$$

In determining the necessary number of stages of compression z using this equation, the quantities τ and ψ are assigned. In practice they are:

$$\tau = 2.5 - 3.5 \quad \psi = 1.1 - 1.25$$

For better use of the volumes of the cylinders, we assume

$$\frac{V_1}{V_2} = \frac{V_2}{V_3} + \dots + \frac{V_{z-1}}{V_z} = \tau$$

where $V_1, V_2, V_3, \dots, V_z$ -- volumes of cylinders respectively 1, 2, 3, ..., of the z -th stage of the compressor.

With the same piston stroke for all cylinders, their diameters correspondingly equal:

$$D_2 = \frac{D_1}{\sqrt{\tau}}; \quad D_3 = \frac{D_2}{\sqrt{\tau}}; \quad D_z = \frac{D_{z-1}}{\sqrt{\tau}}$$

The actual working process of the interstage compression deviates from the theoretical as a consequence of the effect of the reducing compressibility of the real gases. If the gas or the gas mixture is compressed to pressure above 75 atm., the coefficient of compressibility β is introduced into the characteristic equation:

$$pV = \beta RT$$

The adiabatic work of compression for the z -stage cycle with regard for the coefficient of compressibility equals:

$$L_{ad} = \frac{P_1 V_1}{\beta_1} \left\{ \frac{k}{k-1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right] + (\beta_1 - \beta_2) \right\} \text{kg-f x m/kg}$$

This equation can be transformed as follows:

$$L_{ad} = z \frac{P_1 V_1}{\beta_1} \left[\frac{k}{k-1} \cdot \frac{T_1}{273} \left(\tau^{\frac{k-1}{kz}} - 1 \right) + \rho_2 - \rho_1 \right] \text{kg-f x m/kg}$$

where v --specific volume of gas;

β_1 and β_2 --special coefficients of compressibility respectively with pressure of suction of first stage and pressure of injection of z -th stage (β and ρ are linked by the following ratio: $\beta = \rho \times 273/T$).

The volumetric efficiency for real gas in multiple-stage compression to high pressures is determined from the equation

$$\lambda_{\text{vol.}} = 1 - e \left(\tau^{1/k} \frac{\beta_1}{\beta_2} - 1 \right)$$

while the coefficient of supply from the equation:

$$\lambda = \left[1 - e \left(\tau^{1/k} \frac{\beta_1}{\beta_2} \right) \right] (1.01 - 0.022\tau)$$

The power on the compressor shaft N_g with actual volume of the gas V_ϕ fed by the compressor is determined by the equation:

$$N_g = \frac{V_\phi L_{\text{act.}}}{3600 \cdot 102 \eta_{\text{me.}} \eta_{\text{max.}}} \text{ kg-f x m/kg}$$

where v --specific volume of gas with temperature and pressure of suction.

In multiple-stage compressors and multiple-stage cooling, the operation of the compressor depends not only on the temperature of the compressed gas, but on the temperature of the cooling water:

$$L_{\text{act.}} = P_{\text{so.1}} v_{01} \left(1 + \frac{t_{\text{sox.}} - t_{\text{sc.}}}{T_{01}} \cdot \frac{\lg \frac{P_2}{P_1}}{\lg \frac{P_2}{P_{\text{so.1}}}} \right) 2.303 \lg \frac{P_2}{P_{\text{so.1}}} \text{ kg-f x m/kg}$$

where $P_{2\text{sc.1}}$ --initial pressure of gas in suction line of first stage, kg-f/m²;

v_{01} --specific volume of gas before first stage, m³/kg;

$t_{\text{sox.}}$ --temperature of cooling water, °C;

t_{sc} and T_{01} --temperature of gas at suction of first stage, respectively in °C and °K;

P_2 --pressure of injection of first stage, kg-f/m²;

P_z --pressure of injection of z-stage, kg-f/m².

The isothermic power of the z-th stage of the compressor is determined from the equation:

$$N_{is. z} = \frac{T_{cool. z}}{T_{01}} \cdot \frac{10^4}{3600 \cdot 102} \cdot \frac{P_{so. 1} V_{1z}}{\rho_{so. 1}} \left(\frac{T_{01}}{273} \cdot 2.303 \lg \frac{P_z}{P_{so. z}} + \rho_z - \rho_{so. z} \right) \text{kW}$$

where $T_{cool. z}$ --temperature of cooling water, °K;

V_{1z} --output of z-th stage under conditions of suction of first stage, m³/h;

P_z --final pressure after z-th stage, kg-f/cm²;

$P_{gc. z}$ --pressure of gas in interstage cooler before z-th stage, kg-f/cm²;

$\rho_{sc. 1}$ --special coefficient of compressibility with pressure of $P_{sc. 1}$;

ρ_z --the same with pressure of P_z ;

$\rho_{sc. z}$ --the same with pressure of $P_{gc. z}$.

The coefficients of compressibility ρ and their special values ρ are defined in broad limits of pressures and temperatures for the majority of gases and gas mixtures used in equipment (see vol. 1 of Reference Book for the Gas Industry Worker).

Below are the empirical formulas for determining the special coefficients of compressibility of certain gases in pressure intervals from 100 to 1000 atm. and temperatures from 20 to 200°C:

Gas	Equation
Nitrogen	$\rho = 0.801 + 1.244 \frac{P}{1000} + 0.433 \frac{t}{100}$
Hydrogen	$\rho = 0.990 + 0.721 \frac{P}{1000} + 0.376 \frac{t}{100}$
Carbon monoxide	$\rho = 0.757 + 1.298 \frac{P}{1000} + 0.434 \frac{t}{100}$
Nitrogen-hydrogen mixture	$\rho = 0.973 + 0.818 \frac{P}{1000} + 0.381 \frac{t}{100}$
The same for 500°C	$\rho = 0.960 + 0.862 \frac{P}{1000} + 0.374 \frac{t}{100}$
Air	$\rho = 0.787 + 1.207 \frac{P}{1000} + 0.432 \frac{t}{100}$

The isothermic efficiency of the multiple-stage compressor

can be defined as the ratio of work of isothermic compression L_{is} to the sum of indicator works of all stages or the ratio of the power in isothermic compression to the sum of the indicator powers:

$$\eta_{is} = \frac{L_{is}}{L_{ind.1} + L_{ind.2} + \dots + L_{ind.n}} = \frac{N_{is}}{N_{ind.1} + N_{ind.2} + \dots + N_{ind.n}}$$

Below are the nomograms to determine the parameters of the piston compressors and the examples of using them.

1. The volume V_2 of gas compressed to pressure P_2 with regard for the coefficients of compressibility β with assigned temperatures is determined with the help of a nomogram (fig. III-26) constructed from the condition that the equation $PV = \beta RT$ is correct for real gas, i.e.,

$$\frac{P_1}{\beta_1} \cdot \frac{V_1}{T_1} = \frac{P_2}{\beta_2} \cdot \frac{V_2}{T_2} = R$$

From here

$$V_2 = V_1 \frac{P_1 T_2 \beta_2}{P_2 T_1 \beta_1}$$

Here P_1 (kg-f/cm²), V_1 (m³) and T_1 (°K)--respectively the pressure in suction (absolute), actual volume of compressed gas, and its beginning temperature;

P_2, V_2 and T_2 --pressure at end of compression, volume and temperature of compressed gas;

β_1 and β_2 --coefficients of compressibility for initial and final conditions (can be found with the help of curves in fig. III-26).

Example. Dry air in a quantity of $V_1 = 8570$ m³ with initial absolute pressure $P_1 = 1.033$ atm. and initial temperature $t_1 = 0^\circ\text{C}$ ($T_1 = 273^\circ\text{K}$) is compressed to $P_2 = 346$ atm. and $t_2 = 25^\circ\text{C}$ ($T_2 = 298^\circ\text{K}$).

From the nomogram we find for air the value $\beta_1 = 1.0$ and $\beta_2 = 1.15$. Consequently,

$$V_2 = 8570 \frac{1.033}{346} \cdot \frac{298}{273} \cdot \frac{1.15}{1.0} = 32.1 \text{ m}^3$$

2. In order to determine the isothermic power, the nomogram is used for real gases presented in fig. III-27.

The isothermic power in this case is determined from the equation:

$$N_{\text{из.}} = 0.736 \cdot 0.0852 \frac{P_1 V_1}{\beta} \left[\lg \frac{P_2}{P_1} + (C_e - C_a) \right] \text{ kW}$$

The effective power on the shaft of the compressor equals:

$$N_{\text{эф.}} = \frac{N_{\text{из.}}}{\eta_{\text{мех.}}} = \frac{N_{\text{из.}}}{\eta_{\text{из. из.}} \cdot \eta_{\text{из.}}} = \frac{N_{\text{из.}}}{\eta_{\text{мех.}} \cdot \eta_{\text{из.}} \cdot \eta_{\text{из.}}}$$

Here P_a and P_e -- absolute pressure in atm. (kg-f/cm^2) respectively in beginning and end of compression;

C_e and C_a -- coefficients defined from the nomogram (fig. III-27) for pressure in the beginning and end of compression (P_a and P_e) with temperature T_1 ;

$N_{\text{ИИИД}}$ -- indicator effective power on shaft of compressor, kw;
 $\eta_{\text{мех.}}$, $\eta_{\text{из. из.}}$ and $\eta_{\text{из. ИИИД}}$ -- efficiency of compressor (respectively mechanical, effective isothermic and indicator isothermic).

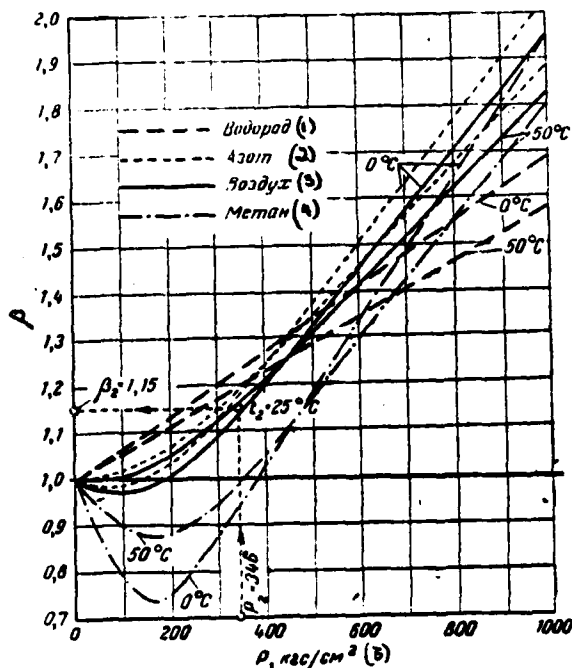


Figure III-26. Nomogram to Determine Coefficient of Compressibility β of Real Gases (for Calculation of Volume of Compressed Gas).

- Key:
1. Hydrogen
 2. Nitrogen
 3. Air
 4. Methane
 5. kg-f/cm^2

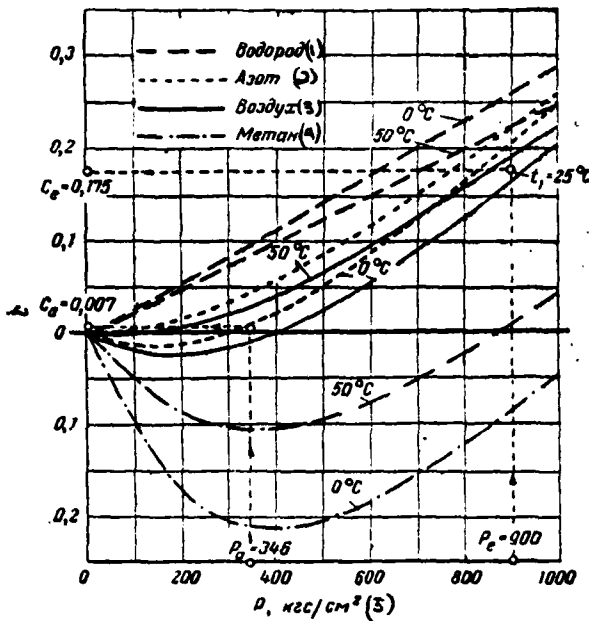


Figure III-27. Nomogram to Determine Coefficient C (for Calculation of Power of Isothermic Compression)

- Key:
1. Hydrogen
 2. Nitrogen
 3. Air
 4. Methane₂
 5. kg-f/cm²

Example. Determine the power of the compressor necessary for isothermic compression of dry air if $V_1=10,000 \text{ m}^3/\text{h}$, P_1 (absolute)=1 atm., $T=25^\circ\text{C}$; the coefficient of compressibility β_1 with P_1 and T_1 equals 1.0; $P=346 \text{ atm}$, $P_e=900 \text{ atm}$.

After determining from the nomogram the quantity $C_a = \frac{0.007}{1.0}$ and $C_e = 0.175$, we obtain:

$$N_{\text{is}} = 0.736 \cdot 0.0852 \frac{1.0 \cdot 10000}{1.0} \left[\lg \frac{900}{346} + (0.175 - 0.007) \right] = 366 \text{ kW}$$

If we assume that $\eta_{\text{м.з.д.}} = 0.65$; $\eta_{\text{мех}} = 0.91$ and $\eta_{\text{м.в.м.}} = 0.714$, then $N_{\text{з.д.}} = 563 \text{ kW}$, $N_{\text{м.в.м.}} = 511 \text{ kW}$. The C values for calculation of the isothermic power during compression of certain gases can also be taken from table III-73.

3. With the help of the nomogram illustrated in fig. III-28, the final temperature of compression t_2 is determined for different indicators of the polytropic curve m depending on the ratio of pressures P_2/P_1 and the temperature for suction.

The numerical example is presented on the nomogram itself.

TABLE III-73. QUANTITIES C FOR CALCULATION OF ISO-THERMIC POWER IN COMPRESSION OF CERTAIN GASES

(1) Абсолютное давление атм	(2) Начальная температура, °C							
	10	20	30	40	10	20	30	40
	(3) Водород				(5) Азот			
50	+0.013	+0.013	+0.012	+0.012	-0.006	-0.004	-0.002	-0.001
100	0.026	0.025	0.025	0.024	-0.009	-0.005	-0.001	+0.001
200	0.053	0.052	0.050	0.049	-0.005	+0.001	+0.007	0.011
300	0.080	0.078	0.078	0.075	+0.009	0.017	0.023	0.029
400	0.109	0.106	0.103	0.100	0.031	0.039	0.046	0.052
500	0.137	0.133	0.129	0.126	0.060	0.069	0.075	0.081
600	0.166	0.161	0.156	0.152	0.084	0.101	0.107	0.112
700	0.194	0.188	0.183	0.178	0.130	0.137	0.142	0.146
800	0.223	0.216	0.210	0.204	0.170	0.175	0.179	0.183
900	0.252	0.244	0.237	0.230	0.210	0.214	0.218	0.220
1000	0.280	0.272	0.264	0.256	0.253	0.256	0.258	0.259
	(4) Воздух				(6) Метан			
50	-0.009	-0.006	-0.004	-0.003	-0.043	-0.038	0.033	0.029
100	-0.014	-0.010	-0.007	-0.004	0.085	0.074	0.065	0.057
200	-0.017	-0.010	-0.004	+0.001	0.149	0.130	0.114	0.099
300	-0.008	+0.001	+0.008	0.015	0.180	0.158	0.138	0.119
400	+0.011	0.020	0.028	0.035	0.185	0.163	0.140	0.121
500	0.035	0.044	0.052	0.059	0.177	0.153	0.131	0.112
600	0.064	0.073	0.080	0.087	0.157	0.134	0.113	0.094
700	0.097	0.105	0.112	0.118	0.130	0.108	0.088	0.070
800	0.133	0.140	0.146	0.151	0.100	0.078	0.057	0.039
900	0.171	0.176	0.181	0.186	0.065	0.044	-0.025	-0.007
1000	0.210	0.215	0.219	0.222	0.028	0.007	+0.011	+0.027

Key:

1. Absolute pressure atm.
2. Initial temperature, °C
3. Hydrogen
4. Air
5. Nitrogen
6. Methane

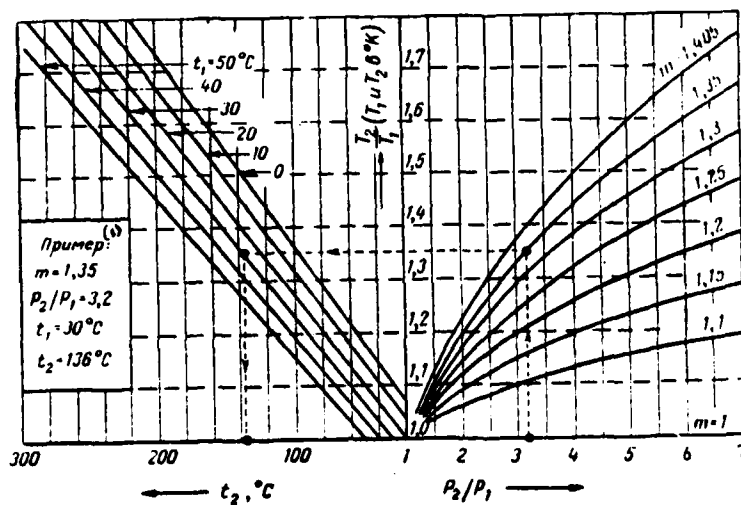


Figure III-28.
Nomogram to Determine
Final Temperature
of Compression

Key:

1. Example

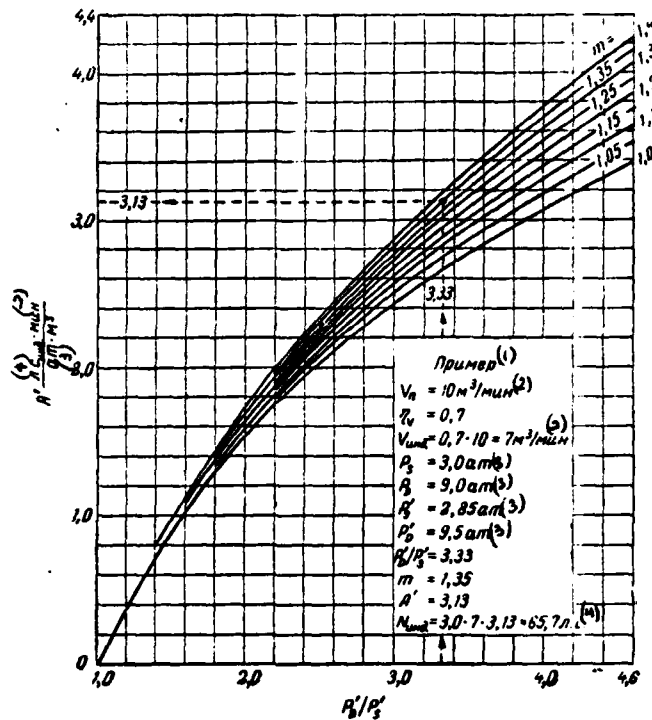


Figure III-29. Nomogram to Determine Indicator Power

Key:

1. Example
2. Min.
3. Atm.
4. H.p.

4. The indicator power of special compressors with forced valves can be determined from the nomogram indicated in fig. III-29. The indicator power can be expressed:

$$N_{\text{инд.}} = P_s V_{\text{инд.}} \frac{10000}{4500} \cdot \frac{m}{m-1} \left[\left(\frac{P'_D}{P'_s} \right)^{\frac{m-1}{m}} - 1 \right] = P_s V_{\text{инд.}} A' \text{ hp инд.}$$

Here P_s and P_D --absolute pressure in suction and injection pipelines, atm;

P'_s and P'_D --absolute pressure in cylinder according to actual line of suction and forced discharge, atm.;

$V_{\text{инд.}} = \eta_v V_n$ --indicator volume of suction with pressure P_s , m^3/min .
 (η_v --volumetric efficiency and V_n --volume described by piston);

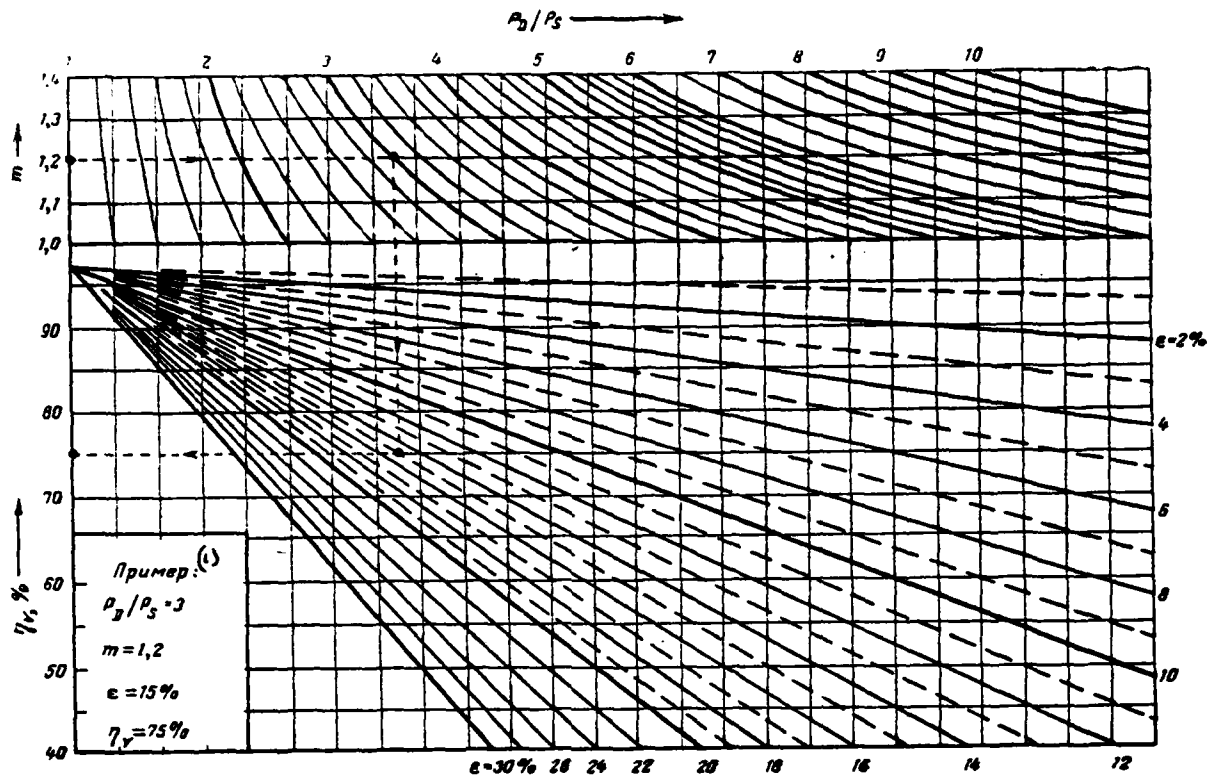


Figure III-30. Nomogram to Determine Volumetric Efficiency (ϵ -- quantity of harmful space)

Key:

1. Example

m --indicator of polytropic curve;

A' --quantity of indicator required power expressed in $\frac{\text{h.p.} \cdot \text{ind}^x \text{ min}}{\text{atm.} \times \text{m}^3}$

The numerical example is presented in fig. III-29.

5. The volumetric efficiency η_v is found with the help of a nomogram depicted in fig. III-30. The numerical example is presented on the nomogram itself. The coefficient of supply λ , as is known, is expressed by the ratio of effective volume of gas (actually fed into the injection line) to the volume described by the piston, consequently:

$$V_{\text{eff}} = \lambda V_{\text{on}}$$

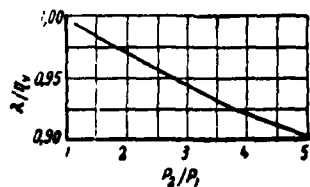


Figure III-31. Graph to Determine Coefficient of Preheating

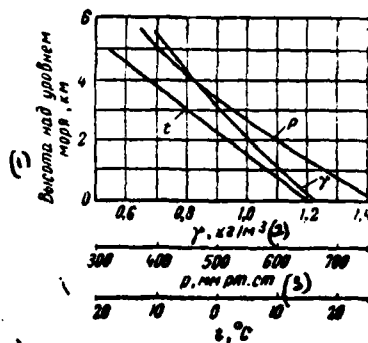


Figure III-32. Graph to Evaluate Atmospheric Pressure Depending on Altitude above Sea Level

Key:

1. Altitude above sea level, km
2. kg/m^3
3. mm Hg

However, λ is smaller than the volumetric efficiency η_v since it does not take into consideration the preheating of the gas because of details of the cylinder. Consequently, in order to determine $V_{\text{до}}$ it is necessary to take into consideration the size of the ratio λ/η_v . Then $V_{\text{до}} = \eta_v \frac{\lambda}{\eta_v} \cdot V_{\text{он}}$.

6. With the help of the graph constructed in fig. III-31, one can determine the coefficient of preheating for piston compressors. The quantity λ/η_v is plotted on the y-axis; the ratio of final pressure P_2 to initial P_1 , i.e., the degree of compression, is plotted on the x-axis.

7. In order to evaluate the change in atmospheric pressure depending on the altitude above sea level, a graph is used (fig. III-32).

Centrifugal Compressors

Because of a rise in the production of nitrogen fertilizers, the unlimited demand for them in agriculture, and the developed need to make large units to synthesize and process the ammonia (1500 T/day and more), the attained level of compressor construction has proven

to be insufficient for the plants of the nitrogen industry. Therefore in the last 10 years, a transition has occurred in the technology of ammonia production from piston multiple-stage compressors of high pressure to centrifugal compressor machines of high pressure which would allow:

- guaranteed supply of over 3000 m³/min. of gas, a quantity sufficient for producing 1500 T/day of ammonia in one production line;
- guaranteed final gas pressure to 320 atm;
- simultaneous circulation of gas in the synthesis unit at high pressure (260-320 atm.) and in the assigned quantity (19,000 m³/min.,).

Figure III-32a depicts the plan and gives the basic parameters of centrifugal compressors which nitrogen plants will be equipped with in future years.

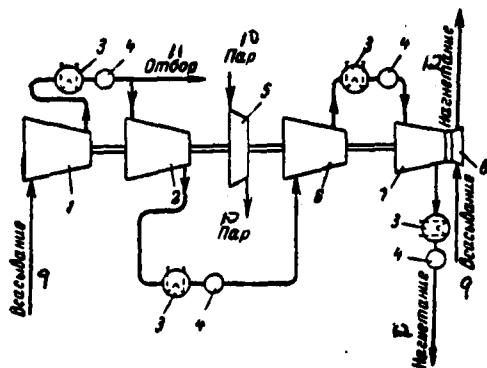


Figure III-32a. Plan of Centrifugal Compressor for Compressing Nitrogen-Hydrogen Mixture Combined with CCC

Key:

1. Cylinder of first stage
2. Cylinder of second stage
3. Cooler
4. Separator
5. Steam turbine
6. Cylinder of third stage
7. Cylinder of fourth stage
8. CCC (centrifugal circulation compressor)
9. Suction
10. Steam
11. Bleed
12. Injection

Specifications of unit

Compressor	
Output, m ³ /h	185,000
Shaft rotation rate, rpm	15,000
Absolute pressure, atm	
in suction pipeline	23
in injection pipeline	256-286
Gas temperature, °C	
suctioned	25-40 (rated 30)
injected	34

Intermediate gas bleeding quantity, m ³ /h		3960-4200
pressure, atm.		41
Recirculator (CCC)		
Output under suction conditions, m ³ /min		70-80
Gas pressure, atm.		
suctioned		256-286
injected		291-321
Temperature of suctioned gas, °C		35
Turbine		
Power, kW	n	28,500
Steam consumption, T/h		392
Shaft rotation rate, rpm		15,000
Absolute steam pressure, atm.		
at entrance to turbine		130
at exit from turbine		37
Steam temperature, °C		
at entrance to turbine		550
at exit from turbine		400-405

The centrifugal compressor with these parameters must have improved reliability in operation and guarantee lengthy faultless (for example, for a year) operation.

The described high-power compressor unit (exceeding 25,000 kW) and with high shaft rotation rate (15,000-17,000 rpm) can be actuated from a steam or gas turbine. In the adopted modern production plans, preference is given to the steam turbines with counterpressure and condensation.

In selecting the centrifugal compressor machine, one should be guided by the gas-dynamic characteristics that are set by the manufacturing plant during testing of the machine on the plant's test stand.

The equations given above for computing the piston compressors are also correct for centrifugal machines.

In order to determine the power consumed by the centrifugal gas-blower machine under the assigned conditions, we use the equation:

$$N = 1.034 \frac{Q P_1}{\eta_b \eta_m \eta_{h.s.}} \cdot \frac{k}{k-1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right] \quad \text{kW}$$

where Q--output with temperature and pressure of suction, m³/min;
 P₁ and P₂--pressure of gas respectively on side of suction and
 injection, kg-f/cm²;
 η_o--volume efficiency (0.98-1.0);
 η_m--mechanical efficiency (0.97-0.99);
 η_{ad}--adiabatic efficiency (0.6-0.75);
 k--indicator of adiabatic curve c_p/c_v=1.4.

Electric motors for compressor drive. Asynchronous motors are usually used for compressors with power to 100 kW, and for machines with power over 100 kW, synchronous. The synchronous number of revolutions of the electric motor is determined from the formula

$$n = \frac{3000}{p} \text{ rpm}$$

where p is the number of pairs of poles.

The following series of synchronous numbers of revolutions n is adopted with the corresponding number of pairs of poles p:

p	24	20	18	16	14	12	10	9	8	7	6	5	4	3	2
n	125	150	167	187	214	250	300	333	375	428	500	600	750	1000	1500

For large synchronous electric motors, a normal series of powers has been set (in kW): 100, 125, 160, 200, 250, 320, 400, 500, 630, 800, 1000, 1250, 1600, 2000, 2500, 3200, 4000, 5000, 6300, 8000, 10,000.

Compressor Lubrication

The consumption of grease for compressor cylinders can be approximately defined from the following equation

$$G_n = \frac{2\pi D s n \cdot 60}{K} \text{ g/h}$$

where D--diameter of cylinder, m;
 s--piston stroke, m;
 n--number of revolutions, min.
 K=400-500.

When gases are compressed in the interval 50-100 atm, the obtained norm of consumption should be increased 1.5-2-fold. It is

increased 3-4-fold in the interval 220-350 atm.

The consumption of grease for the gaskets with metal packing can be determined from the equation:

$$g_0 = \frac{2\pi d n \cdot 60}{33} \text{ g/h}$$

where d--diameter of rod, m.

Depending on the wear of the gasket packing and other factors, the consumption of grease obtained by calculation rises 1.5-2-fold.

Below are the properties of the compressor oils (according to GOST 1861-54):

Indicators	Brands	
Viscosity, kinematic at 100°C, cSt	12(M) 11-14	19(T) 17-21
Acid number, mg KOH/g of oil, no more	0.15	0.10
Stability (precipitate after oxidation), % , no more	0.30	0.02
Ash content, % no more	0.015	0.010
Content of mechanical admixtures, %, no more	0.007	0.007
Content of water-soluble acids and alkalis, water	Missing	
Flash point, determined in open crucible, °C, no below	216	242
Corrosion, determined by method of Pinkevich on plate made of lead brand S1 or S2 (GOST 3778-65), g/m ² , no more	60	5

The nitrogen industry mainly uses compressor oil of brand 19(T) for lubricating the moving parts and cylinders of large compressors.

The properties of aviation oils (according to GOST 1013-49):

Indicators	Brands	
	MS-20	MK-22
Viscosity, kinematic, at 100°C, cSt, no less	20	22
Stability, % no more	0.3	0.7
Acid number, mg KOH/g of oil, no more	0.05	0.1
Ash content, % no more	0.003	0.004
Content of selective solvents, water-soluble acids and alkalis, mechanical admixtures and water	Missing	
Flash point (determined in closed crucible), °C, no lower	225	230

Pour point, °C no higher	-18	-14
Corrosion, determined by method of Pinkevich on plate of lead brand S2 (GOST 3778-65), g/m ² , no more	45	2

Aviation oils of the presented brands have recommended themselves in lubricating the cylinders and moving parts of large gas compressors of high pressure.

The properties of the oil for rolling mills of brand P-28 (according to GOST 6480-53):

Indicators	
Viscosity at 100°C kinematic, cSt	26-30
conventional corresponding to it, °CV	3.68-4.20
Stability, %, no more	1.0
Acid number, mg KOH/g of oil, no more	0.1
Content of water soluble acids and alkalis, mechanical admixtures and water	Missing
Flash point determined in open crucible, °C no lower	285
Pour point, °C, no higher	-10
Testing for corrosion of steel plates at 100°C for 3 h	Withstands

Oil of brand P-28 has recommended itself as the best for lubricating high pressure compressors in units of air separation by the method of deep cooling.

The properties of oil for cooling machines of brand KhZ (frigus) according to GOST 5546-66:

Indicators	
Viscosity, kinematic at 50°C, cSt	11.5-14.5
Acid number, mg KOH/g of oil, no more	0.10
Ash content, %, no more	0.01
Testing for corrosion	Withstands
Content of water-soluble acids and alkalis, mechanical admixtures and water	Missing
Flash point, determined in open crucible, °C no lower	160
Pour point, °C, no higher	-40

The "frigus" oil is used in the nitrogen industry for lubricating cylinders of ammonia compressors of cooling units.

The properties of turbine oils of different brands (according to GOST 32-53):

Indicators	Brands			
	22(I.)	30(UT)	46(T)	57(turbo-reducer)
Viscosity, kinematic at 50°C, cST	20-23	28-32	44-48	55-59
Acid number, mg KOH/g of oil, no more	0.02	0.02	0.02	0.05
Stability precipitate after oxidation, %, no more	0.10	0.10	0.15	-
acid number after oxidation, mg KOH/g of oil, no more	0.35	0.35	0.45	-
Ash content, %, no more	0.005	0.005	0.020	0.040
Rate of deemulsification, min. no more	8	8	8	8
Content of water soluble acids and alkalis, mechanical admixtures	Missing			
Flash point determined in open crucible, °C no lower	180	180	195	195
Pour point, °C, no higher	-15	-10	-10	-
Sodium test with acidification, points, no more	2	2	2	2
Transparency at 0°C	Oil in glass test tube, diameter 30-40 mm must remain transparent			

For lubricating electric motor with a large number of revolutions, and average gas blower power, turbine oil of brand 22 is used; for turbocompressors with reducers, oil of brands 30 and 44 is mainly used.

Technical Data of Compressors

Gas-turbine unit GTT-3 which is included in the unit for producing weak nitric acid under absolute pressure of 7.3 atm. includes an axial compressor, separator blower, gas turbine and alternating current generator. The characteristics of the axial compressor and the separator blower are presented in table III-74.

TABLE III-74. CHARACTERISTICS OF AXIAL COMPRESSOR AND SEPARATOR BLOWER WITH RATED OUTPUT OF 1000 m³/min FOR COMPRESSED AIR ($\rho_{\text{air}} = 1.293 \text{ kg/m}^3$)

Link of Type unit	Final press. (gage), atm.	Suction conditions		Rotor rotation rate rpm	Power kW	Weight of unit, T		
		temp. °C	press. (abs.) atm.			com-pressor	reducer	heaviest parts
Axial GT-600-compress* 1.5	3.53	20	0.97	5100	7060	42	5.6	11.5
Separat. 360-21-	7.30	42	3.47	7400	Joint	5.2	-	-

blower

ly with
compres-
sor

* Four-axle reducer, type R-3600
Water consumption is 360 T/h.

Below are the characteristics of the gas turbine that operates on natural gas, and the alternating current generator:

Gas turbine		Alternating current generator	
Power, kW	7250	Type of generator with energizer	G-2b-1.5-2
Gas consumption, T/h	82.1	Type of booster engine	MPS-300-3000
Absolute gas pressure, atm.		Surplus power on coupling, kW	280
incoming	5.4	Weight, T	10.4
outgoing	1.06		
Gas temperature, °C			
incoming	720		
outgoing	408		
Shaft rotation rate, rpm	5100		
Weight, T	26		

TABLE III-75. VERTICAL FANS OF SPECIAL PURPOSE WITH OUTPUT OF 100,000 m³/h

Type	Density of mixed gas, kg/m ³	Temp. °C	Static press. mm wat. col.	Wheel diam. mm	Consumed power kW	Electric motor			Total weight, kg-f	
						type	power kW	shaft rotation rate rpm		
For unit in granulation towers										
S1530	1.06	from -20 to +60	40	1540	24	Dgne87-8	29	725	1885	
VVO-2	1.4-1.06	from -20 to +60	40	1520	40	A02-91-8	40	735	2679	
For degasification units										
S1530	1.19	30	100	1550	46.5	DO ne 96/8	55	975	2600	
VVO-1	1.18	30	70	1520	40	AO 2-91-8	40	735	3426	

Note: Fans type S1530 are made by the firm Nema (GDR); fans type VVO-1 and VVO-2 are made by the Ordzhonikidze Podol'sk Mechanical Plant.

TABLE III-76. RECOVERY MACHINES

Тип машины	2	3	4	5	6	7	8	9		12		15
								10	11	13	14	
	Производительность по свежему раствору, м ³ /ч	Число двойных ходов за 1 ч	Ход поршня, мм	Внутренний диаметр цилиндра, мм	Высота цилиндра, мм	Давление отработанного раствора, атм	Рабочее давление магнетана, атм	Производительность, м ³ /ч	напор, атм	мощность, кВт	скорость вращения вала, об/мин	Общий вес, кгс
RS60/320	60	66	2450	500	3115	323	340	75	10	45	1450	62 400
RS120/320	120	70	2800	650	3520	323	340	150	25	175	1470	88 153
RS120/150	120	70	3100	650	3720	114.5	130	150	15	130	1450	64 115

Key:

1. Type of machine
2. Output for fresh solution, m³/h
3. Number of double strokes in 1 h
4. Piston stroke, mm
5. Inner cylinder diameter, mm
6. Cylinder height, mm
7. Pressure of spent solution, atm.
8. Working pressure of injection, atm.
9. Pump for fresh solution
10. Output, m³/h
11. Pressure, atm.
12. Electric motor
13. Power, kW
14. Shaft rotation rate, rpm
15. Total weight, kg-f

Note: The manufacturer is the firm "Investa" of the CSSR.

TABLE III-77. CHARACTERISTICS OF PISTON COMPRESSORS USED IN THE

Compressor brand	Type	Compressible gas	Gas density kg/m ³	Pressure, atm			No. of stgs.	Piston stroke mm
				Out-put m ³ /h	beg. (abs)	final		
Special High Pressure								
1G-266/320	Horizontal double-row	Nitrogen-hydrogen mixture	0.41-0.48	16 000	1.02	320	6	1000
7G-166/320	The same	The same	0.41-0.48	10 000	1.02	320	6	1000
3/4G-125/200	"	Air	1.293	7500	1.018	200	5	800/550
3G-117-200	"	Nitrogen	1.250	7000	1.01	200	5	800
3G-50-200	Horizontal single-row	Air	1.293	3000	1.01	200	5	800
2RA-3/350	Double-row	Nitrogen	1.250	180	1.0	350	4	150
Separating High								
2G-420/25-320	Double-row	Nitrogen-hydrogen mixture	0.41-0.48	25 000	25	320	3	900
3G-83/10-320	The same	The same	0.41-0.48	5000	10.0	320	4	800
4G-80/5.5-220	"	Air	1.293	4800	5.5	220	4	550
4G-40/5.5-220	Single-row	Air	1.293	2400	5.5	220	4	550
Circulation								
5G-6/285-320	Horizontal double-row	Nitrogen-hydrogen mixture	0.41-0.48	360	285	320	1	450
5G-3/285-320	Horizontal single-row	The same	0.41-0.48	180	285	320	1	450
Average and Low								
3G-142/13	Double-row	Coking gas	0.530	8500	1.0	12.0	2	800
3.5G-108/35	The same	Hydrocarbon gases	~0.6	6500	1.02	35.0	4	650
Compressors on								
6M40-320/320		Nitrogen-hydrogen mixture	0.41-0.48	18 600	1.01	320	6	450
6M40-320/200		Nitrogen	1.25-0.09	18 200	1.02-1.3	200	5	450
6M40-450/22.5		Hydrogen	-	27 000	1.12	70-150	4	450
4M25-117/200		Coking gas	-	7000	1.02	201	5	400
50T-130/200		Nitrogen	1.293	8000	1.0	200	5	400
50T-130/200		Air	1.250	5890	1.01	201	5	400
50TG-130/200		Nitrogen	0.09	6350	1.01	76-154	5	400
4M16-100/200		Hydrogen	-	4850	1.03	201	5	320
		Carbon dioxide	1.8	4850	1.03	201	5	320

- Notes: 1. Compressors of the presented brands have direct drive from a synchronous electric motor. Compressor of brand 2RA-3/350 has drive from an asynchronous motor through a V-belt gear. The rotation rate of the shaft of the compressor is 400 rpm.
2. The output is given for gas, relative to normal conditions: for compressors of brand 1G-266/320, 5G-6/285-320, 6M40-320/320, 6M40-320/200, 6M40-450/22.5, 2RA-3/350; 5G-3/285-320--for gas under suction conditions.

NITROGEN INDUSTRY

Power on shaft kW	Consumption		Electric motor Brand	Power kW	Velocity rpm	Voltage V	Weight, T		
	water m ³ /h	oil kg/h					Compressor with app.	Mo-torest	Heavi-part
Compressor									
3760	320	2.3	SDS 4650-125	4000	125	6000	290	80.0	30.0
2860	250	2.1	SDS 3750-125	3200	125	6000/3000	230	72.0	25.0
1102	90	1.18	SM 1350-125	1135	125	6000	108.7	41.5	18.26
1660	200	0.2	SDS 2400-125	2000	125	6000/3000	150	57.8	30.0
930	84.0	0.6	MS 340-6/48	1200	125	6000/3000	80	37.35	-
58	7.5	-	MA 36-41-4	75	1480	380/220	3.475	0.72	0.5
Pressure Compressor									
3300	280	2.3	SDS 4650-125	4000	125	6000	173	80	25
925	85	0.38	SM 1350-125	1135	125	6000/3000	71.4	41.5	11.0
760	70	0.6	DSK 260/34-36	840	167	6000/3000	44.5	13.6	11.0
380	35	0.3	DSK 260/20-36	420	167	6000/3000	23.6	10.8	10.0
Compressors									
530	-	1.4	SDS 780-125	630	125	6000	23.6	23.8	15.0
268	-	0.7	SDKZ 18-19-48	320	125	6000	12.2	21.5	10.5
Pressure Compressor									
1120	125	1.8	SDKI 19-36-48	1250	125	6000/3000	110	23.5	20
1190	96	0.6	SDS 1500-167	1250	167	6000	84.7	19.8	11.2
Opposite Bases									
4410	550	2.1	SDKI 19-54-20	5000	300	6000	206	36.2	20
4400	467	2.2	SDKI 19-54-20	5000	300	6000	227	38.2	20
-	370	2.0	SDKP 19054-24	4000	250	6000	171.6	31.2	18
1650	150	0.6	SDKP 48-39-20	2000	300	6000	84	16	11
-	160	-	SD 18-39-20	2000	300	6000	100.0	13.4	7.0
1800	160	1.7	SDSP 18-39-20	2000	300	6000	97.4	18.5	12.6
1680									
1208	125	1.09	SDK 16-51-16	1250	375	6000	67.8	11.2	11.2

TABLE III-78. CHARACTERISTICS OF CENTRIFUGAL COMPRESSORS USED IN

Brand of compressor	Compressible gas	Gas density kg/m ³	Rated operating regime				No. of rotor rpm	Power on shaft kW	Water consumption m ³ /h
			Output in suction m ³ /min	Final pressure (abs) atm.	Suction condition Temp. °C	Pressure (abs) atm			
K-1500-62-1	Air	1.293	1290	7.5	30	0.97	4370	6300	774
K-1500-62-2	"	1.293	1590	7.5	30	0.97	4470	7300	774
K-1300-91-1	Nitrogen	1.250	1300	1.12	25	0.0545	4500 (I цил.) 7850 (II цил.)	605	143
K-500-61-1	Air	1.293	525	9.0	20	1.0	7600	3000	193
K-500-61-2	"	1.293	510	7.5	20	0.97	7400	2500	193
K-480-42-1	Nitrous gas	1.290	480	3.8	53	0.958	8100	1700	20
K-505-121-1	Gases of methane pyrolysis	0.625	500	10.0	35	0.98	7650	2900	508
K-350-62-1	Air	1.293	420	7.35	20	0.97	8846	2060	183
K-250-61-1	"	1.293	250	9.0	20	1.0	11 230	1500	220
K-405-121-1	Gases of pyrolysis	1.19	450	42	15	1.3	6920 (I цил.) 14 050 (II цил.) 15 200	5100	132
TsK-100-61	Air	1.293	100	6.5	—	1.0	15 200	600	80
TsK-135/8	"	1.293	135	7.8	30	1.0	13 645	880	110
KTK-12.5/35	Oxygen	1.41— 1.429	208	35	—	1.02	13 800	2700	420
KTK-7/15	"	1.41— 1.429	117	15	—	1.00	13 645	1050	140
2TsTsK-10/300-12-10	Nitrogen-hydrogen mixture	0.41— 0.48	10.6	313.5 (при γ = 80 кгс/см ²)	35	290	2970	—	—
1TsTsK-7-300-14/12	The same	0.41— 0.48	7.5	318 (при γ = 94 кгс/см ²)	35	290	2970	450	—
TsKO-7	"	0.41— 0.48	7.5	320	35	290	2970	510	—

- Note: 1. The output is given for gas under suction conditions; for compressors of brand K-480-42-1, TsK-100-61, KTK-7/15--for gas relative to normal conditions.
2. An expander, recovering about 700 kW of drive power is built into one circuit with compressors of brand K-480-42-1 and K-505-121-1.
3. Compressors of the last three brands are centrifugal circulation compressors with electric motors placed inside the high pressure housing.

THE NITROGEN INDUSTRY

Fly-wheel moment of rotor relat. to rotor coupl. kg/m ²	Type of inducer	Electric motor Type	Rated power kW	Rotation rate of shaft rpm	Dimensions of unit			Weight of unit, T			
					Length	Width	Hgt of base-ment	com-pressor machine	re-ducer	elec-ric cer	hea-est part
2800	R $\frac{7000}{1.45}$	SIM-9000-2	900	3000	14.1	5.1	4.8	55	6.3	41.5	18.0
3000	R $\frac{8000}{1.49}$	STM-9000-2	900	3000	14.1	5.1	4.8	55	6.3	41.5	18.0
3200	R $\frac{200}{1.74}$	ATMF-850-2	850	—	12.3	5.1	4.8	58	1.6	7.0	16.6
	R $\frac{600}{1.51}$								0.7		
850	R $\frac{3000}{2.55}$	STM-2500-2	3500	3000	10.0	3.4	3.6	22	2.5	18.5	15.0
815	R $\frac{2700}{2.48}$	STM-3500-2	3500	3000	10.3	3.4	3.6	22	2.5	18.5	15.0
475	R $\frac{1800}{2.72}$	AZP-1600/6000	1600	2980	7.7	3.3	4.2	13.2	1.6	7.8	6.6
2000	R $\frac{2800}{2.56}$	STMP-4000-2	4000	3000	19.0	14.0	6.0	35	3.1	22.0	12.0
480	R $\frac{2000}{2.87}$	STM-3500-2M	2500	3000	9.8	3.15	3.5	12.5	2.5	18.5	15.0
	R $\frac{1500}{3.74}$	STM-1500-2	1750	3000	9.1	4.2	3.25	11.0	1.77	10.5	10.5
300	R $\frac{5100}{2.3}$	STMS-6000-2a	6000	3000	5.0	4.0	4.8	16	4.1	31.5	5.5
1000	R $\frac{2500}{2.03}$								1.4		
—	—	AZ-630/6000	630	2970	7.9	3.7	6.0	9.12	—	6.0	—
—	Pm 1500	AZ-1000/6000	1000	2970	9.0	4.6	5.0	(with apparatus) 2.44	19	6.6	6.6
—	—	STM-3500-2	3500	3000	14.0	5.0	4.5	5.05	1.7	15.5	10.5
—	Pm 1500	STM-1500-2	1500	3000	11.0	4.0	4.2	18.2	2.7	10.5	6.0
—	with-out re-ducer	ATMK 750-2	750	2970	6.3	1.25	—	(with apparatus) 2.6	—	2.9	27.6
—	—	ATMK 470-2	470	2970	6.5	1.06	—	19.0	—	2.05	21.05
—	—	ATMK 600-2	600	2970	6.5	1.25	—	25.1	—	2.9	25.1

TABLE III-79. SPECIFICATIONS OF FOREIGN PISTON COMPRESSORS

Country and firm supplying equipment	Type and brand of compressor	Compressible gas	Gas density kg/m ³	Rated operating pattern			
				Output m ³ /h	Final pres. (abs) atm.	Suction condit.	
						Tem per °C	Abs. pres. atm.
Czechoslovakia, ChKD	Horizontal double-row 2KhLK-1420	Nitrogen-hydrogen mixture	0.41-0.48	15 900*	321	30	1.02
The same	Horizontal single-row R1-K-920	Nitrogen	1.25	3 000	201	30	1.01
"	Opposite, six-row, 6ChVK-355	Nitrogen-hydrogen mixture	0.41-0.48	25 200	326	—	12.0
"	Opposite, eight-row, 8TBK-300	Coking gas	0.515	17 000	16	—	1.01
"	Opposite, eight-row, 8PBK-800	Nitrogen	1.25	8 400	201	—	1.02
"	Opposite, four-row, 4IBKO-240	Mixture of gases	—	37 750	66	—	26.0
France, Du-jarend-Clark	Opposite, ten-row, CLBA-10	Coking gas	0.515	32 000	19	—	1.02
The same	Opposite, six-row, CLBA-6	Nitrogen-hydrogen mixture	0.38	24 000	330	—	13.5-16.0
"	Opposite, six-row CLRA-6	Nitrogen	1.25	9 000	180-200	—	1.02
France SFAK (by license of Kupper-Bessemer)	Opposite, ten-row multiservice (KM5+KM5); including: a) pressing compressor (7 cylinders) b) recirculator (2 cylinders) c) ammonia compressor (1 cylinder)	Nitrogen-hydrogen mixture	0.41-0.48	40 000	320.8	35	25
		The same	0.41-0.48	15 600	350.9	35	321.8
		Ammonia	—	7 700	18.55	-10	3.0
FRG Borzig	Opposite, eight-row	Nitrogen-hydrogen mixture	0.41-0.48	25 000	320	28	1.01
FRG Manesman-Meyer	Opposite, four-row BFV/320	Expander gas	1.8	4 850	200	—	1.03

No. of stages	Rotation rate of shaft rpm	Piston stroke mm	Power on shaft kW	Consumption		Electric motor Type	rated power kW	Weight, T		
				water T/h	oil kg/h			compressor	motor	heaviest parts
6	125	1000	3760	320	2.3	Synchronous	4100	290	115	30
5	125	800	—	100	—	"	930	78	37.2	—
4	300	450	4247	550	—	Synchronous EVOE280/72-20	5000	155	26.3	12
3	300	380	—	210	—	The same	2500	114.5	21.4	10.5
5	300	380	2208	300	1.4	Synchronous EVOE280/40-20	2500	104	19.7	10.5
1	250	450	1718	45	0.78	Synchronous	1900	45.5	—	19.0
3	273	425	4520	625	4.5	"	5000	240	29.6	14.0
3	330	425	3560	495	1.6	"	3900	125	24.7	11.45
5	333	210	2184	300	0.4	"	2500	105	20.5	9.6
3	333	356	5100	480	—	Synchronous SSW efpEh	6780	167.8	34.12	—
1	333	356	920	—	—					
1	333	356	565	7	—					
6	214	560/500	7065	550	—	Synchronous SSW efpEW	7500	240	68.5	29.5
5	300	320	1100	114	—	Synchronous efSSW 8126D3/206	1250	52.5	15.6	10.5

[Continuation of Table III-79 from p.528]

Italy, Nuovo-Pin- yoni	Opposite, pressing, four row 4HC/4ap	Nitrogen-hydro- gen mixture	0.38	35 000	360	—	24
The same	Opposite, pressing, four- row 4HC/4ap	Air	1.293	21 200	200	—	5.4 5.6
"	Opposite, pressing, two- row 2HB/200ap	Natural gas	0.73	12 000	36	—	19
"	Opposite, three- row, 3HF/3	Nitrogen	1.25	11 000	27-31	—	1.03
"	Opposite, pressing, four- row 4HG/4ap	Gas for methanol synthesis	0.448	20 800	501	—	16
"	Opposite, pressing, four- row 4HG/4ap	Nitrogen-hydro- gen mixture	0.38	19 500	501	—	15
"	Opposite four-row 4HF/5	Nitrogen	1.25	8 250	200	—	1.0
"	Opposite, four row, 4HD/4	Hydrogen	0.1	5 200	60	—	1.015
FRG, Demag	Opposite, pressing, four row	Nitrogen-hydro- gen mixture	0.38	21 300- 22 400	550	—	10.3
"	Opposite, pressing	Oxygen	1.427	8 950	27.0	—	7.0
FRG, SYUET	Opposite, six- row	Nitrogen	1.25	5 900	200	—	1.04
FRG, Borzig	Opposite, four- row	Carbon dioxide	1.8	4 850	200	—	1.03
"	Horizontal, circulation one-row	Gas mixture	0.41-0.48	360*	320	—	2:1
France, Burton	Horizontal, pressing	Nitrogen-hydro- gen mixture	0.41-0.48	2 778	40.0	—	1.40
The same	Opposite 3HC-8BS	Air	1.293	860	7.0	—	1.0

Note: The output is given for gas relative to normal conditions. For compressors 2ShLK-1420 (Czechoslovakia) and circulation horizontal one-row (FRG, firm "Borzig")--for gas under suction conditions.

[continuation of Table III-79 from p. 529]

4	250	450	4 520	443	2.5	Synchronous	4 900	125.8	35.8	15.0
4	250	450	3 590	350	1.82	"	3 850	110	30.8	7.0
1	600	205	345	33	0.21	-	380	7.5	7.5	2.0
3	300	420	1 820	190	1.25	-	1 950	64.7	16.3	4.75
4	214	450	3 370	323	1.75	Synchronous GGE AG-28-4050	3 700	~ 70	36	-
4	214	450	3 370	320	1.75	Synchronous GGE AT-28-4050	3 700	~ 70	36	-
5	300	420	2 100	217	1.002	Synchronous AT-20-2480	2 250	54	25.2	-
4	375	320	1 073	95	-	Synchronous	1 180	42.5	-	-
4	250	450	-	-	-	"	3 900	115	-	-
1	500	-	-	-	-	-	765	24.6	-	-
6	300	-	-	-	-	Synchronous	1 440	61.5	-	-
5	300	400	1 170	103	-	"	1 280	54.0	14.5	-
1	147	560	662	-	-	-	750	18.5	17.0	-
1	375	-	70	-	-	Asynchronous	92	4.7	0.6	-
2	600	-	-	-	-	Asynchronous	92	4.21	0.785	-

TABLE III-80. CHARACTERISTICS OF FOREIGN CENTRIFUGAL COMPRESSORS

Country and firm supplying equip.	Type and brand of compressor	Compressible gas	Gas density kg/m ³	Rated operating pattern		
				output m ³ /min	final pres. (gage) atm.	absolute pressure of suction, atm.
FRG, Gutehofnungs-Hutte	Two-housing TKD 11-7/18	Gases of pyrolysis	0.52	400	10.0	0.99
The same	Two-housing, four row, TKD 11-7/14	The same	0.618	466	9.2	1.04
"	Two-housing TKD 11-7/15	"	0.6	433	9.5	-
France, Rato	-	Air	1.293	410	35.0	0.98 (T _{suc.} = 25°C)
The same	Two-housing of "barrel" type	Natural gas	0.73	296	38.2	8.2 (T _{suc.} = 20°C)
FRG, Demag	-	Air	1.293	785	6.3	1.00
The same	-	Oxygen	1.427	149	7.0	1.04
Italy, Nuovo Pinoni	-	Air	1.293	715	6.3	0.97
FRG, Gutehofnungs-Hutte	Circulation CP4/14/12	Nitrogen-hydrogen mixture	0.5	6.06	324.7	300
The same	Circulation CP4/14/10	Gas for methanol synthesis	0.448	8.33	370	350
Italy, Clark	Turbo-vacuum pump 3MX-8	Acetylene	1.261	216	1.35	0.15
France, Alkatel	Screw HC 250-15GV	Nitrogen	1.25	166	5.0	3.0
United States Italy, Japan, France	-	Nitrogen-hydrogen mixture	0.5	45-120	150, 240, 320	23-25

Note: The output is given for gas relative to normal conditions. For compressors of brands CP 4/14 and CP4/14/10 (FRG, Gutehofnungs-Hutte) it is given for gas under suction conditions.

Rate of shaft rotation rpm	Power kW	Consumption of water m ³ /h	Type of gear	Electric motor Type	Power kW	Rate of shaft rotation rpm	Weight of compressor T	Electric motor	heaviest parts
7 500	3 120	320	Reducer and recovery machine	Asynchronous ep RV 348/43-4	3 800	1 488	43.0 (with apparatus)	—	6.8
7 500	3 320	290	Reducer	Asynchronous 384/41-4-D5	3 900	1 484	8.5	13.5	—
7 500	—	290	"	348/41-4D5	3 600	1 488	8.7	12.5	—
12 580	—	—	Reducer of Krupp firm	Asynchronous	4 800	1 490	53.8	13.1	—
16 500	1 375	—	Reducer	"	1 650	1 490	22.3	7.0	—
—	—	—	"	"	4 500	1 500	45.0 (with apparatus)	—	—
—	—	—	"	"	1 075	1 500	18.5	—	—
4 250	3 970— 4 130	380	"	"	4 600	1 500	49.9 (with apparatus)	—	22
2 970	402	—	Without reducer	Asynchronous SSW	450	2 970	20.5	—	17.5
2 970	476	—	The same	The same PR-260/37-2	550	2 970	20.5	—	17.5
8 500	225	—	Reducer	Asynchronous COR-2681-48	340	1 480	12.1	3.15	—
7 620	382	6.0	Reducer Alkatel NA-20	Asynchronous Alston 81.5-39	440	2 960	4.23	3.8	—
11 000— 15 000	До 30000	—	Without reducer	—	—	—	—	—	—

TABLE III-81. CHARACTERISTICS OF CENTRIFUGAL BLOWERS

Type of machine	Compressible gas	Gas density at 0°C and 750 mm Hg, kg/m ³	Rated operating				Consumed power kW	Rotor rotation rate rpm
			output m ³ /h	regime rise in pressure mm wat.col.	suction temp. °C	absolute suction pres.		
610-11-1	Flue	1.250	36 000	450	400	1.0	80	2 950
540-41-1	Nitrous gases	1.290	33 600	3.96 am	50	0.906	2 040	8 455
360-21-1	Semiwater	0.86	22 500	4400	40	0.95	320	6 290
360-22-1	Air	1.293	18 500	2.4 am	20	1.0	700	7 775
360-22-2	Air	1.293	16 200	1.75 am	20	1.0	380	6 280
1050-13-1	Sulfurous	1.4	65 000	2 800	50	0.94	560	2 975
750-23-2	Semiwater	0.94	42 500	4 500	35	0.96	605	4 250
400-12-2	Sulfurous	1.4	25 000	1 800	40	0.96	175	2 965
0-325-11M	Semiwater	0.892	19 500	2 800	40	0.98	200	7 525
101-11-2M	Sulfurous	1.4	6 000	2 000	50	0.96	50	700
TG-500-1.3	Nitrous gases	1.285	32 000	3 000	50	0.94	335	2 970
TG-450-1.08	Ammonia-air mixture	1.238	27 000	800	20	0.985	85	2 960
TG-250-1.12	Nitrous gases	1.24	15 000	1 200	40	0.93	80	2 950
TG-200-1.25	Ammonia-air mixture	1.238	12 000	2 500	20	1.0	115	2 955
TG-150-1.12	Return gases	1.3	9 000	1 200	20	0.98	42	2 950
TG-125-1.1	Ammonia-air mixture	1.234	7 500	1 000	20	0.97	40	2 950
TG-80-1.8	Oxygen	1.43	5 000	8 500	20	1.0	155	2 960
TG-80-1.4	"	1.43	5 000	4 500	25	0.98	92	2 950
TG-60-1.8	"	1.43	3 500	9 000	20	1.0	110	2 950
TG-50-1.9	Nitrogen	1.25	3 000	9 000	20	1.0	120	2 950
TG-25-1.4	Converted gas	0.7	1 500	4 000	20	1.02	35	2 950
TG-25-1.05	Nitrous gases	1.285	1 500	1 500	35	0.9	15	2 950

Electric motor Type	Rotation rate of shaft rpm	Power kW	Machine parameters operating in air under standard conditions			Unit di- mensions		Weight, kg-f		
			out- put m ³ /h	rise in press. mm wat.col.	con- sum. po- wer kW	length	width	with out elec- tric motor	elec- tric mo- tor	heaviest parts
KOM-732	2950	100	Not designed for working in air			2960	3360	3 800	700	1400
AZD ¹⁶⁰⁰ / ₈₀₀₀	2980	1600	The same			4650	3300	13 200	8400	6400
KAMO-350-3 ATD-630	2975	400 630	22 500	1.8 atm	530	6200	3200	6 700	3750	3750
ATD-800	2980	800	—	—	—	6400	3200	5 300	4900	4160
KAMO-350-2	2975	400	—	—	—	6100	3200	5 300	3750	3750
ATD-630	2975	630	66 000	3000	800	5000	3000	26 700	4460	4460
ATD-800-2	2975	800	—	—	—	6850	3700	10 500	4880	4880
A-103-2	2975	250	25 000	1850	180	4500	300	5 000	1220	3000
A-113-2	2970	320	19 500	7600	300	2650	2800	2 300	1780	2300
MA-146-1/4	1480	68	6 000	2160	53	2850	2550	2 200	740	2200
ATD-500	2970	500	—	—	—	—	—	—	—	—
A02-92-2	2960	100	27 000	850	90	2230	1950	2 187	597	1745
A02-92-2	2960	100	Not designed for working in air			2120	1600	1 330	597	905
A-101-2	2955	160	12 000	2700	120	2996	1685	4 118	980	1700
K0-42-2	2950	50	Not designed for working in air			2120	1695	1 230	765	790
A0-83-2	2950	50	7 500	1100	45	2215	1450	1 586	560	470
A-102-2	2960	200	5 000	8000	143	3270	1550	4 690	1100	1940
A-92-2	2950	125	5 000	4000	79	2790	1550	3 846	685	1340
A2-92-2	2950	125	3 600	8000	105	2960	1550	5 173	519	1930
MA36-50/2	2970	125	3 000	9500	130	3250	1550	6 160	1160	2130
K0-42-2	2950	50	1 500	7500	90	3065	1550	5 340	720	1915
A0-73-2	2950	28	Not designed for working in air			2042	1290	1 575	325	550

TABLE III-82. SPECIFICATIONS OF MPT (MOTOR-PUMP-TURBINE) UNITS

MPT Unit			
Output, m ³ /h	900	1500	2100
Number of revolutions in 1 min.	1485	1490	1490
Turbine			
Pressure, m wat. col. at inlet	270 (gage)	260-280	270
at outlet	0-40(gage)	10-15	25-30
Maximum power, kW			
at P=270 m wat. col.	550	880	1120
at P=230 m wat. col.	450	800	-
Total weight, kg-f	7700	8840	9515
Pump			
Pressure, m. wat. col. at inlet	0	0	9
at outlet	310	320	320
Maximum consumable power, kW	1000	1600	2500
Total weight of pump with foundation slab, kg-f	1100	11,400	9000
Electric motor			
Type	DAMSO-1510-4	DAZ-1612-4	DAZ-1616-4
Rated power on shaft, kW	850	1500	2000
Voltage on stator winding, V	6000	6300	6000
Total weight of electric motor with foundation slab, kg-f	5050	5100	11,600

Note: Manufacturere, Ural'sk Plant of Hydromachines.

5. Pumps

The basic parameters that charaterize the operation of any pump are:

output of pump Q which is determined by the volume of liquid fed by the pump in a unit of time;

pressure H which is expressed in meters of a column of pumped liquid;

power consumed by the pump, N, kW.

The catalogues present pump characteristics with the maximum number of wheel rotations n which cannot be increased without the agreement of the manufacturing plant.

When the number of revolutions is changed from n_1 to n_2 , the

pump parameters also change according to the following law of proportionality:

$$\frac{Q_1}{Q_2} = \frac{n_1}{n_2} \quad \frac{H_1}{H_2} = \left(\frac{n_1}{n_2}\right)^2 \quad \frac{N_1}{N_2} = \left(\frac{n_1}{n_2}\right)^3$$

The power of the electric motor is indicated by the manufacturing plant. It must be somewhat greater than the power on the pump shaft because of its possible overloading.

The power consumed by the pump is determined from the formula:

$$N = \frac{Q\gamma H}{102\eta} = \frac{Q\rho g H}{1000\eta} \quad \text{KW}$$

where Q--pump output, m³/s;

H--complete pressure of pump, m;

γ--specific weight of pumped liquid, kg-f/m³;

ρ--density of pumped liquid, kg/m³;

g--acceleration of gravity force, m/s²;

η--complete efficiency of pump (in fractions of a unit) equal to the ratio of useful pump power (QγH/102, or QρH) to the consumed.

The nitrogen industry makes the greatest use of blade pumps which are designed to pump chemically active liquids (both pure and contaminated) which contain abrasive inclusions of size to 0.2 mm in a quantity of not more than 0.2% weight.

The blade pumps are made in three types:

Kh--cantilever on individual stand;

KHG--hermetically sealed, monoblock with electric motor;

KHP--submersible.

Pumps of types Kh and KhG are made with horizontal and vertical arrangement of the shaft, pumps of type KhP are only made with vertical arrangement of the shaft.

TABLE III-83. DESIGN AND AREA OF APPLICATION OF Kh AND KhG TYPE PUMPS (GOST 10168-62)

Design	Designation	Area of application	
		pressure in loop, kg-f/cm ²	temperature of liquid, °C
Kh Type Pump			
With soft gasket	1	-	-
With end packing	2		
With standing packing	3		
KhG Type Pump			
With common loop for circulation of pumped liquid in pump and motor	1	to 25	to 50
	4	25-50	
	7	50-350	
With common loop of circulation of pumped liquid in pump and motor and with additional cooling of motor	2	to 25	50-100
	5	25-50	
	8	50-350	
With separate loop of circulation of liquid in pump and motor and with additional cooling of motor	3	to 25	100-400
	6	25-50	
	9	50-350	

TABLE III-84. TYPE-SIZES AND RATED OPERATING REGIME OF PUMPS (GOST 10168-62)

Type-size	Q, l/s	H, m	n, rpm	$\Delta h_{m \text{ non}}$	Type-size	Q, l/s	H, m	n, rpm	$\Delta h_{m \text{ non}}$
1Kh-2; 1KhV-2	0.6	30.5	2900	3	1½KhV-4	2.4	30	2900	5
1Kh-2P;					1½KhG-6x3;	2.4	53.3	2900	5
1Kh-2F					1½KhGV-6x3				
1KhV-2F					1½KhG-6x2	2.4	35.4	2900	5
1KhG-2; 1KhGV-2					1½KhGV-6x2				
1KhP-2					1½Kh-6	2.4	17.8	2900	5
1½Kh-2;	0.9	40	2900	4	1½KhV-6				
1½KhV-2					1½Kh-6P				
1½Kh-2P					1½KhV-6P				
1½KhV-2P					1½KhG-6				
1½KhG-2					1½KhGV-6				
1½KhGV-2					1½Kh-4x2	3	70	2900	5
1½Kh-2	1.8	63	2900		1½KhV-4x2				
1½Kh-2P					2Kh-2F	1.8	25	1450	3
1½KhV-2P					2KhV-2F				
1½KhP-2					2Kh-3F	1.8	14.6	1450	3
1½Kh-4	2.4	30	2900	5	2KhV-3F				
					4Kh-4F	12.5	36	1450	4
2Kh-4x2	5.5	106	2900	5	4KhV-4F				
2KhV-4x2					4Kh-6; 4KhV-6	25	85	2900	6
2Kh-4; 2KhV-4	5.5	53	2900	5	4KhG-6				
2Kh-4P					4KhGV-6				
2KhV-4P; 2KhP-4					4KhG-7x2	25	143	2900	6
2KhG-5x2	5.5	80	2900	5	4KhGV-7x2				
2KhGV-5x2					4Kh-9; 4KhV-9	25	49	2900	6
2KhG-6x2	5.5	61.6	2900	5	4KhG-9				

[continuation of table]

2KhGV-6x2					4KhGV-9				
2Kh-6; 2KhV-6	5.5	30.8	2900	5	4KhP-9				
2Kh-6P					4Kh-12	25	33.5	2900	6
2KhV-6P					4KhV-12				
2KhG-6; 2KhGV-6					4KhG-12				
2KhP-6					4KhGV-12				
2Kh-9; 2KhV-9	5.5	18	2900	5	4KhP-12				
2Kh-9P					4Kh-18	25	19.5	2900	6
2KhV-9P					4KhV-18				
2KhG-9					4KhP-18				
2KhGV-9					5KhP-6	45	49.5	1450	4.5
2KhP-9					5KhP-9	45	29	1450	4.5
3Kh-3F	5.5	30.8	1450	4	5Kh-12; 5KhV-12	45	49.5	2900	8
3KhV-3F					5Kh-18; 5KhV-18	45	29	2900	8
3Kh-6x2	12.5	108	2900	5	5Kh-24; 5KhV-24	45	19.7	2900	8
3KhV-6x2					7KhP-9	80	42.2	1450	6
3Kh-6; 3KhV-6	12.5	54	2900	5	7KhP-12	80	29	1450	6
3Kh-6P					8Kh-6; 8KhV-6	80	72.5	1450	6
3KhV-6P					8Kh-9; 8KhV-9	80	42.2	1450	6
3KhG-6					8Kh-12; 8KhV-12	80	28.9	1450	6
3KhGV-6									
3KhP-6									
3KhG-7x2	12.5	90	2900	5	9KhP-9	150	37.2	960	6
3KhGV-7x2									
3Kh-9; 3KhV-9	12.5	31	2900	5	9KhP-12	150	25.3	960	6
2Kh-9; 3KhV-9				5	9KhP-12	150	44	1450	10
3Kh-9P									
3KhV-9P					9KhP-18	150	25.3	1450	10
3KhG-9					10Kh-9; 10KhV-9	150	37.2	960	6
3KhGV-9									
3KhP-9					10Kh-12	150	25.3	960	6
3Kh-12	12.5	21.1	2900	5					
3KhV-12; 3Kh-12P									
3KhV-12P									

- Note: 1. In order to avoid cavitation, increase in pressure of the liquid at the entrance to the pump, the height of suction is diminished or backwater is used. The quantity Δh_{on} is the permissible height of suction (or minimum backwater) necessary for cavitation-free operation of the pump (expressed in meters of column of pumped liquid).
2. The designation of the pump type-size includes: a) first number is the diameter (in mm) in the intake (for KhP type pumps--the pressure) connection reduced 25-fold; b) the capital letters (before the hyphen) designate the type (for pump with vertical arrangement of the shaft, the letter V is added to the designation); c) the numbers after the hyphen are the coefficient of high speed reduced 10-fold; d) numbers after the multiplication sign are the number of stages (if there are two and more); e) the capital letters after the number of stages (and if the pump is one-stage, then after the coefficient of high

speed) is the conventional designation of nonmetal materials of which the parts of the flow-through part are made (P--plastic, F--porcelain, ceramic or graphite). The absence of these letters means that the parts of the flow-through part are made of metals. When the parts are made of metals, as well as when different coatings are applied, it is permitted to add the conventional designation set by the approved technical documents, instead of the letter.

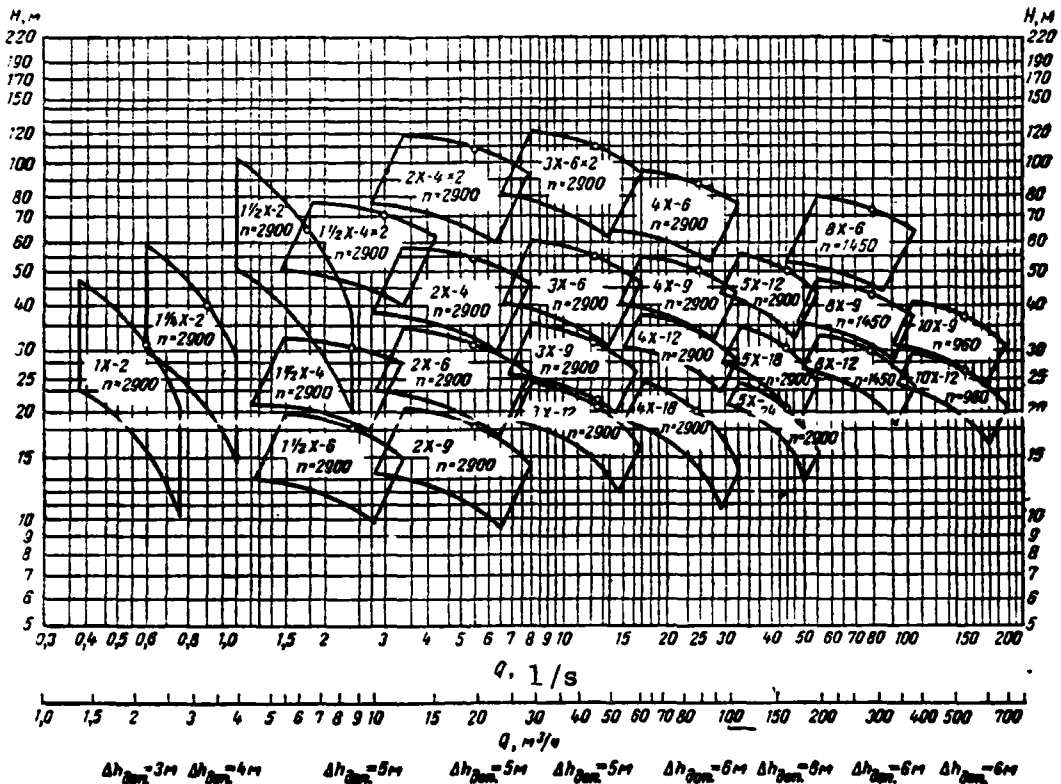


Figure III-33. Parameters of Pumps of Type Kh with Parts of the Flow-Through Part Made of Metals

TABLE III-35. CHARACTERISTICS OF PISTON (PLUNGER) PUMPS

Pumped medium (temp. of med.)	Design of pump	Type, brand	Input m ³ /h	Inject. pres. kg _f /cm ²	Backwater at inlet, atm.	Rotation rate of shaft, rpm	Piston di- ameter, mm	Stroke, mm	Overall dimensions, mm			Wgt. kg-f
									Length	width	hgt	
Copper-ammonia solution (at 25°C)	Horizontal, three- plunger with drive from reducer	T-25/340	25	340	3*	—	78	350	6491	4655	2400	—
Copper-ammonia solution (at 20-20°C)	Horizontal, four- plunger	6H-CZ1-FPE	25	340	—	138	63	—	2910	2610	—	13710
4% ammonia water	Horizontal, three plunger	SIGMA CHTP- 25/70-CZ1-FE	0.51- 1.02	340	—	102- 205	—	—	—	—	—	1200
Liquid ammonia (from -5 to +30°C)	Horizontal, three- plunger, with elec- tric drive, con- trollable	KhTR-1.5/200A	0.75- 1.5	200	—	200	32	60	1880	1000	1300	980
35% nitric acid (at 20-40°C)	Horizontal, three- plunger, with elec- tric drive, con- trollable	KhTP-8/110A	4-8	110	2.0	182	55	120	2335	1150	1330	1040
Mixture of li- quid nitric oxides with ni- tric acid (from -2 to +15°C)	Horizontal triple action with drive from electric motor through worm globoid reducer	KhT-8/52A	8	52	—	205	62	85	2115	785	1100	785

[continuation of table]

Water	Horizontal, three-plunger	GA-364	1.2	120	—	350	36	80	1 (100)	2 (80)	855
Liquid ammonia (at 40°C)	Horizontal, four-plunger	SIGMA 6N-CZL-COC F/2PE	32.1	230	15	138	70	290	3 (250)	3 (50)	1 (100)
25% ammonia water (at 36°C)	Horizontal, three-plunger	SIGMA CHNP-111 5/50 C5-FE	3	25	1	240	45	50	900	750	570
Liquid ammonia (at 25°C)	Horizontal three-plunger	SIGMA 14-CZL-ax-FE	8	200	7-15	184	48	—	1 (610)	2 (00)	1 (100)
Solution of ammonium carbonate (at 60°C)	Horizontal three-plunger	SIGMA CHNP 85/140 -D4-FVE	13-24	25	2	98-180	88	140	2 (120)	1 (30)	1 (170)
Solution of ammonium carbonate (at 90°C)	Vertical three-plunger	VTE-H79x152	18.5	200	19	146	79	152	1 (640)	1 (350)	3 (070)
Solution of ammonium carbonate (at 55°C)	Vertical three-plunger	VTE-257x127	10	25	2	100	57	127	1 (167)	1 (100)	1 (90)

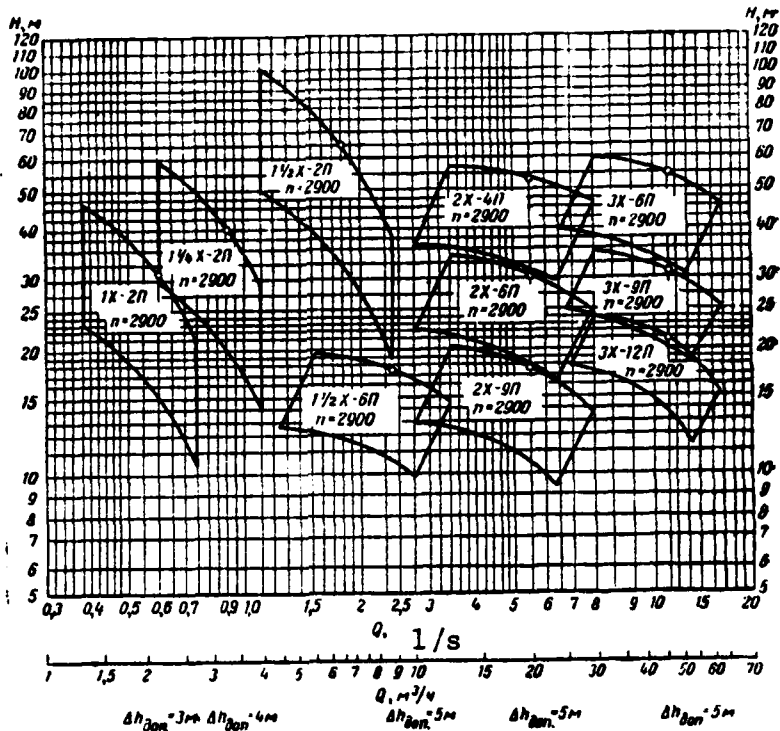


Figure III-34. Parameters of Kh Type Pumps with Parts of Flow-Through Section Made of Plastic

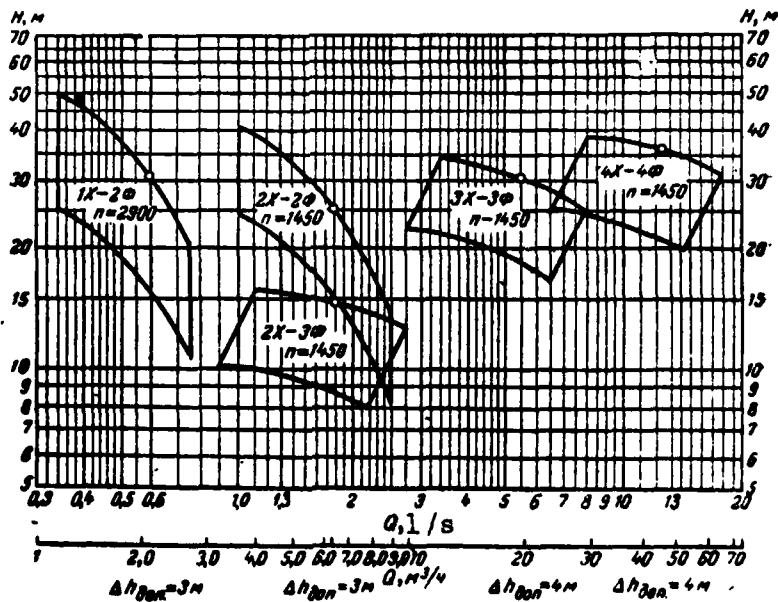


Figure III-35. Parameters of Kh Type Pumps with Parts of Flow-through Section Made of Porcelain, Ceramic or Graphite

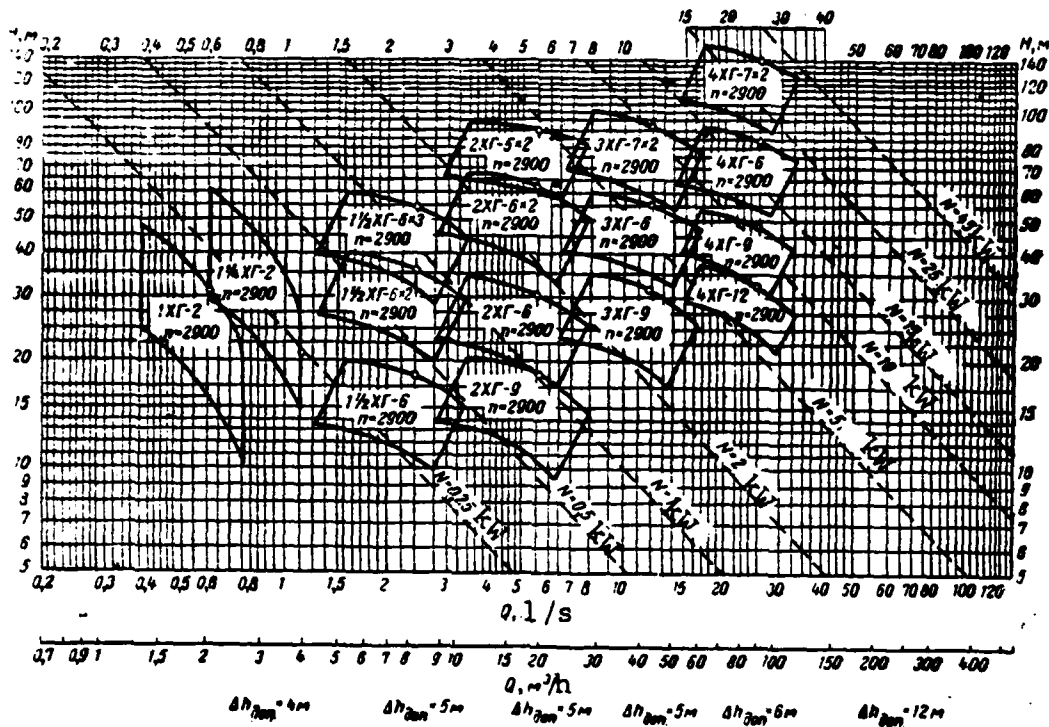


Figure III-36. Parameters of KhG Type Pumps with Parts of Flow-Through Section Made of Metals (N --useful power of pump with specific weight of liquid 1000 kg-f/m^3)

6. High Pressure Vessels 62-65

The phenomena of metal creep, hydrogen corrosion and nitriding of the inner surface of the apparatus or pipeline are especially dangerous for equipment that operates under conditions of high pressures ($P_{\text{pab}} = 320 \text{ atm}$ and higher).

It has recently been found that during transporting of a nitrogen-hydrogen mixture that contains ammonia (for example, circulation gas of synthesis), at high pressure and temperature above 300°C , the phenomenon of nitriding of steel is observed (effect of atomic nitrogen). The solid nitride film that is formed in this case is exposed to brittle cracking. In the final analysis, this may result in destruction of the apparatus housing or the pipeline.

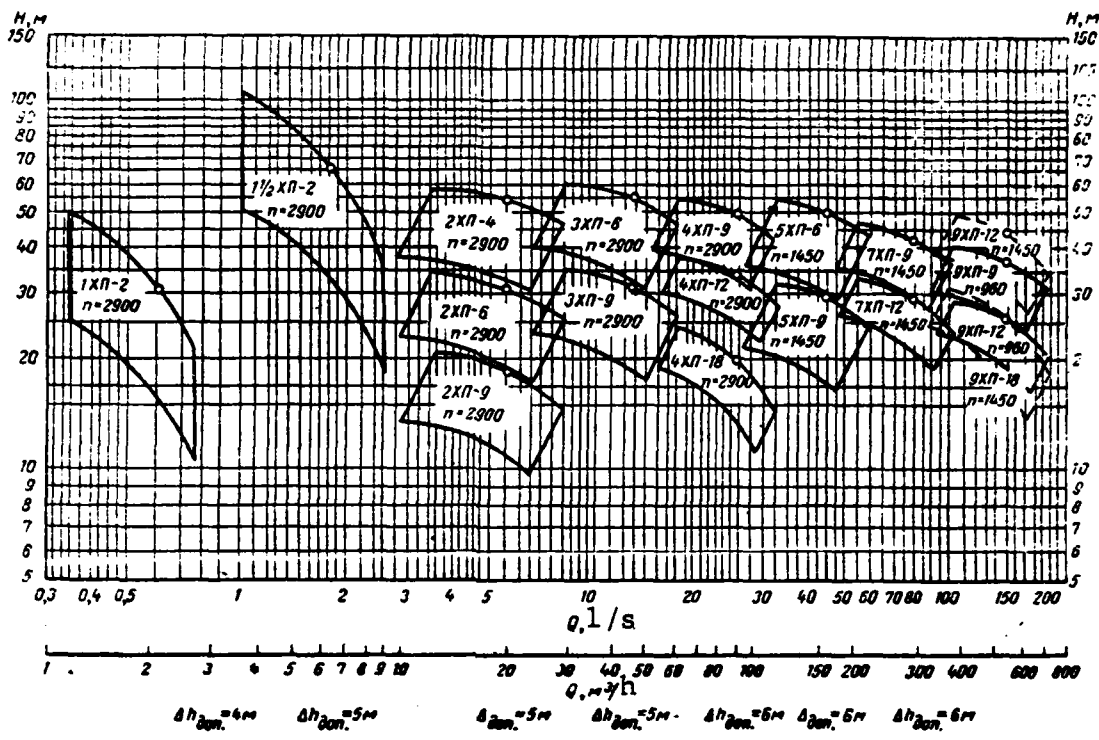


Figure III-37. Parameters of KhP Type Pumps with Parts of Flow-Through Section Made of Metals

Conducted studies have shown that high-alloy steels of type 25/20 (25% Cr, 20% Ni) are less exposed to nitriding, however there are still no sufficient data on this question.

In order to protect steel from nitriding, it is possible to use lining, for example, copper or aluminum.

High pressure equipment is conventionally divided into "cold" operating at temperatures to 200°C, and "hot" operating in temperature intervals from 200 to 400 °C and higher.

The "hot" units include synthesis columns for ammonia and methanol, columns of precatalysis, hydrogenation, etc. The housing of the "hot" units, covers, packing (pressure) rings are made from steel 25Kh3NM according to RTM 121-65.

The chemical composition of steel 25Kh3NM (in %) must satisfy

the following requirements:

C	0.15-0.35	Mo	0.25-0.6
Si	0.17-0.37	P	no more than 0.045
Mn	0.25-0.55	S	no more than 0.04
Cr	3.0-4.0	P + S	no more than 0.07
Ni	0.6-2.0		

In order to increase the resistance of steel to hydrogen corrosion at high pressures and temperatures, it is necessary to have the minimum content of nickel and carbon and the maximum of chrome.

Pins of the main fastening are made of steel 25Kh1MF (GOST 10500-63); nuts are made of steel 30KhMA (GOST 4543-61); washers are made of steel 30Kh(GOST 4543-61). The chemical composition of the listed brands of steels must correspond to the indicated GOSTs.

The "cold" units include condensation columns, oil filters, scrubbers, separators and other apparatus. The housings of the "cold" apparatus, covers, packing (pressure) rings are made of boiler steel of brand 22K according to TUKhK 1-00 of the Izhorskiy Plant according to RTM 121-65.

The pins and nuts of the main fastening are made of steel 30KhMA and 40Kh, and the washers are made of steel 30Kh.

The material in the parts of the high pressure vessels in the form of forged pieces must correspond in mechanical properties to the requirements presented in table III-86.

Figure III-38 shows the high pressure apparatus of different shape used in the nitrogen industry. Depending on the purpose and diameter, apparatus of a certain shape is used:

Apparatus	Inner diameter, mm				
	600	800	850	1000	1200
Columns of synthesis of ammonia and methanol	-	A	A	B	B
Condensation columns	A	A	-	B	-
Filters and separators	B	C	-	C	-
Scrubbers, copper-ammonia and alkali	A	A	-	B	B
		or B			

The following forms of housings are the most frequently used for "cold" apparatus: for condensation columns: type A; for copper-ammonia and alkali scrubbers: type B; for filters and separators: type C.

TABLE III-86. MECHANICAL PROPERTIES OF STEEL FORGED PIECES FOR MAKING PARTS OF HIGH PRESSURE VESSELS

1 Марка стали	2 Температура °C	3 Предел прочности кгс/мм ²	4 Предел текучности кгс/мм ²	5 Относитель- ное удлинение %	6 Относитель- ное сужение %	7 Ударная вязкость кгс·м/см ²
25Kh3NM	20	≥65	≥50	≥15	≥32	5
	300	≥58	≥37	—	—	—
25Kh1MF	20	85	65	15	40	8
	300	—	50	—	—	—
30KhMA	400	—	45	—	—	—
	20	75	55	14	42	7
	300	—	40	—	—	—
30Kh	400	—	35	—	—	—
	20	70	50	14	42	8
	300	—	35	—	—	—
22K	400	—	32	—	—	—
40Kh	—	≥44	≥22	≥20	≥48	≥5
		≥70	≥50	≥14	≥42	6

Key:

1. Brand of steel
2. Temperature, °C
3. Ultimate strength, kg-f/mm²
4. Yield limit, kg-f/mm²
5. Relative elongation, %
6. Relative constriction, %
7. Impact viscosity, kg-f x m/cm²

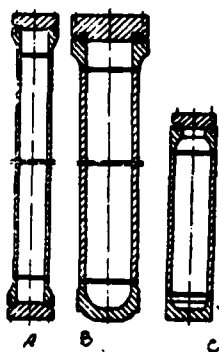


Figure III-38. Shapes of Housings of High Pressure Apparatus

Below are certain formulas for computing the parts of high pressure apparatus (fig. III-39). In all the formulas, $[\sigma]$ is the permissible tension (in kg-f/mm²).

$$[\sigma] = \frac{\sigma_s}{n_s} \quad \text{or} \quad [\sigma] = \frac{\sigma_T}{n_T}$$

where σ and σ_T -- respectively the ultimate strength and yield limit in stretching, kg-f/mm²;

n_s and n_T --margin of strength respectively for ultimate strength and yield limit.

Determination of Thickness of Housing Wall

$$S = (0.5D + C)(\beta - 1) + C + C_1$$

where C--addition for corrosion;

C_1 --addition for permissible deviations from inner and outer diameters;

β --coefficient of thick-wall, whereupon

$$\ln \beta = \frac{P}{[\sigma] \phi}$$

here P--working pressure in apparatus, atm.;

ϕ --coefficient of strength of welded seam;

$n_s = 2.6$; $n_T = 1.5$.

Determination of Height of Roof

$$H = 0.5 \sqrt{\frac{38Q(D_w - D_{cp}) + D_{cp}^2 P}{(D_w - 2d - \sum_{i=1}^n d_i) [\sigma]}}$$

where Q--calculated force (in kg-f) equal to $Q_s + Q_n$;

Here Q_s --equivalent force of inner pressure;

Q_n --component of equivalent force of inner pressure on packing;

$n_T = 3.5$.

Determination of Diameter of Pin Neck

$$d_w = \sqrt{\frac{4kQ}{\pi s [\sigma]} + d^2}$$

where k--coefficient that takes into consideration the torque

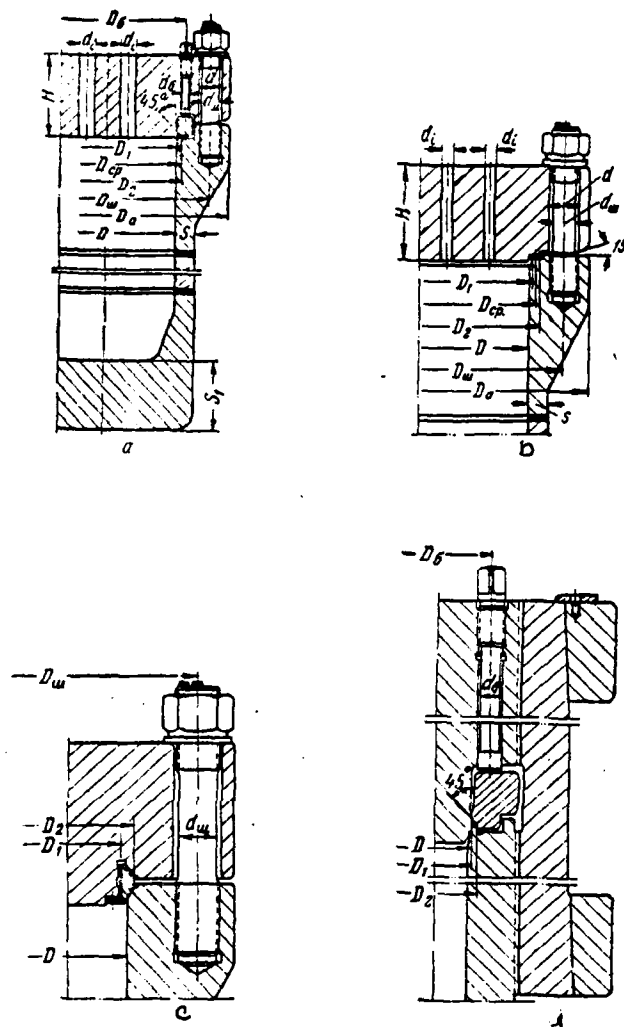


Figure III-39. Basic Dimensions Needed to Compute Flange, Cover, Bottom and Gates of Varying Design

Key:

- a. With metal packing of triangular section
 - b. With flat metal packing
 - c. With two-cone packing ring and packing made of sheet aluminum
 - d. With basic fastening in form of coupling made of two halves
- D. inner diameter of apparatus
D and H. outer diameter and height of roof respectively
 D_1, D_{cp}, D_2 . inner, middle and outer diameter of packing respectively
 D_w and D_f . Diameter of circumference of pin and pressure bolts respectively
S and S_1 . Thickness of wall of housing and bottom respectively
d. Diameter of opening for pin and for pressure bolt

d_w and d_r . Diameter of pin neck and pressure bolt respectively
 d_i . Diameter of hole in cover.

during tightening of the pin;
 d_a -- diameter of central hole in pin;
 z -- number of pins;
 $n_T = 2 - 2.25$.

Determination of Thickness of Bottom

$$s_1 = D \sqrt{\frac{0.3P}{[\sigma] \phi}}$$

where P --working pressure in apparatus, atm.;
 ϕ --coefficient of strength of welded seam;
 $n_s = 2.6$; $n_T = 1.5$

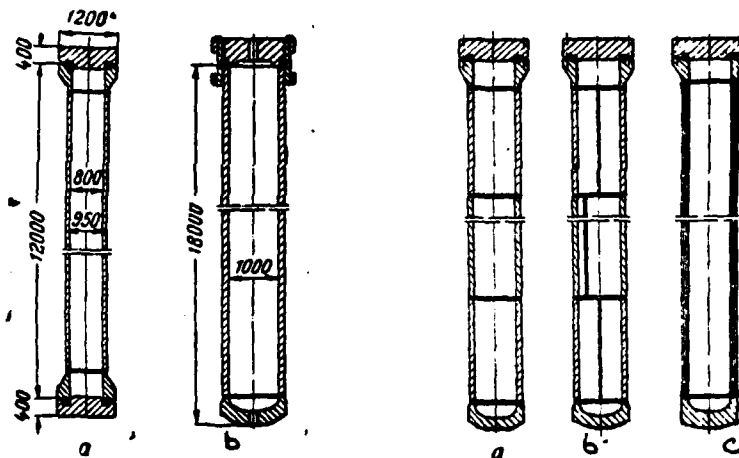


Figure III-40. High Pressure Housing for Column of Ammonia and Methanol Synthesis

Key:

- a. With main fastening in form of pins and detachable bottom
- b. With main fastening in form of coupling of two halves and welded bottom

Figure III-41. Types of High Pressure Vessels Depending on Method of Their Fabrication

Key:

- a. Forged-welded
- b. Stamped-welded (stamp-U-shaped, made of thick-sheet rolled piece and longitudinal welding of them)
- c. multilayer

Calculation of the high pressure housings is done according to RTM 121-65.

Depending on the conditions for the use of high pressure vessels, there are different methods of making them.

Recently, because of the installation of large units for ammonia synthesis (over 1000 T of NH_3 per day), high pressure columns are used with large internal diameter (over 2000 mm) made by the method of rolling (multilayer) which make it possible to obtain the housing of columns of unlimited dimensions.

Calculation of Pipes under Internal Pressure⁶⁵

The thickness of the wall of pipe S (in mm);

$$\text{with } \frac{P}{\sigma_R} < 0.4 \quad S = \frac{D_n P}{2\sigma_R \phi + P} + C$$

$$\text{with } \frac{P}{\sigma_R} \geq 0.4 \quad S = 0.5 D_n \frac{10^{P/3.3\sigma_R} - 1}{10^{P/3.3\sigma_1}} + C$$

The pressure in the pipe wall during hydraulic testing σ (in kg-f/mm^2):

$$\sigma = \frac{[D_n + (S - C)] P_n}{2(S - C)\phi}$$

where P--working internal pressure, kg-f/cm^2 ;

P_n --calculated internal pressure in testing, kg-f/cm^2 ;

σ_R --permissible pressure in stretching, kg-f/mm^2 ;

D_n and D_s --outer and inner diameters of pipe respectively, mm;

ϕ --coefficient of strength in axial direction;

C--addition for calculated thickness of wall, mm:

$$C = C_1 + C_2 + C_3$$

here C_1 --addition for corrosion, mm;

C_2 --addition for erosion (if there is any), mm;

C_3 --addition for minus tolerance for sheet thickness, mm.

7. Steel Gas Holders with Water Basin^{66,67}

Steel gas holders with a water basin (wet gas holders) of low pressure and variable volume are designed for storing, regulating the consumption and pressure of gases: argon, nitrogen, oxygen, hydrogen, ammonia, methane, acetylene, fractions of carbon monoxide, carbon dioxide, gas-generator, converted, coking and other gases that do not cause strong corrosion of the metal.

Wet gas holders have become the most popular in the chemical industry and a number of other sectors because of the simplicity of design and the great safety of operation as compared to dry.

The component parts of the wet gas holder are:

tank (water basin);

bell (mobile tank without bottom);

telescope (in two-, three- and multiple-link gas holders, a mobile tank without bottom or cover);

internal and external guides (vertical or screw) for moving the bell and the telescope using rollers installed above and below them.

When the gas holder is filled, the bell is lifted under the influence of gas pressure; with further filling of gas, the bell, attached by a lower gate to the upper gate of the telescope, lifts it. In this case the water from the water basin is captured, and as a result, a gas-impermeable hydraulic gate is formed.

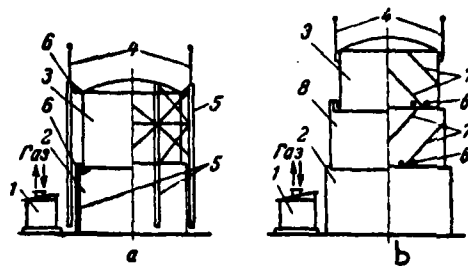
The bell and the telescope of the gas holder are elements which create and maintain gas pressure in the gas holder. The minimum gas pressure under the bell equals 125, the maximum equals 400 mm wat. col.

The wet gas holders are divided by design into gas holders with vertical guides (see fig. III-42,a) and gas holders with screw guides (see fig. III-42,b).

Gas holders with vertical guides are manufactured with capacity from 100 to 30,000 m³ according to standard plans 7-07-01/66-7-07-10/66 that were developed by the GIAP jointly with the Central Scientific Research and Planning Institute for Designing Steel Structural Parts and the institute "Proyektkhimzashchita." Gas holders with screw guides are manufactured with capacity from 1000 to 30,000 m³ according to standard plans 7-07-30-7-07-36 developed by the same institutes:

With vertical guides (manufactured in 1966)		With screw guides (manufactured in 1964)	
Capacity of gas holder m ³	Number of standard plan	Capacity of gas holder m ³	Number of standard plan
100	7-07-01/66	1 000	7-07-30
300	7-07-02/66	3 000	7-07-31
600	7-07-03/66	6 000	7-07-32
1 000	7-07-04/66	10 000	7-07-33
3 000	7-07-05/66	15 000	7-07-34
6 000	7-07-06/66	20 000	7-07-35
10 000	7-07-07/66	30 000	7-07-36
15 000	7-07-08/66		
20 000	7-07-09/66		
30 000	7-07-10/66		

Figure III-42. Gas Holders with Vertical (a) and Screw (b) Guides



Key:

1. Gas input shelter
2. Tank
3. Bell
4. Lightning protection
5. Vertical guides
6. Rollers
7. Screw guides
8. Telescope

Determination of Gas Pressure in Gas Holder

Gas pressure in the gas holder with upper position of the bell without telescope is roughly determined by the formula:

$$P = \frac{Q_k}{F} \text{ kg-f/m}^2 \text{ (or mm wat. col.)}$$

where Q_k -- weight of bell, kg-f;
 F -- area of bell base, m².

$$P = \frac{1}{4} \pi D_k^2$$

where D_k -- diameter of bell, m.

Then:

$$P = \frac{Q_g}{0.785 D_k^2} = 1.273 \frac{Q_g}{D_k^2} \text{ kg-f/m}^2 \text{ (or mm wat. col.)}$$

The minimum gas pressure under the bell (when one bell is lifted) is determined by the formula:

$$P_{\text{min}} = \frac{1.273}{D_k^2} \left[Q_g - \frac{Q_g}{7.85} - v_g (\gamma_a - \gamma_g) \right]$$

For gas holders with telescope in the working position, the pressure in the gas holder with regard for losses from submersion of the telescope and the bell into the water and the difference in densities of air and gas are determined from the formula:

$$P = \frac{1.273}{D_k^2} \left[Q_g + Q_t + g - \frac{Q'_g}{7.85} - (v_g + v_t) (\gamma_a - \gamma_g) \right]$$

where P -- pressure of gas, mm wat. col.;

Q_k, Q_T -- weight of bell and telescope respectively, kg-f;

g -- weight of water in hydraulic gate of telescope, kg-f;

Q'_k and Q'_T -- respectively the weight of the submerged part of the bell and the telescope, kg-f;

v_k, v_T -- respectively the volume of the bell and the telescope, m^3 ;

γ_a, γ_r -- respectively the specific weight of air and gas under normal conditions, kg-f/m^3 ;

7.85 -- specific weight of steel, kg-f/m^3 .

The gas pressure in the gas holders is not constant. It depends on the position of the bell and the telescope. If necessary, the pressure can be increased by additional loading on the bell using pig iron and concrete loads. The weight of the additional load x (in kg-f) with an increase in pressure by a mm wat. col. is determined from the equation:

$$x = \frac{(P + g) D_k^2}{1.273} - Q_g$$

where Q_k --weight of bell, kg-f;

P --gas pressure under bell, mm wat. col.

Calculation of Volume of Gas Holder

The useful volume of wet gas holders is determined as follows.

For a one-link gas holder

$$v = 0.785 D_k^2 (H_k - h_0)$$

where v --volume of gas in gas holder, m^3 ;

D_k, H_k --diameter and height of bell, m;

$$h_0 = h_n + h_m$$

Here h_n --height of column of liquid corresponding to the greatest gas pressure in the gas holder, m;

h_m --addition of 2mm for every 1000 mm of bell diameter.

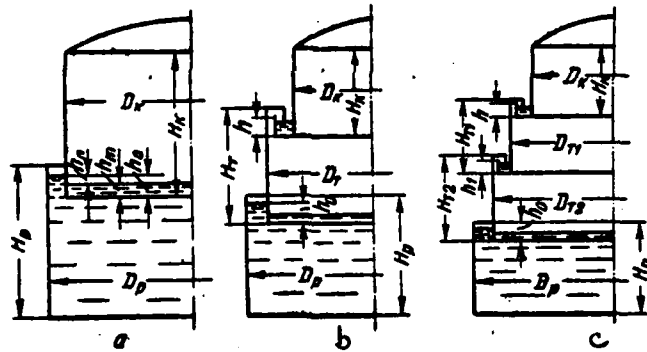


Figure III-43. Determination of Useful Volume of Gas Holder

Key:

- a. One-link
- b. Two-link
- c. Three-link

Figure III-43 shows the dimensions necessary for determining the useful volume of the gas holder (D_p and H_p --diameter and height of tank).

For a two-link gas holder

$$v = 0.785 D_k^2 H_k + 0.785 D_k^2 (H_k - h - h_0)$$

where D_k and H_k --diameter and height of bell, m;
 D_T and H_T --diameter and height of telescope, m;
 h --height of bell dish, m;

$$h_0 = h_n + h_m$$

For a three-link gas holder

$$v = 0.785 D_k^2 H_k + 0.785 D_{T_1}^2 (H_{T_1} - h) + 0.785 D_{T_2}^2 (H_{T_2} - h_1 - h_0)$$

where D_k and H_k --diameter and height of bell, m;
 D_{T_1} and H_{T_1} --diameter and height of first telescope, m;
 D_{T_2} and H_{T_2} --diameter and height of second telescope, m;
 h and h_1 --height of bell dish and telescope, m;

$$h_0 = h_n + h_m$$

Selection of Gas Holder Capacity

In the majority of cases, the capacity of the gas holders is selected from a calculation of the gas reserve needed to guarantee operation of the consumer for 10-60 min.

The capacity of the gas holder (in m^3) is determined based on the time needed to stop the compressors and the gas blowers when gas stops coming into the gas holder:

$$v = \frac{0.8Q_t}{60} \approx 0.02Q_t$$

where Q --consumption of gas, m^3/h ;

t --time of emptying gas holder, min;

0.8--coefficient of useful volume of gas holder.

Table III-87 presents the overall dimensions and weight of the one-, two- and three-link gas holders.

The tank is filled with water from an industrial water line. The overflow pipeline from the gas holder is connected to the industrial drainage system.

TABLE III-87. MAIN DIMENSIONS AND WEIGHT OF GAS HOLDERS

1 Емкость газополь- зователя, м ³	2 Размеры, мм								7 Общая высота стальных конструк- ций, мм	8 Минимальное дав- ление газа для об. ст.	9 Общий вес, Т
	3 резервуар		4 колокол		5 первый телескоп		6 второй телескоп				
	D _р	H _р	D _к	H _к	D _{т1}	H _{т1}	D _{т2}	H _{т2}			
10 С вертикальными направляющими											
100	7 400	3 450	6 800	3 845	—	—	—	—	7 480	220	14
300	9 308	5 920	8 500	5 715	—	—	—	—	12 555	200	27
600	11 480	7 390	10 880	7 150	—	—	—	—	15 435	200	40
1 000	14 500	7 390	13 700	7 140	—	—	—	—	15 436	170	55
3 000	21 050	9 800	20 250	9 550	—	—	—	—	20 258	150	120
6 000	28 900	11 750	28 100	11 455	—	—	—	—	24 358	150	211
10 000	28 140	9 800	26 100	9 420	27 120	9 400	—	—	29 588	160	276
15 000	31 170	11 750	29 050	11 350	30 110	11 350	—	—	35 538	160	354
20 000	35 860	11 750	33 700	11 350	34 780	11 350	—	—	35 538	140	416
30 000	43 600	11 750	41 400	11 310	42 500	11 330	—	—	35 538	125	624
11 С винтовыми направляющими											
1 000	16 450	5 820	15 350	5 660	—	—	—	—	10 990	160	64.7
3 000	24 550	7 400	23 450	7 200	—	—	—	—	14 050	130	122.8
6 000	25 850	7 400	23 450	7 188	24 550	7 188	—	—	20 440	150	183.4
10 000	31 700	7 850	29 500	7 630	30 600	7 650	—	—	21 790	150	255.6
15 000	38 200	7 850	38 000	7 680	37 100	7 638	—	—	21 790	140	333.3
20 000	39 300	7 000	38 000	6 780	37 100	6 788	38 200	6 788	25 280	135	397.5
30 000	44 900	7 850	41 800	7 630	42 700	7 638	43 800	7 638	28 880	130	525.8

Key:

1. Capacity of gas holder, m³
2. Dimensions, mm
3. Tank
4. Bell
5. First telescope
6. Second telescope
7. Total height of steel structures, mm
8. Minimum gas pressure, mm. wat. col.
9. Total weight, T
10. With vertical guides
11. With screw guides

Note: 1. Maximum gas pressure is 500 mm wat. col.
 2. The total weight only includes the weight of the steel structures.

Plans of Gas Inlet of Gas Holder

The gas holders can be connected in technological plan to a "dead end" or to a "passage" with discharge and without discharge of the surplus gas into the atmosphere.

The plan for connecting the gas holder to a "dead end" and to a "passage" with discharge of the gas into the atmosphere

TABLE III-88. DIAMETERS OF GAS PIPELINES AND WATER PIPELINES

1 Емкость газголь- дера м ³	2 Диаметр газового ввода мм	3 Диаметр трубопро- водов, мм		6 Едино- времен- ный рас- ход воды м ³	7 Емкость газголь- дера м ³	2 Диаметр газового ввода мм	3 Диаметр трубопро- водов, мм		6 Едино- времен- ный рас- ход воды м ³
		4 пода- чи воды	5 слива воды				4 по- дачи воды	5 слива воды	
7 С вертикальными направляющими					8 С винтовыми направляющими				
100	200	80	100	150	1 000	400	80	100	1 200
300	200	80	100	430	3 000	600	125	150	3 500
600	400	80	100	770	6 000	600	150	200	3 800
1 000	400	80	100	1 220	10 000	800	150	200	6 100
3 000	600	125	150	3 410	15 000	1 000	200	200	8 900
6 000	600	150	200	6 700	20 000	1 200	200	250	8 400
10 000	800	150	200	8 180	30 000	1 200	200	300	12 200
15 000	1 000	200	200	9 000					
20 000	1 200	200	250	11 900					
30 000	1 200	200	300	17 500					

- Key:
1. Capacity of gas holder, m³
 2. Diameter of gas inlet, mm
 3. Diameter of pipelines, mm
 4. Water supply
 5. Water overflow
 6. One-time water consumption, m³
 7. With vertical guides
 8. With screw guides

- Note:
1. The useful volume of the gas holder is 80% of its rated capacity.
 2. The diameters of the gas inlets are taken from the condition of minimum losses of gas pressure in the gas line which must not exceed 30-50 mm wat. col. For gases with density of 1 kg/m³, these losses are obtained with gas velocity in the gas line of roughly 8-10 m/s.
 3. In designing the gas inlets, it is taken into consideration that the normal velocity of movement of the mobile links (bell, telescope) on the vertical must not exceed 1.5 m/min.

(fig. III-44) is used for all gases, except, those whose discharge into the atmosphere is not allowed: gas mixtures with content of ammonia, methane and CO higher than 3.5% vol. and acetylene over 15% vol.

The plan for connecting the gas holder to a "dead end" and to "passage" without discharge of gas into the atmosphere (fig. III-45) is used for gases and gas mixtures whose discharge into the atmosphere is not allowed.

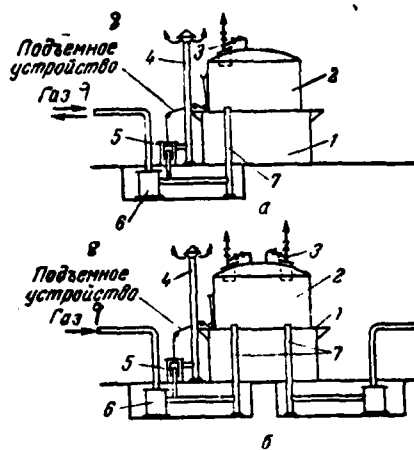


Figure III-44. Plan for Connecting Gas Holder with Discharge of Gas into the Atmosphere

Key:

- a. to "dead end"
- b. to "passage"
- 1. tank
- 2. bell
- 3. relief device
- 4. gas-discharge pipe
- 5. valve box
- 6. hydraulic gate
- 7. gas riser
- 8. lifting device
- 9. gas

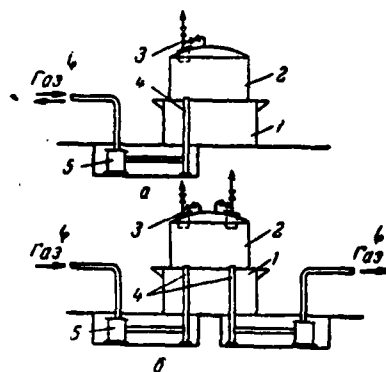


Figure III-45. Plan for Connecting Gas Holder without Discharge of Gas into the Atmosphere

Key:

- a. to "dead end"
- b. to "passage"
- 1. tank
- 2. bell
- 3. relief device
- 4. gas riser
- 5. hydraulic gate
- 6. gas

Construction Designs; Heating and Ventilation

The foundation under the gas holder consists of a ground fill, a sand cushion, insulation layer and protective layer made of sand. The foundation of the precast monolithic structure under the tank wall is made in the form of a ring. The walls of the heated shelter (chamber) are brick. The areaway, tunnel and designs of the between-story flooring are made of monolithic reinforced concrete. The roofing is made of precast reinforced concrete elements. The heating wall of the gas holders is made of brick on a foundation beam.

The gas holders are heated to maintain in the tank and the hydraulic gate of the telescope water temperature no lower than

+5°C. The heat carrier is saturated steam with absolute pressure of 4 atm. Depending on the duration of the heating season and the cost of the steam, the gas holders can be used without heating of the tanks (for regions with calculated winter temperature to -20 - -30°C) and with heating of the tank by a brick wall (for regions with calculated winter temperature below -20- -30°C). Table III-89 presents the consumption of steam to heat wet gas holders under winter conditions.

The chamber of the gas inlet provides for intake mechanical ventilation in the inner areaway in a volume of 10-12-fold the volume per hour. This ventilation is periodic. It is turned on for 10 min before the entrance of the service crew into the gas inlet chamber.

Electrical Equipment and Lightning Protection; Protection from Corrosion

The electrical power is supplied to the gas holder by one seven-cable line for 380/220 V. The gas holder is protected from direct lightning strikes with the help of lightning receivers installed on the pipes of gas discharge and outer guides of the gas holder (in this case it is necessary to create a ground with total resistance of no more than 10 Ohm). The production equipment and the pipelines are protected from static electricity by reliable grounding by connection to the nearest grounding device of lightning protection.

Depending on the climate conditions and the gas in the gas holder, three methods are possible for anticorrosion protection of the metal structures.

First method: use of protective liquid and partial coating with varnish 177 and paint AL-177;

Second method: coating made of perchlorovinyl materials and red lead on natural tin;

Third method: coating made of red lead and iron oxide on

natural tin.

Below are the recommended methods of protection for gas holders of varying purpose:

For storage of argon, nitrogen, hydrogen, carbon dioxide, water, air, converted, gas-generator gases, mixture of hydrocarbon and water gases
For storage of gases of hydrogenation, methane and other hydrocarbon gases
For storage of ammonia

For storage of oxygen

Methods

1,2,3

1,3

1,2,3 (inner surface of housing and cover of bell not protected)
3 (first and second cannot be used)

Control and Signalling

Each gas holder is equipped with:

sensors for measuring and signalling the volume of gas with command apparatus of the synchrotransmitter type;

secondary instruments of the selsyn receiver type for continuous indication of the volume of gas in the shops that issue or receive the gas;

signal panel of stepped signalling of the positions of the gas holder bell ("minimum," "preminimum," "normal," "premaximum," "maximum") installed in the shops that issue or receive the gas;

mercury thermometer to measure the water temperature in the gas holder tank.

Content of Standard Plans*

For gas holders with vertical guides

Album I. Per sheet assembly

" II. Assembly by enlarged panels.

" III/66. Assembly by rolling method.

" IV. Per-sheet assembly made of low-alloy steel.

* Standard plans of wet gas holders are distributed by the Minsk branch of the Central Institute of Standard Plans, Minsk, Kozlova, 2.

- Album V. Rollers, hatches, manholes (standard plan 7-07-11).
- " VI. Anticorrosion protection.
- " VII. Gas inlet; control and automatics; electrical engineering devices.
- " VIII. Architectural-structural part; heating and ventilation with heating of tank.
- " IX. Architectural-structural part, heating and ventilation without heating of tank.
- " X. Estimates

For gas holders with screw guides

- Album I. Gas inlet; heating and ventilation; electrical engineering devices.
- " II. Control and automatics.
- " III. Architectural-construction part.
- " IV. Steel structures.
- " V. Rollers, hatches, manholes.
- " VI. Anticorrosion protection.
- " VII. Estimates.

Initial Calculation Data as the Basis for Standard Plans

The carrier metal structures of the gas holders are rated for the following loads:

- gas pressure under the bell--from 125 to 400 mm wat. col.;
- weight of the actual structures and water pressure;
- snow loads-- 100 kg-f/m^2 ;
- wind loads-- 70 kg-f/m^2 (main wind);
- seismic oscillations--to 7 points.

The construction designs (foundations, heating brick wall, etc.) are designed for the following conditions:

- dry, nonsagging ground, with rated resistance with central compression 2 kg-f/cm^2 , with eccentric compression-- 2.4 kg-f/cm^2 at edge of footing;
- wind load-- 70 kg-f/m^2 ;
- snow load-- 100 kg-f/m^2 .

Similar data used as the basis for developing plans of metal designs and the construction parts are given in the explanatory notes for the corresponding parts of the plan.

TABLE III-89. CONSUMPTION OF STEAM FOR HEATING GAS HOLDERS UNDER WINTER CONDITIONS (in kg/h)

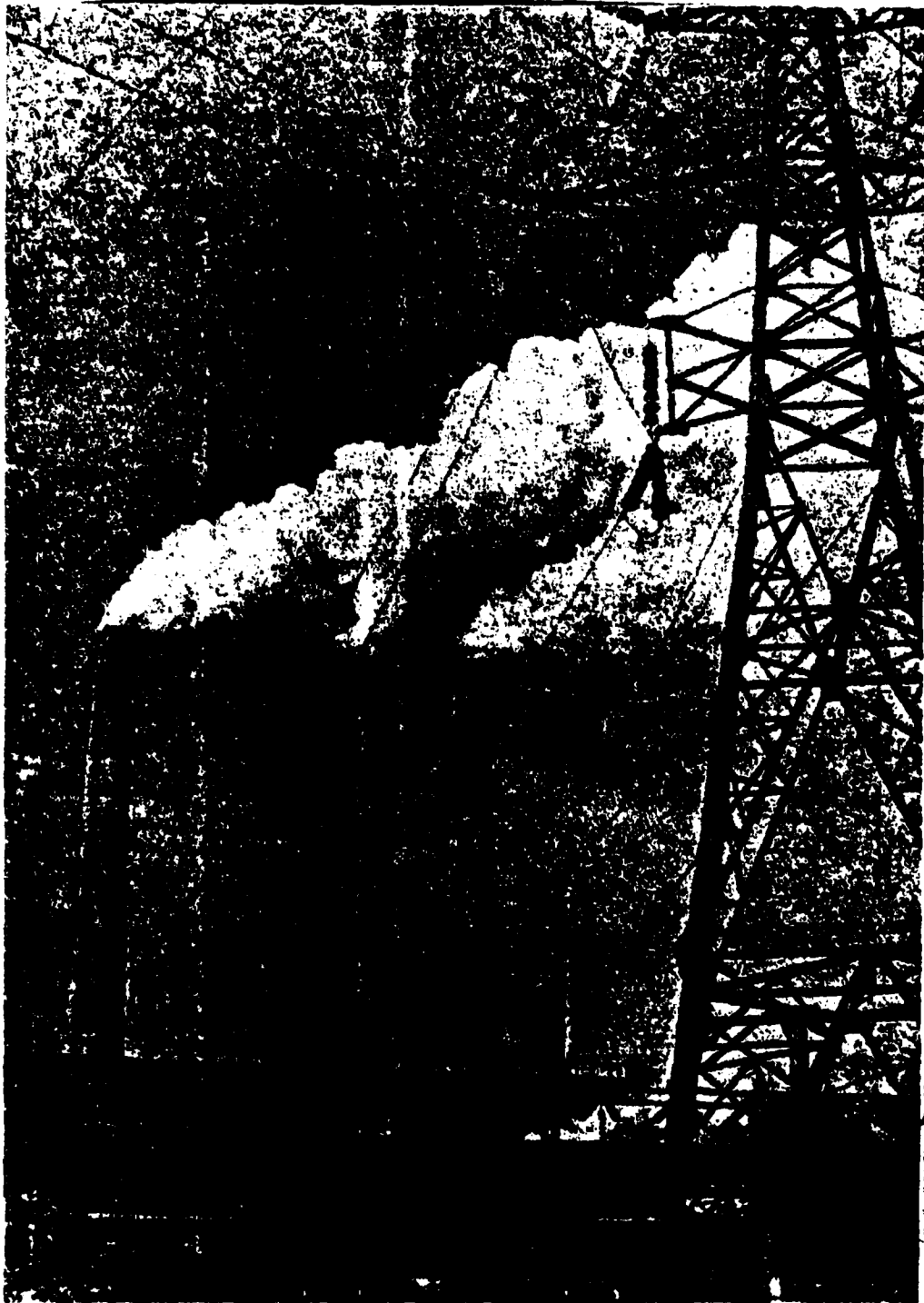
1 Емкость газодержателя, м ³	2 Расчетная внешняя температура, °C									
	3 с утепленным резервуаром					4 без утепленного резервуара				
	-20	-25	-30	-35	-40	-10	-15	-20	-25	-30
5 С вертикальными направляющими										
100	30	33.5	37	43.5	70	91	121.5	164	125.5	167
200	79	95.5	107	123.5	140	181	136.5	219	266.5	307
300	119	140.5	162	186.5	210	261	267.5	334	400.5	467
400	155	182.5	215.5	243.5	271	298.5	342.5	430	512.5	600.5
500	231	351	405	465	520	497	691	830	966	1148
600	330	521	610	695	780	757	1001	125	1301	1548
8000	605	722	842.5	958	1075	902.5	1070	1335	1362	1600.5
15000	795	952	1107.5	1258	1415	1062.5	1415	1766	2102	2467.5
20000	915	1092	1267.5	1443	1620	1222.5	1625	2025	2422	2907.5
30000	1195	1317	1532	1748	1980	1482.5	1970	2480	2932	3407.5
6 С винтовыми направляющими										
100	133.8	169.2	185.5	211.9	237.2	250.6	306.15	361.7	456.2	530.7
200	258	307	341	412	461	440	564	725	890	1040
300	416	502	546	672	751	680	744	930	1104	1280
400	550	654	770	871	970	725	800	1200	1430	1672
500	655	794	915	1041	1170	870	1156	1446	1736	2007
600	845	1059	1230	1401	1570	938	1286	1576	1861	2192
8000	1125	1344	1506	1761	1985	1210	1611	2006	2404	2785

- Key:
1. Capacity of gas holder, m³
 2. Calculated external temperature, °C
 3. With heating of tank
 4. Without heating of tank
 5. With vertical guides
 6. With screw guides

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IV. Power Supply

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Heat Engineering^{1,2}

Thermodynamic Properties of Water Vapor

TABLE IV-1. SATURATED WATER VAPOR

Pressure atm.*	Satura- tion temp. °C	Specific volume, m ³ /kg		Enthalpy, kcal/kg	
		water	saturated vapor	liquid	vapor
0.01	6.988	0.0010001	131.6	6.73	600.2
0.02	17.204	0.0010013	68.25	17.25	604.9
0.03	23.772	0.0010027	46.52	23.81	607.8
0.04	28.641	0.0010040	35.48	28.67	609.8
0.05	32.55	0.0010052	28.72	32.57	611.5
0.06	35.82	0.0010063	24.19	35.83	612.9
0.08	41.16	0.0010084	18.45	41.16	615.2
0.10	45.45	0.0010101	14.95	45.45	617.0
0.15	53.60	0.0010138	10.20	53.59	620.5
0.20	59.67	0.0010169	7.789	59.65	623.1
0.25	64.56	0.0010196	6.318	64.54	625.0
0.30	68.68	0.0010220	5.324	68.66	626.8
0.40	75.42	0.0010261	4.066	75.41	629.5
0.50	80.88	0.0010296	3.299	80.86	631.6
0.60	85.45	0.0010327	2.782	85.47	633.5
0.70	89.45	0.0010355	2.406	89.49	635.1
0.80	92.99	0.0010381	2.125	93.05	636.4
0.90	96.18	0.0010405	1.903	96.26	637.6
1.0	99.09	0.0010428	1.725	99.19	638.8
2.0	119.62	0.0010600	0.9018	119.94	646.3
3.0	132.88	0.0010726	0.6169	133.4	650.7
4.0	142.92	0.0010829	0.4709	143.7	653.9
5.0	151.11	0.0010918	0.3817	152.1	656.3
6.0	158.08	0.0010996	0.3214	159.3	658.3
7.0	164.17	0.0011071	0.2776	165.7	659.9
8.0	169.61	0.0011139	0.2448	171.4	661.2
9.0	174.53	0.0011202	0.2189	176.5	662.3
10	179.04	0.0011262	0.1980	181.3	663.3
11	183.20	0.0011319	0.1808	185.7	664.1
12	187.08	0.0011373	0.1663	189.8	664.9
13	190.71	0.0011426	0.1540	193.6	665.6
14	194.13	0.0011476	0.1434	197.3	666.2
15	197.36	0.0011525	0.1342	200.7	666.7
16	200.43	0.0011572	0.1261	204.0	667.1
17	203.35	0.0011618	0.1189	207.2	667.5

* Here and further, absolute pressure.

[continuation of table IV-1]

18	206.14	0.0011662	0.1125	210.2	667.8
19	208.81	0.0011706	0.1067	213.1	618.2
20	211.38	0.0011749	0.1015	215.9	668.5
22	216.23	0.0011833	0.09245	221.2	668.9
24	220.75	0.0011914	0.08486	226.2	669.2
26	224.99	0.0011992	0.07838	230.9	669.4
28	228.98	0.0012067	0.07282	235.4	669.5
30	232.76	0.0012142	0.06797	239.6	669.6
32	236.35	0.0012215	0.06370	243.7	669.6
34	239.77	0.0012286	0.05995	247.6	669.5
35	241.42	0.0012321	0.05819	249.5	669.5
36	243.04	0.0012356	0.05654	251.3	669.4
38	246.17	0.0012425	0.05352	254.9	669.2
40	249.18	0.0012493	0.05077	258.4	669.0
42	252.07	0.0012561	0.04829	261.8	668.8
44	254.87	0.0012628	0.04601	265.0	668.5
46	257.56	0.0012694	0.04394	268.2	668.2
48	260.17	0.0012759	0.04203	271.3	667.9
50	262.70	0.0012825	0.04026	274.3	667.5
55	268.69	0.0012986	0.03639	281.5	666.6
60	274.29	0.0013147	0.03313	288.3	665.4
65	279.54	0.0013308	0.03036	294.8	664.0
70	284.48	0.0013466	0.02798	301.0	662.6
75	289.17	0.0013626	0.02569	307.0	661.0
80	293.62	0.0013787	0.02405	312.8	659.3
85	297.86	0.0013950	0.02243	318.4	657.6
90	301.92	0.0014115	0.02086	323.8	655.7
95	305.80	0.0014282	0.01965	329.1	653.8
100	309.53	0.0014453	0.01846	334.2	651.7
110	316.58	0.001480	0.01638	344.2	647.2
120	323.15	0.001517	0.01463	353.9	642.5
130	329.30	0.001557	0.01313	363.4	637.2
140	335.09	0.001600	0.01182	372.7	631.7
150	340.58	0.001644	0.01066	381.9	625.6
160	345.74	0.001693	0.009625	391.1	618.9
170	350.66	0.001748	0.008681	400.4	611.5
180	355.35	0.001812	0.007803	410.1	602.8
190	359.82	0.001890	0.00697	420.4	593.0
200	364.08	0.001967	0.00618	431.3	581.4
210	368.16	0.00213	0.00535	444.5	565.9
220	372.1	0.00238	0.00436	463.0	542.3
224	373.6	0.00267	0.00373	479.0	520.7
225.65	374.15	0.00326	0.00326	—	—

*Here and further on, pressure is absolute

Main Equations for Calculating Heat Engineering Equipment

Steam Turbines

1. Power on generator terminals

$$N = \frac{D_0 H_0}{860} \eta_{oe} \eta_r \eta_p \quad \text{kW}$$

where D_0 -- quantity of steam fed into turbine, kg/h;

H_0 -- adiabatic drop in heat, kcal/kg;

η_{oe} -- relative effective efficiency ($\eta_{oe} = 0.7-0.8$ with $N=1000-6000$ kW; $\eta_{oe} = 0.82-0.85$ with $N=12,000-50,000$ kW);

η_r -- efficiency of generator ($\eta_r = 0.93-0.95$ with $N=750-6000$ kW; $\eta_r = 0.96-0.97$ with $N=12,000-25,000$ kW);

η_p -- efficiency of reducer (≈ 0.98).

2. Specific consumption of steam

$$d_s = \frac{D_0}{N} = \frac{860}{H_0 \eta_{oe} \eta_r \eta_p} \quad \text{kg/(kW x h)}$$

Steam Boilers

1. Hourly consumption of fuel

$$B = \frac{D (i_s - i_n)}{Q_p^H \eta_k} \quad \text{kg/h}$$

where D -- steam productivity of boiler unit, kg/h;

i_n and i_s -- enthalpy of feed water and steam generated in boiler, kcal/kg;

Q_p^H -- lowest calorific value of fuel (according to working mass), kcal/kg;

η_k -- efficiency of boiler unit,

2. Intensity of continuous blowing through of boiler (in percents of steam-output of boiler)

$$P = \frac{a_s - a_n}{a_{kp} - a_s} \cdot 100\%$$

where a_s -- content of salts (or silicon compounds) in feed water, mg/l, or alkalinity of feed water, mg-equi/l;

a_n and a_{kp} -- the same for saturated steam and for boiler water (from calculated norms).

Smokestacks

1. Quantity of natural draft of pipe

$$h_s = H \left(\rho_a \frac{273}{t_a + 273} - \rho_r \frac{273}{t_r + 273} \right) \quad \text{mm. wat. col.}$$

where H--height of smokestack, m;

ρ_a and ρ_r --specific weight of air and exhaust flue gases, kg-f/m³;
 t_a and t_r --temperature of external air and exhaust flue gases, °C.

With $t_a = 20^\circ\text{C}$, $\rho_a = 1.2 \text{ kg-f/m}^3$ and average value of $\rho_r = 1.34 \text{ kg-f/m}^3$, the presented equation adopts the following appearance:

$$h_s = H \left(1.2 - \frac{365}{273 + t_r} \right) \quad \text{mm wat. col.}$$

If t_r is 180°C , we obtain the following values of h_s :

H, m	h_s mm wat. col.	H, m	h_s mm wat. col.
40	15.7	100	39.4
60	23.6	120	47.5
80	31.5		

2. Cooling of flue gases in the pipe (for 1 m of pipe height)

$$\Delta t = \frac{A}{\sqrt{D}} \quad \text{deg/m}$$

where A--coefficient which has the following values:

for steel unlined pipes	2
for steel lined pipes	0.8
for brick pipes with average thickness of laying $\leq 0.5 \text{ m}$	0.4
the same, with average thickness of laying $> 0.5 \text{ m}$	0.2

D--total steam output of boilers connected to pipe, T/h.

3. Rate of gas output from pipe w (in m/s) is:

in the case of natural draft	
with least consumption of gases	4
with calculated consumption of gases	6-10
in the case of artificial draft	10-20

TABLE IV-2. ENTHALPY OF SUPERHEATED WATER VAPOR

Pressure atm.	Temperature, °C																				Pressure atm.		
	200	220	240	260	280	300	320	340	360	380	400	420	440	460	480	500	550	600	700	800		1000	
5	681.7	691.7	701.6	711.5	721.5	731.4	741.4	751.4	761.4	771.4	781.5	791.5	801.7	811.7	821.9	832.1	854.0	884.1	917.5	952.7	1049.5	1107.0	5
6	680.6	690.7	700.7	710.7	720.7	730.7	740.8	750.9	760.9	771.0	781.1	791.1	801.3	811.5	821.7	831.9	857.8	894.0	937.4	982.6	1049.4	1107.0	6
7	679.4	689.7	699.8	709.9	720.0	730.1	740.2	750.3	760.3	770.5	780.6	790.8	801.0	811.2	821.4	831.7	857.8	893.8	937.3	982.5	1049.3	1107.0	7
8	678.2	688.7	698.9	709.2	719.4	729.6	739.8	749.9	760.0	770.1	780.3	790.5	800.6	810.8	821.0	831.4	857.2	893.4	937.1	982.3	1049.1	1107.0	8
9	677.0	687.5	697.8	708.1	718.3	728.5	738.7	748.8	758.9	769.0	779.1	789.3	800.3	810.5	820.8	831.2	857.2	893.4	936.9	982.2	1049.0	1107.0	9
10	675.8	686.3	696.7	707.0	717.2	727.4	737.6	747.7	757.8	767.9	778.0	788.1	798.2	808.3	818.5	828.8	854.9	891.2	935.8	981.2	1048.0	1107.0	10
11	674.6	685.1	695.5	705.8	716.0	726.2	736.4	746.5	756.6	766.7	776.8	786.9	797.0	807.1	817.3	827.6	853.8	890.1	934.7	980.1	1048.0	1107.0	11
12	673.4	683.9	694.3	704.6	714.8	725.0	735.2	745.3	755.4	765.5	775.6	785.7	795.8	805.9	816.1	826.4	852.6	888.9	933.6	979.0	1048.0	1107.0	12
13	672.2	682.7	693.1	703.4	713.6	723.8	733.9	744.0	754.1	764.2	774.3	784.4	794.5	804.6	814.8	825.1	851.3	887.6	932.3	977.7	1048.0	1107.0	13
14	671.0	681.5	691.9	702.2	712.4	722.6	732.7	742.8	752.9	763.0	773.1	783.2	793.3	803.4	813.6	823.9	850.1	886.4	931.0	976.4	1048.0	1107.0	14
15	669.8	680.3	690.7	701.0	711.2	721.4	731.5	741.6	751.7	761.8	771.9	782.0	792.1	802.2	812.4	822.7	848.9	885.2	929.8	975.2	1048.0	1107.0	15
16	668.6	679.1	689.5	700.0	710.2	720.4	730.5	740.6	750.7	760.8	770.9	781.0	791.1	801.2	811.4	821.7	847.9	884.2	928.8	974.2	1048.0	1107.0	16
17	667.4	677.9	688.3	698.8	709.0	719.2	729.3	739.4	749.5	759.6	769.7	779.8	789.9	800.0	810.2	820.5	846.7	883.0	927.6	973.0	1048.0	1107.0	17
18	666.2	676.7	687.1	697.6	707.8	718.0	728.1	738.2	748.3	758.4	768.5	778.6	788.7	798.8	809.0	819.3	845.5	881.8	926.4	971.8	1048.0	1107.0	18
19	665.0	675.5	685.9	696.4	706.6	716.8	726.9	737.0	747.1	757.2	767.3	777.4	787.5	797.6	807.8	818.1	844.3	880.6	925.2	970.6	1048.0	1107.0	19
20	663.8	674.3	684.7	695.2	705.4	715.6	725.7	735.8	745.9	756.0	766.1	776.2	786.3	796.4	806.6	816.9	843.1	879.4	924.0	969.4	1048.0	1107.0	20
22	661.4	671.9	682.3	692.8	703.0	713.2	723.3	733.4	743.5	753.6	763.7	773.8	783.9	794.0	804.2	814.5	840.7	877.0	921.6	967.0	1048.0	1107.0	22

25	-	-	682.5	685.1	707.4	718.4	729.9	741.4	752.1	763.0	773.4	784.5	795.3	805.9	816.5	827.2	833.0	839.4	845.9	850.7	854.1	1048.1	1105.8	21	
26	-	-	680.1	693.1	705.4	717.1	728.6	740.1	751.2	762.1	773.0	783.8	794.7	805.3	816.0	826.8	833.5	840.4	847.7	850.9	854.3	1047.9	1105.6	26	
28	-	-	677.6	691.1	703.7	715.6	727.3	738.8	750.1	761.2	772.2	783.1	794.0	804.6	815.3	826.1	833.0	840.0	847.3	850.3	853.7	1047.7	1105.5	28	
30	-	-	675.0	688.9	701.9	713.2	724.1	735.7	746.2	756.4	767.4	778.4	789.3	800.1	810.9	821.7	828.6	835.8	843.1	849.9	856.9	1047.6	1105.4	30	
32	-	-	672.4	686.7	699.7	711.1	722.7	734.4	745.9	757.4	768.5	779.5	790.4	801.2	812.0	822.8	829.7	837.0	844.3	851.3	858.5	1047.5	1105.3	32	
34	-	-	669.8	684.5	697.5	708.5	720.5	732.5	744.0	755.5	766.4	777.3	788.2	799.0	809.8	820.6	827.5	834.8	842.1	848.9	856.1	1047.2	1105.1	34	
36	-	-	682.7	696.6	709.6	722.0	734.3	746.0	757.5	768.9	780.1	791.2	802.2	813.2	824.1	835.1	841.9	848.9	855.9	862.8	869.7	1047.0	1104.9	36	
38	-	-	689.3	694.9	708.1	720.7	733.0	744.8	756.4	768.0	779.3	790.5	801.5	812.5	823.5	834.5	841.3	848.3	855.3	862.2	869.1	1046.8	1104.7	38	
40	-	-	678.0	693.4	706.6	719.6	731.9	743.9	755.6	767.2	778.5	789.8	801.0	812.0	823.0	834.0	840.8	847.7	854.7	861.6	868.5	1046.7	1104.6	40	
42	-	-	671.6	687.0	702.5	716.4	728.7	741.2	753.3	765.1	776.8	788.1	799.3	810.5	821.7	832.9	839.7	846.6	853.5	860.4	867.3	1046.5	1104.4	42	
44	-	-	682.7	698.4	712.5	725.8	738.5	750.8	762.8	774.7	786.3	797.7	809.1	820.3	831.5	842.7	849.5	856.4	863.3	870.2	877.1	1046.4	1104.3	44	
46	-	-	671.0	689.0	705.1	719.8	733.1	746.1	758.7	770.9	782.7	794.3	805.9	817.5	829.0	840.5	847.3	854.2	861.1	868.0	874.9	1046.3	1104.2	46	
48	-	-	678.7	697.1	713.0	727.4	741.0	754.1	766.8	779.1	791.1	803.0	814.7	826.5	838.1	849.8	856.6	863.5	870.4	877.3	884.2	1046.2	1104.1	48	
50	-	-	687.0	698.0	705.8	721.5	735.9	748.3	760.3	772.4	784.2	796.0	807.8	819.5	831.2	842.9	849.7	856.6	863.5	870.4	877.3	1046.1	1104.0	50	
52	-	-	677.7	696.0	715.1	730.4	744.8	758.3	771.4	784.2	796.7	809.0	821.3	833.6	845.9	858.2	864.9	871.7	878.5	885.3	892.1	1045.9	1103.8	52	
54	-	-	668.0	688.2	708.0	724.6	738.8	754.1	767.6	780.9	793.8	806.1	818.5	830.8	843.1	855.4	862.1	868.9	875.7	882.5	889.3	1045.8	1103.7	54	
56	-	-	688.2	692.7	711.9	728.3	745.3	758.9	773.7	787.1	800.1	813.5	826.8	839.8	852.8	865.8	872.5	879.3	886.1	892.9	899.7	1045.7	1103.6	56	
58	-	-	642.8	674.4	698.0	718.2	736.1	751.9	766.1	780.4	794.1	808.0	821.8	835.6	849.3	863.0	870.0	877.0	884.0	891.0	898.0	1045.6	1103.5	58	
60	-	-	651.0	681.9	705.6	725.8	742.6	758.3	773.4	787.8	801.6	815.4	829.2	843.0	856.8	870.5	877.5	884.5	891.5	898.5	905.5	1045.5	1103.4	60	
62	-	-	620.3	662.8	691.4	714.3	733.2	750.3	766.3	781.6	796.6	811.6	826.6	841.6	856.6	871.6	878.6	885.6	892.6	899.6	906.6	1045.4	1103.3	62	
64	-	-	638.6	678.0	702.2	723.2	741.8	759.0	775.0	790.0	804.0	818.0	832.0	846.0	860.0	874.0	881.0	888.0	895.0	902.0	909.0	1045.3	1103.2	64	
66	-	-	470.0	623.0	698.1	695.3	718.5	736.1	757.9	789.2	834.8	903.0	968.9	1029.5	1091.2	230									
68	-	-	440.2	525.8	618.0	690.7	692.8	716.1	739.2	784.4	824.1	895.9	961.5	1025.5	1088.1	230									

TABLE IV-3. SPECIFIC VOLUME OF SUPERHEATED WATER VAPOR (in m³/kg)

Pressure atm.	Temperature, °C										
	200	220	240	260	280	300	320	340	360	380	400
5	0.4334	0.4537	0.4736	0.4935	0.5131	0.5327	0.5521	0.5715	0.5908	0.6101	0.6294
6	0.3591	0.3763	0.3932	0.4099	0.4264	0.4428	0.4591	0.4753	0.4915	0.5077	0.5237
7	0.3059	0.3209	0.3356	0.3501	0.3644	0.3785	0.3926	0.4066	0.4206	0.4345	0.4483
8	0.2662	0.2795	0.2925	0.3054	0.3180	0.3305	0.3429	0.3552	0.3674	0.3796	0.3918
9	0.2353	0.2472	0.2589	0.2704	0.2818	0.2930	0.3040	0.3150	0.3260	0.3369	0.3477
10	0.2103	0.2214	0.2321	0.2426	0.2529	0.2630	0.2731	0.2829	0.2929	0.3028	0.3126
11	0.1900	0.2002	0.2100	0.2197	0.2292	0.2386	0.2478	0.2568	0.2658	0.2748	0.2838
12	0.1728	0.1825	0.1918	0.2007	0.2095	0.2181	0.2265	0.2348	0.2432	0.2515	0.2598
13	0.1584	0.1675	0.1762	0.1846	0.1928	0.2008	0.2086	0.2163	0.2241	0.2318	0.2394
14	0.1460	0.1547	0.1629	0.1708	0.1784	0.1859	0.1933	0.2005	0.2077	0.2150	0.2220
15	0.1352	0.1436	0.1513	0.1587	0.1660	0.1731	0.1800	0.1867	0.1936	0.2003	0.2070
16	—	0.1338	0.1411	0.1482	0.1551	0.1618	0.1683	0.1747	0.1811	0.1875	0.1937
17	—	0.1251	0.1322	0.1389	0.1455	0.1519	0.1581	0.1641	0.1701	0.1762	0.1821
18	—	0.1175	0.1242	0.1307	0.1369	0.1430	0.1490	0.1548	0.1605	0.1661	0.1717
19	—	0.1105	0.1172	0.1235	0.1294	0.1352	0.1408	0.1464	0.1518	0.1572	0.1625
20	—	0.1043	0.1108	0.1168	0.1225	0.1281	0.1334	0.1386	0.1438	0.1491	0.1542
22	—	0.0937	0.0998	0.1052	0.1106	0.1158	0.1207	0.1255	0.1303	0.1351	0.1397
24	—	—	0.0905	0.0958	0.1007	0.1055	0.1102	0.1146	0.1190	0.1234	0.1277
26	—	—	0.0826	0.0877	0.0924	0.0968	0.1011	0.1053	0.1095	0.1136	0.1177
28	—	—	0.0758	0.0807	0.0851	0.0894	0.0935	0.0974	0.1012	0.1051	0.1089
30	—	—	0.0699	0.0746	0.0789	0.0829	0.0868	0.0905	0.0942	0.0978	0.1013
32	—	—	0.0646	0.0692	0.0734	0.0773	0.0810	0.0845	0.0880	0.0914	0.0947
34	—	—	0.0600	0.0645	0.0685	0.0723	0.0758	0.0792	0.0825	0.0857	0.0889
36	—	—	—	0.0603	0.0642	0.0678	0.0712	0.0744	0.0776	0.0807	0.0837
38	—	—	—	0.0565	0.0603	0.0638	0.0671	0.0702	0.0732	0.0762	0.0791
40	—	—	—	0.0530	0.0568	0.0602	0.0634	0.0664	0.0693	0.0721	0.0749
45	—	—	—	0.0457	0.0493	0.0526	0.0556	0.0583	0.0609	0.0636	0.0661
50	—	—	—	—	0.0433	0.0465	0.0493	0.0519	0.0543	0.0567	0.0590
60	—	—	—	—	0.0340	0.0371	0.0398	0.0421	0.0443	0.0464	0.0484
70	—	—	—	—	—	0.0303	0.0329	0.0351	0.0371	0.0390	0.0408
80	—	—	—	—	—	0.0250	0.0276	0.0298	0.0317	0.0335	0.0351
90	—	—	—	—	—	—	0.0234	0.0255	0.0274	0.0291	0.0307
100	—	—	—	—	—	—	0.0199	0.0221	0.0240	0.0256	0.0271
120	—	—	—	—	—	—	—	0.0168	0.0187	0.0202	0.0217
140	—	—	—	—	—	—	—	0.0125	0.0147	0.0163	0.0177
160	—	—	—	—	—	—	—	—	0.0115	0.0133	0.0147
180	—	—	—	—	—	—	—	—	0.0086	0.0108	0.0123
200	—	—	—	—	—	—	—	—	—	0.0087	0.0103
250	—	—	—	—	—	—	—	—	—	0.0023	0.0064
300	—	—	—	—	—	—	—	—	—	0.0019	0.0031

Temperature, °C

Pressure,
atm.

420	440	460	480	500	550	600	700	800	900	1000	
0.6485	0.6676	0.6867	0.7058	0.7248	0.7724	0.8198	0.9144	1.0088	1.1032	1.1976	5
0.5398	0.5558	0.5717	0.5876	0.6036	0.6432	0.6829	0.7818	0.8407	0.9192	0.9977	6
0.4621	0.4759	0.4896	0.5033	0.5169	0.5510	0.5851	0.6528	0.7204	0.7878	0.8552	7
0.4039	0.4159	0.4280	0.4400	0.4519	0.4819	0.5117	0.5711	0.6303	0.6894	0.7483	8
0.3586	0.3693	0.3800	0.3907	0.4014	0.4280	0.4546	0.5074	0.5601	0.6127	0.6651	9
0.3223	0.3320	0.3417	0.3513	0.3609	0.3851	0.4088	0.4565	0.5040	0.5513	0.5985	10
0.2927	0.3015	0.3103	0.3191	0.3279	0.3499	0.3716	0.4149	0.4581	0.5012	0.5441	11
0.2679	0.2761	0.2842	0.2922	0.3003	0.3205	0.3405	0.3802	0.4198	0.4593	0.4987	12
0.2470	0.2546	0.2621	0.2696	0.2770	0.2956	0.3141	0.3509	0.3875	0.4239	0.4603	13
0.2291	0.2361	0.2431	0.2501	0.2570	0.2744	0.2915	0.3257	0.3597	0.3936	0.4274	14
0.2136	0.2201	0.2267	0.2332	0.2397	0.2559	0.2720	0.3039	0.3356	0.3673	0.3989	15
0.2009	0.2062	0.2123	0.2184	0.2245	0.2398	0.2548	0.2848	0.3146	0.3443	0.3739	16
0.1889	0.1938	0.1996	0.2054	0.2112	0.2255	0.2398	0.2680	0.2961	0.3240	0.3519	17
0.1773	0.1829	0.1884	0.1938	0.1992	0.2129	0.2264	0.2529	0.2796	0.3059	0.3322	18
0.1678	0.1730	0.1783	0.1835	0.1885	0.2016	0.2143	0.2397	0.2648	0.2898	0.3148	19
0.1592	0.1642	0.1692	0.1741	0.1790	0.1913	0.2035	0.2276	0.2515	0.2753	0.2990	20
0.1444	0.1490	0.1535	0.1580	0.1625	0.1739	0.1848	0.2068	0.2285	0.2502	0.2718	22
0.1329	0.1383	0.1404	0.1446	0.1487	0.1591	0.1692	0.1894	0.2094	0.2293	0.2491	24
0.1217	0.1256	0.1295	0.1333	0.1371	0.1467	0.1561	0.1748	0.1932	0.2116	0.2299	26
0.1126	0.1164	0.1200	0.1235	0.1270	0.1360	0.1448	0.1622	0.1794	0.1965	0.2135	28
0.1048	0.1084	0.1118	0.1151	0.1185	0.1269	0.1350	0.1512	0.1673	0.1833	0.1992	30
0.0980	0.1014	0.1046	0.1077	0.1108	0.1187	0.1264	0.1417	0.1568	0.1719	0.1867	32
0.0929	0.0951	0.0981	0.1012	0.1041	0.1117	0.1189	0.1333	0.1475	0.1616	0.1756	34
0.0887	0.0898	0.0925	0.0954	0.0982	0.1053	0.1122	0.1258	0.1393	0.1526	0.1659	36
0.0819	0.0847	0.0875	0.0902	0.0929	0.0996	0.1062	0.1191	0.1319	0.1446	0.1571	38
0.0776	0.0803	0.0829	0.0855	0.0882	0.0945	0.1008	0.1131	0.1252	0.1373	0.1493	40
0.0686	0.0710	0.0734	0.0757	0.0780	0.0838	0.0894	0.1004	0.1112	0.1220	0.1326	45
0.0613	0.0635	0.0657	0.0679	0.0700	0.0752	0.0803	0.0902	0.1000	0.1097	0.1193	50
0.0505	0.0523	0.0542	0.0560	0.0578	0.0623	0.0666	0.0749	0.0832	0.0913	0.0993	60
0.0428	0.0443	0.0460	0.0476	0.0492	0.0530	0.0568	0.0640	0.0711	0.0781	0.0851	70
0.0367	0.0383	0.0398	0.0412	0.0426	0.0461	0.0494	0.0559	0.0621	0.0683	0.0744	80
0.0322	0.0336	0.0350	0.0363	0.0376	0.0407	0.0437	0.0495	0.0551	0.0606	0.0660	90
0.0285	0.0298	0.0311	0.0323	0.0335	0.0364	0.0392	0.0444	0.0495	0.0545	0.0594	100
0.0229	0.0241	0.0253	0.0263	0.0274	0.0299	0.0323	0.0368	0.0411	0.0453	0.0494	120
0.0189	0.0200	0.0211	0.0221	0.0230	0.0253	0.0274	0.0313	0.0351	0.0387	0.0423	140
0.0159	0.0170	0.0179	0.0189	0.0197	0.0218	0.0237	0.0272	0.0306	0.0338	0.0369	160
0.0135	0.0145	0.0155	0.0164	0.0172	0.0191	0.0208	0.0240	0.0271	0.0299	0.0328	180
0.0115	0.0126	0.0135	0.0144	0.0151	0.0169	0.0185	0.0215	0.0242	0.0269	0.0294	200
0.0079	0.0090	0.0099	0.0107	0.0114	0.0130	0.0144	0.0169	0.0192	0.0214	0.0234	250
0.0052	0.0065	0.0074	0.0082	0.0089	0.0104	0.0117	0.0139	0.0158	0.0177	0.0195	300

Reduction-Cooling Units (RCU)

1. Consumption of cooling water:

$$B = \frac{D_1 (i_1 - i_2)}{\phi i_1 + (1 - \phi) q_2 - t_2} \quad \text{kg/h}$$

or

$$B = \frac{D_2 (i_1 - i_2)}{\phi i_1 + (1 - \phi) q_2 - t_2} \quad \text{kg/h}$$

where D_1 and D_2 --quantity of steam before and after RCU, kg/h;
 i_1 and i_2 --enthalpy of steam before and after RCU, kcal/kg;
 q_2 --enthalpy of liquid at vapor pressure after RCU, kcal/kg;
 t_2 --temperature of cooling water, °C;
 ϕ --coefficient which takes into consideration the percentage of evaporating water (0.65).

2. Consumption of steam before RCU

$$D_1 = D_2 - \phi B \quad \text{kg/h}$$

3. 3. Minimum area of passage section of RCU mixing pipe

$$F = \frac{D}{0.0752\mu} \sqrt{\frac{p_1}{v_1}} \quad \text{cm}^2$$

where D --maximum steam consumption, T/h;
 μ --consumption coefficient (0.85);
 p_1 --vapor pressure before mixing pipe, atm.;
 v_1 --specific volume of vapor before mixing pipe, m³/kg.

Diameter of passage section

$$d = \sqrt{\frac{F}{0.785}} \quad \text{cm}$$

4. Diameter of opening in restraining diaphragm with $\frac{p_2}{p_1} < 0.577$ is determined from the formula:

$$D = 72 \frac{\pi d^2}{4} \sqrt{\frac{p_1}{v_1}} = 56.5 d^2 \sqrt{\frac{p_1}{v_1}} \quad \text{kg/h}$$

where d --diameter of opening, cm;
 D --quantity of transmitted steam, kg/h;

p_1 and p_2 --vapor pressure before and after RCU, atm;
 v_1 --specific volume of steam before RCU with p_1 and t_1 , m³/kg.

Quality Indicators of Water

Hardness--measure of the content in the water of Ca and Mg salts dissolved in it.

Constant (noncarbonate) hardness H_n is governed by the presence in the water of sulfates and chlorides of Ca and Mg (CaSO_4 , MgSO_4 , CaCl_2 , MgCl).

Temporary (carbonate) hardness H_{bp} is governed by the content in the water of bicarbonates $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$.

The total hardness H_o

$$H_o = H_n + H_{bp}$$

The hardness of water is expressed in mg-equi/l. In practice, degrees of hardness (°) are used and they are interlinked by the following correlations:

	Degree			mg-equi/l
	German	British	French	0.3566
	British			0.2848
	French			0.1998
	American			0.0199
	Degree			
1 mg-equi/l	German	British	French	American
	2.8	3.5	5.0	50

The alkalinity is expressed in mg-equi/l.

A_k --carbonate alkalinity governed by the presence in water of CO_3^{2-} anions;

A_r --hydrate alkalinity governed by the presence in the water of OH^- anions;

A_g --bicarbonate alkalinity governed by the presence in water of HCO_3^- anions.

Natural waters mainly contain HCO_3^- , therefore usually $A_g = A_k$.

Important indicators of water quality are the sum of metal oxides (ΣM , mg-equi/l) and the sum of acid residues (ΣK , mg-equi/l):

$$\Sigma M = \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{R}_2\text{O}_3$$

where $\text{R}_2\text{O}_3 = \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$.

$$\Sigma K = \text{SO}_3 + \text{Cl}_2 + \text{CO}_{2,\text{unb.}} + \text{N}_2\text{O}_3 + \text{SiO}_2$$

A check of the water analyses is made based on the condition

$$\Sigma M = \Sigma K$$

Mineral residue (mg/l)

$$S_{\text{unb.}} = \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{R}_2\text{O}_3 + \text{SO}_3 + \text{Cl}_2 + \text{CO}_{2,\text{unb.}} + \text{N}_2\text{O}_3 + \text{SiO}_2$$

$$S_{\text{unb.}} = a - b$$

(where a--dry residue; b--losses in calcination).

The mineral residue can be defined from the formula:

$$S_{\text{unb.}} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{Cl}^- + \text{SO}_3^{2-} + \text{NO}_3^- + \text{CO}_3^{2-} + \text{SiO}_2^- + \text{R}_2\text{O}_3$$

Hydrogen indicator pH

with pH = 7	neutral medium
with pH > 7	alkaline medium
with pH < 7	acid medium

Below are the quantities of different admixtures in water (in mg/l), corresponding to 1 mg-equi/l:

Ca ²⁺	20.04	Na ⁺	23.00	HCO ₃ ⁻	61.02
CaO	28.04	Na ₂ O	31.00	CO ₂	22.00
Ca(OH) ₂	37.00	NaOH	40.00	CO ₃ ²⁻	30.00
CaCO ₃	50.00	Na ₂ CO ₃	53.00	SO ₃	40.03
Mg ²⁺	12.16	NaCl	58.45	SO ₄ ²⁻	48.03
MgO	20.16	Cl ⁻	35.46	SiO ₂	30.03
Mg(OH) ₂	29.17	HCl	36.46	SiO ₃ ²⁻	38.03
MgCO ₃	42.16	H ₂ SO ₄	49.00	R ₂ O ₃	26.60

Information on Boiler-Turbine Units

TABLE IV-4. CHARACTERISTICS OF STEAM TURBINES WITH COUNTERPRESSURE OF THE KALUGA TURBINE PLANT

1 Мощность кВт	2 Тип турбины и обозначение	3 Параметры острого пара		6 Номиналь- ное противо- давление и пределы регулиру- вания атм	7 Температура при номиналь- ном противо- давлении, °С	8 Номиналь- ный расход пара (в т/ч) при режимах		11 Вес, т		
		4 давление атм	5 температура, °С			9 без отбора	10 с от- бором	12 турбины с масляной системой	13 роtores тур- бины	14 верхней по- ловой кор- пуса
15 Турбины без промежуточного отбора пара										
12 000	R-12-90/31	90	535	31 (29-33)	401	189	—	20.7	2.3	4.3
	R-12-90/18	90	535	18 (15-21)	340	131	—	22.0	2.5	4.5
	R-12-90/13	90	535	13 (10-16)	305	113	—	22.0	2.5	4.5
	R-12-90/7	90	535	7 (5-9)	245	87	—	24.8	3.0	7.5
	R-12-35/5	35	435	5 (4-7)	224	114.7	—	25.0	3.0	7.0
6 000	R-6-35/11	35	435	11 (8-13)	301	93.5	—	17.5	1.8	6.0
	R-6-35/10	35	435	10 (8-13)	293	87.7	—	17.5	1.8	6.0
	R-6-35/8	35	435	8 (4-7)	244	66.6	—	17.5	2.1	5.6
	R-6-35/5	35	435	5 (4-7)	226	60.0	—	17.5	2.1	5.6
	R-6-35/3	35	435	3 (2-4)	186	50.5	—	17.5	2.1	5.6
4 000	R-4-35/15	35	435	15 (13-17)	339	85.4	—	15.4	1.6	6.0
	R-4-35/11	35	435	11 (8-13)	308	65.0	—	15.2	1.6	5.0
	R-4-35/8	35	435	8 (4-7)	247	44.8	—	15.0	2.0	5.5
	R-4-35/3	35	435	3 (2-4)	192	35.6	—	16.4	1.9	5.5
2 500	R-2.5-35/15	35	435	15 (13-17)	342	56.3	—	15.4	1.6	6.0
	R-2.5-35/11	35	435	11 (8-13)	307	41.9	—	15.2	1.6	5.0
	R-2.5-35/8	35	435	8 (4-7)	250	29.2	—	16.0	1.9	5.5
	R-2.5-35/3	35	435	3 (2-4)	200	22.6	—	16.0	1.9	5.5
1 500	R-1.5-35/15	35	435	15 (13-17)	345	35.5	—	14.7	1.5	5.0
	R-1.5-35/11	35	435	11 (8-13)	313	26.6	—	15.0	1.6	5.0
2 500	R-2.5-15/8	15	350	8 (4-7)	256	63.0	—	15.4	1.6	6.0
	R-2.5-15/3	15	350	3 (2-4)	193	34.3	—	17.5	1.9	5.3
1 500	R-1.5-15/8	15	350	8 (4-7)	260	35.2	—	14.0	1.6	5.2
	R-1.5-15/3	15	350	3 (2-4)	190	21.8	—	16.0	1.9	5.5
16 Турбины с промежуточным отбором пара										
12 000	PT-12-90 (15) 7	90	535	7 (5-9)	268	101.0	117.0	32.0	3.2	7.0
6 000	PT-6-35 (15) 5	35	435	5 (4-7)	235	62.6	84.5	19.3	2.2	7.0
	PT-6-35 (10) 5	35	435	5 (4-7)	243	63.6	80.5	19.3	2.2	7.0
	PT-6-35 (10) 1.2	35	435	1.2 (0.7-2.5)	180	41.5	68.8	20.5	2.6	7.0
	PT-6-35 (8) 1.2	35	435	1.2 (0.7-2.5)	180	41.5	55.2	20.5	2.6	7.0

Key:

1. Power, kW
2. Type of turbine and designation
3. Parameters of live steam
4. Pressure, atm.
5. Temperature, °C
6. Rated counterpressure and limits of rebgulation, atm.
7. Temperature with rated counterpressure, °C
8. Rated steam consumption (in T/h) with regimes
9. Without bleeding
10. With bleeding

11. Weight, T
12. Turbine with oil system
13. Turbine rotor
14. Upper half of housing
15. Turbines without intermediate steam bleeding
16. Turbines with intermediate steam bleeding

Note: 1. Absolute pressure.
 2. Height of arrangement of grapple above machine hall floor is 4 m for turbines without intermediate steam bleeding and 4.5 m for turbines with intermediate steam bleeding.
 3. Below are the characteristics for controllable bleeding for turbines with intermediate steam bleeding:

Type of turbine	Rated pressure and limits of regulation, atm.	Temperature with rated pressure, °C	Rated production bleeding, T/h
PR-12-90(15)7	15(12-18)	325	75
PR-6-35(15)5	15(13-17)	300	35
PR-6-35(10)5	10(8-13)	298	50
PR-6-35(10)1.2	10(8-13)	299	50
PR-6-35(5)1.2	5(4-7)	237	40

Below are the requirements for the quality of the feed water for evaporators and steam-formers:

Hardness, mg-equi/kg	0.03
Hardness with softening of highly-mineralized waters (salt content over 200 mg/kg), mg-equi/kg	0.075
Content, mg/kg of oxygen	0.03
of phosphates*	5-7

Below are the calculated norms for the quality of intra-boiler water for different types of boilers and intraboiler devices at different pressures:¹

Boiler	Maximum permissible content, mg/kg		Alkaline number mg/kh
	dry residue	sludge	
	at 15 atm. and lower		
Flue	10,000-20,000	6,000-8,000	500-1000
Fire-tube	4,000-6,000	4,000-6,000	300-700
Water-tube with lower drums and sludge pans	4,000-6,000	5,000-25,000	300-700
Water-tube without lower drums and sludge pans	2,500-3,000	1,500-2,500	300-500
Without stepped evaporation and bubbling washing of steam	2,000-2,500	-	300-400

* Phosphating is necessary with absolute pressure of secondary steam of 8 atm.

Boiler

	Maximum permissible content mg/kg		
	dry residue	dry residue	silicic acid (in conversion for SiO_3^{2-})
	At 15-45 atm		At 45-100 atm.
Without stepped evaporation and bubbling washing of steam	500-3000	300-1000	2-5
The same, but with bubbling washing of steam by feed water of normed quality	-	1500	40
With stepped evaporation (intradrum or extension sections engaged in parallel to drum in pairs), but without bubbling washing of steam	4000-6000	4000	20
With stepped evaporation (intradrum salt compartments) and with bubbling washing of steam by feed water of normed quality	-	5000	80
With stepped evaporation and bubbling washing of steam by feed water of normed quality with pre-included extension compartments II and III of evaporation stages	10,000-15,000	10,000	150

Note: For steam with pressure 15-45 atm. and 45-100 atm., the smaller numbers refer to boilers with one drum, up to 1300 mm in diameter and with purely volumetric separation, and the larger numbers refer to boilers with diameter of the drum over 1300 mm and to boilers with separating drum.

TABLE IV-5. CHARACTERISTICS OF STEAM CONDENSATION TURBINES OF KALUGA TURBINE PLANT

1 Тип турбины и обозначение	2 Мощность, кВт	3 Вакум, %	4 Температура пита- тельной воды, °C	5 Номиналь- ный регули- руемый отбор			6 Номинальный рас- ход пара (в т/ч) при режимах				7 Охла- ждающая вода		8 Вес, т		
				6 давление, ат	7 температура, °C	8 расход пара т/ч	9 с отбором	10 с конденс- ацией	11 с конденса- цией с охл. без регенерации	12 температура, °C	13 полный расход, м ³ /ч	14 турбины с мас- ляной системой	15 ротора турбины	16 наиболее тяже- лого узла тур- бины	
20 Турбины с двумя промежуточными отборами пара															
PT-12-35/10	12 000	91	150	10	295	50	108.84	58.5	53.2	20	2100	39.0	5.68	11.5	
PT-12-35/13T	12 000	86	150	1.2	108	40	112.0	59.8	54.3	40	3800	39.3	5.70	14.5	
				1.2	124	40									
21 Турбины с производственным отбором пара															
P6- 5/5	6 000	95	150	5	230	40	55.8	28.2	26.0	20	1970	31.5	4.93	10.0	
p-4-35/5	4 000	93	150	5	235	25	35.7	19.9	18.5	20	900	28.0	4.17	7.0	
P2,5-35/5	2 500	95	150	5	240	18	26.2	13.1	12.0	20	870	22.5	3.25	5.5	
22 Турбины с теплофикационным отбором пара															
T12-35/1.2	12 000	—	150	1.2	105	45	78.0	53.8	50.3	—	—	—	—	—	
T-6-35/1.2	6 000	95	150	1.2	120	35	40.7	27.6	25.3	20	1970	31.5	4.94	10.0	
AT-4 (old)	4 000	95	146	1.2	120	22	—	—	—	—	—	—	—	—	
23 Турбины без отбора пара															
K-12-35	12 000	95	152	—	—	—	—	53.2	48.0	20	3460	39.7	6.96	14.0	
K-12-35T	12 000	87	145	—	—	—	—	58.0	52.5	35	3800	31.3	5.02	7.6	
K-6-35T	6 000	89	147	—	—	—	—	30.7	—	35	1970	30.5	5.00	10.0	
K-6-35	6 000	95	146	—	—	—	—	27.2	25.0	20	1970	30.0	4.85	10.0	
AK-44 (old)	4 000	90	—	—	—	—	—	19.36	18.4	30	1300	19.0	3.68	8.0	

Key:

1. Type of turbine and designation
2. Power, kW
3. Vacuum, %
4. Temperature of feed water, °C
5. Rated controllable bleeding
6. Pressure, atm.
7. Temperature, °C
8. Consumption of steam, T/h
9. Rated consumption of steam (in T/h) with regimes
10. With bleeding
11. Condensation
12. Condensation without regeneration
13. Cooling water
14. Temperature, °C
15. Complete consumption, m³/h
16. Weight, T
17. Turbine with oil system
18. Turbine rotor
19. Heaviest turbine assembly
20. Turbines with two intermediate steam bleedings
21. Turbines with production steam bleeding

22. Turbines with central heating bleeding of steam
 23. Turbines without steam bleeding

Note: 1. Absolute pressure.

2. The pressure of the steam fed to the turbine is 35 atm., temperature 435°C; the rate of turbine rotor rotation is 3000 rpm.

3. Height of arrangement of crane grapple above machine hall floor is 4.5 m (for turbine P-2.5-35/5 it equals 4 m).

TABLE IV-6. CONSUMPTION OF COOLING WATER BY STEAM-TURBINE UNITS OF POWER PLANT (in m³/h)

(1) Потребители охлаждающей воды	(2) Для турбин среднего давления мощностью (в тыс. квт)							
	1,5	2,5	4	6	12	25	50	100
Конденсаторы(3)	330— 650 (20)	770— 1000 (20)	900— 1400 (20)	1800— 2000 (20)	2100— 3500 (20)	4500— 5500 (15—25)	11 000— 13 000 (15)	20 000— 26 000 (15)
Воздухоохладители(4) генераторов	20	60	60	80	100	300	275	450—600
Маслоохладители(5)	40	40	40	40	40	60—100	120—150	180—300
(6) Всего	390— 710	870— 1100	1000— 1500	1920— 2120	2240— 3640	4860— 5900	11 395— 13 425	20 630— 26 900

(1) Потребители охлаждающей воды	(7) Для турбин высокого давления мощностью (в тыс. квт)		
	25	50	100
Конденсаторы(3)	4000—5000 (20)	7000—10 000 (20)	16 000—20 000 (20)
Газоохладители генераторов(8)	200	200	400
Маслоохладители(5)	60—80	120—140	180—200
(6) Всего	4260—5280	7320—10 340	16 580—20 600

Key:

1. Consumers of cooling water
2. For turbines of medium pressure with output (in thousand kW)
3. Condensers
4. Air-coolers of generators
5. Oil-coolers
6. Total
7. For turbines of high pressure with output (in thousand kW)
8. Gas coolers of generators

Note: The temperature of cooling water is given in°C in parentheses.

TABLE IV-7. REQUIREMENTS FOR QUALITY OF FEED WATER FOR STEAM BOILERS OF HEAT AND ELECTRIC POWER PLANT

(1) Показатели	(2) Барбанные котлы под давлением, ат			(5) Прямоточные котлы	(6) Прямоточные сепараторные котлы при давлении 40 ат
	(3) менее 40	40-100	(4) более 100		
(7) Жесткость, мг-экв/кг	0.015	0.01	0.005	0.003	0.01
(8) Содержание, мг/кг					
(9) кислорода	0.03	0.02	0.01	0.01	0.03
(10) железа	0.07	0.035	0.02	0.02	0.1
(11) меди	0.04*	0.02	0.01	0.01(18)	0.05(18)
(12) масла	3	1	0.5	Следы	Следы
(13) кремниевой кислоты в пересчете на SiO ₂ ⁻	-	2*	1-0.2*	0.02	-
(14) избытка сульфита (при сульфитировании)		(19) Менее двух		(18) Следы	-
(15) свободной угольной кислоты	0	0	0	<0.02	-
(16) нитритов и нитратов (в сумме)	-	-	<0.02	<0.02	-
(17) солей	500*	250*	100-50*	0.05	400

Key:

1. Indicators
2. Drum boilers under pressure, atm.
3. less than
4. more than
5. Direct-flow boilers
6. Direct-flow separator boilers at 40 atm. pressure
7. Hardness, mg-equi/kg
8. Content, mg/kg
9. Oxygen
10. Iron
11. Copper
12. Oil
13. Salicylic acid in conversion for SiO₂⁻
14. Surplus of sulfite (in sulfiteization)
15. Free carbon dioxide
16. Nitrites and nitrates (in sum)
17. Salts
18. Traces
19. Less than two

Note: 1. The hydrogen indicator pH must be 7.0-8.5
 2. The norms are taken from the "Rules of Technical Operation of Power Plants and Networks." The numbers marked by an asterisk are taken from the "Reference Book of the Chemical Power Engineer." For direct-flow separator boilers, the norms are given which are recommended by the Moscow division of the Central Boiler-Turbine Institute).

TABLE IV-8. REQUIREMENTS FOR QUALITY OF STEAM GENERATED BY TETS STEAM BOILERS

Admixtures	Content of admixtures in steam (in mg/kg) for boilers with pressure		
	40 atm.	40-100 atm.	100 atm.
Compounds of sodium (in conversion for Na_2SO_4)	0.3	0.2	0.08
Silicic acid (in conversion for SiO_3^{2-})	-	0.03*	0.03
Free carbon dioxide	20	10	7

*For boilers with pressure 70 atm. and higher.

TABLE IV-9. HEAT RELEASE IN MACHINE HALL OF LOW POWER TETS (FOR 1 TURBINE UNIT) (IN THOUS. kcal/h).

(1)	(2)	(3)	(4)	(5)	(1)	(2)	(3)	(4)	(5)
Мощность турбины кВт	Тип турбины	В турбинном зале	В деаэрационной	Всего	Мощность турбины кВт	Тип турбины	В турбинном зале	В деаэрационной	Всего
1500	(6) Конденсационная с отбором пара	115	55	170	6 000	P-6-35	270	103	373
					12 000	K-12-35/1	318	110	428
					12 000	T-12-35/1	428	172	600
					12 000	T-12-35/1	458	172	630
2500	K-2,5-35	145	68	213	12 000	P, T-12-35/1	491	172	663
2500	T-2,5-35	155	65	220	12 000	PR-12-35/2	416	147	563
3000	K-3-35	160	73	233					
4000	K-4-35	183	79	262					
4000	T-4-35	207	82	289					

Key:

1. Power of turbine, kW
2. Type of turbine
3. In turbine hall
4. In deaerator
5. Total
6. Condensation with steam bleeding

TABLE IV-10. STEAM LOSSES (MOISTURE RELEASE) IN STEAM TURBINES OF LOW POWER (in kg/h)

(1) Мощность турбины кВт	(2) В конденсационных			(3) В турбинах с отбором		
	(4) от паровых труб	(5) от прочих частей	(6) всего	(4) от паровых труб	(5) от прочих частей	(6) всего
1500	60	94	154	60	118	178
2500	70	110	180	70	144	214
3000	74	118	192	74	158	232
4000	79	131	210	79	175	254
6000	90	150	240	90	210	300

Key:

1. Power of turbine, kW
2. In condensation
3. In turbines with bleed
4. From overflow pipes
5. From other parts
6. Total

2. Electrical Engineering

General Part³⁻⁶

Certain Most Important Physical Constants

Magnetic constant μ_0	$4\pi \times 10^7$ H/m
Electric constant ϵ_0	8.86×10^{-12} F/m
Velocity of light in vacuum c	2.9979×10^8 m/s
Wave resistance of vacuum $\sqrt{\frac{\mu_0}{\epsilon_0}}$	376.7 Ohm
Charge of electron e	1.602×10^{-19} C
Rest mass of proton	1.6724×10^{-24} g
Planck's constant h	6.624×10^{-27} erg/sec
Rest mass of electron	$9.1085 \cdot 10^{-28}$ g

Basic Equations

Ohm's law

$$I = \frac{U}{Z}$$

where I--current, a; U--voltage, V;
Z--resistance, Ohm.

Complete resistance:

$$Z = \sqrt{R^2 + (X_L - X_C)^2}$$

where $R = \rho \frac{l}{s}$ --active resistance;

$X_L = 2\pi fL$ --inductive resistance;

$X_C = \frac{1}{2\pi fC}$ --capacitive resistance;

ρ --specific electrical resistance, Ohm x mm²/m;

l --length of conductor, m;

s --section of conductor, mm²;

f --frequency, number of periods per second;

L --inductance, H;

C --capacitance, f.

The rotation rate of the magnetic flux in the electric motor

stator n_c (in rpm):

$$n_c = \frac{60f}{p}$$

(p --number of pairs of poles of stator winding);

The torque of the electric motor:

$$M = 975 \frac{P}{n}$$

where M --moment, kg-f x m;

P --power, kW;

n --rotation rate, rpm.

Mechanical constant of warm-up time of electric motor:

$$T_w = \frac{CD^2 m}{375M}$$

where CD --Mach moment, kg-f/m².

The sag of the conductor of the line f (in m);

$$f = \frac{l^2 \gamma}{8\sigma}$$

where l --length span between supports, m;

γ --specific load of conductor, kg-f/m x mm²;

σ --mechanical stress in conductor, kg-f/mm².

The number of oscillation periods of the busbars per second

$$n = 112 \sqrt{\frac{EI}{gl}}$$

where ϵ --modulus of elasticity, kg-f/cm² (for copper $\epsilon = 1.25 \times 10^6$, for aluminum of quantity $\epsilon = 0.72 \times 10^6$);

I --moment of inertia of busbars, cm⁴; for flat busbars $I = hb^3/12$ (h and b --sides of section), for round busbars $I = 0.05d^4$ (d --diameter of busbar);

l --length of span, cm;

g --weight, kg-f/cm.

TABLE IV-11. BASIC CHARACTERISTICS OF CURRENT-CONDUCTING METALS AND ALLOYS⁵

Metals and alloys	(1) Плотность г/см ³	(2) Температура плавления °C	(3) Предел прочности при растя- жении кгс/мм ²	(4) Удельное электриче- ское сопро- тивление ом·мм ² /м	(5) Температур- ный коэффициент сопротивле- ния 10 ⁴ ·град ⁻¹	(6) Теплопро- водность вт/см·град	(7) Средняя теплоемкость в интервале температур 0-100 °C кал/г·град	(8) Коэффициент линейного расширения в интервале температур 20-100 °C α·10 ⁶ , град ⁻¹
Aluminum	2.7	657	7.5-18	0.026-0.029	44	2.1	0.21	23
Bronze	8.3-8.9	885-1050	35-135	0.021-0.052	40	0.4-0.8	0.095	17
Tungsten	18.0-19.3	3400	200-400	0.053-0.050	45	0.92-1.88	0.034	43
Cadmium	8.6	321	6	0.076	40	0.093	0.06	31
Constantan	8.7-8.9	1270	40-70	0.45-0.52	0.03-0.05	—	—	0.13
Brass	8.4-8.7	900-960	30-70	0.031-0.079	20	1.09-1.25	0.093	18
Magnesium	1.74	650	20	0.04	38	1.53	0.25	27.6
Manganese	8.1-8.4	960	50-70	0.42-0.50	0.3-0.6	—	0.10	0.19
Copper	8.71-8.94	1083	25-40.9	0.0175-0.018	41	3.93-4.10	0.098	17
Molybdenum	9.7-10.3	2570-2620	80-250	0.048-0.054	49	1.46	0.062	4
Argentan	8.4	1000	35-60	0.30-0.45	2.5-3.6	—	—	0.20
Nickel	8.8-8.9	1452	60-70	0.068-0.072	68	0.58-0.62	0.106	13
Nichrome	8.1-8.25	1370-1420	60-75	1.00-1.27	1.25-1.4	—	—	0.14
Tin	7.3	232	2-5	0.124-0.116	44	0.64	0.054	23
Platinum	21.45	1755-1778	15-35	0.096-0.105	26-40	0.7	0.034	9
Mercury	13.5	-38.5	—	0.943-0.952	90	0.11	0.033	180
Lead	11.35	327	0.98-1.6	0.217-0.227	40	0.34-0.35	0.03	29
Silver	10.5	960	15-30	0.015-0.016	36	4.20-4.22	0.055	19
Steel	7.87	1400-1530	70-175	0.103-0.14	60	0.45-0.48	0.12	10
Antimony	6.67	630	—	0.41	37	0.17	0.05	16.8
Fechral	7.1-7.3	1460-1490	60-70	1.26-1.35	0.55-1.8	—	—	0.14
Chromal	6.95-7.1	1500	70-75	1.45	0.4-0.5	—	—	0.145
Zinc	6.86-7.14	419-428	14-29	0.053-0.062	0.004	1.12	0.06	30
Pig iron	7.2-7.6	1200	12-32	0.5-0.41	0.001	0.49	0.11	10

Key: 1. Density, g/cm³; 2. Melting point, °C; 3. Ultimate strength in stretching, kg-f/mm²; 4. Specific electrical resistance, Ohm x mm²/m; 5. Temperature coefficient of resistance, 10⁴ x deg⁻¹; 6. Heat conductivity, W x cm x deg; 7. Average heat capacity in interval of temperatures 0-100°C cal/g x deg; 8. Coefficient of linear expansion in interval of temperatures 20-100°C α x 10⁶, deg⁻¹.

The coefficient k which takes into consideration the change in the permissible current load on the apparatus and the conductors depending on the heating conditions

$$k = \sqrt{\frac{\theta_a - \theta_p}{\theta_a - \theta_0}}$$

where θ_a -- permissible temperature, °C;

θ_p and θ_0 -- calculated and actual ambient temperature, °C.

The order of highest harmonics generated by the multiple-phase rectification unit on the side of alternating current

$$v = np \pm 1$$

where v -- order of highest harmonics;

n -- whole number (1, 2, 3, 4, etc.);

p -- number of phases of rectification unit.

The amount of currents of the highest harmonics of the rectification unit

$$I_v = \frac{I}{v}$$

where I -- quantity of current of first (main) harmonics;

I_v -- quantity of current of highest harmonics.

TABLE IV-12. CHARACTERISTICS OF SEMICONDUCTOR MATERIALS

Main parameters	Copper-oxide	Selenium	Germanium	Silicon
Current density, a/cm ² with cooling				
natural	0.04	0.07	40	80
artificial	0.14	0.20	100	200
Inverse voltage (effective), V	6	25	110	380
Maximum working temperature, °C	50	85	65	140
Efficiency, %	78	92	98.5	99.6
Comparative volume of elements	30	15	3	1
Inner drop in voltage, V	0.2	0.6	0.5	0.7

Calculation of Loads

The maximum required power P_n (in kW) is determined from the

TABLE IV-13. SPECIFIC ELECTRICAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF ELECTROLYTES AT 18°C $10^4 \text{ Ohm}^{-1} \times \text{cm}^{-1}$

Содержание безводного электролита %	KCl	NaCl	NH ₄ Cl	ZnSO ₄	CuSO ₄	KOH	NaOH	H ₂ SO ₄	HCl
5	690	672	918	191	189	—	1969	2085	3948
10	1359	1211	1776	321	320	3125	3093	3915	6302
15	2020	1642	2586	415	421	—	3490	5432	—
20	2877	1957	3385	469	—	—	3284	6527	7615
25	—	2135	4025	480	—	—	2717	—	—
30	—	—	—	444	—	5555	2074	7388	6620
40	—	—	—	—	—	4595	1206	6800	5152
50	—	—	—	—	—	—	820	5405	—
90	—	—	—	—	—	—	—	1075	—

Key:

1. Content of anhydrous electrolyte, %

Note: With a change in temperature by 1°C in the interval 18-26°C, the specific electrical conductivity increases by 1.5-3%.

quantity of established power of the current receivers P_y and the coefficient of demand k_c from the equation:

$$P_n = k_c P_y$$

The quantity of the coefficient of demand k_c and the annual number of hours of use of the maximum load T for the chemical industry are assumed to be equal to:

	k_c	T , thous. h
For high output plants	0.60-0.65	7-8
For low output plants	0.17-0.50	5.8-6.2

If the complete power of the load in relative units (S_*) changes according to the equation

$$S_* = t^a$$

then the losses of power (in relative units) will be:

$$\Delta P_* = t^{a+1}$$

Then the time for use of the maximum load in a year (relative quantity)

$$T_* = \int_0^1 t^a dt = \frac{1}{a+1}$$

The time of energy loss in a year (relative quantity) equals:

$$\tau_0 = \int_0^1 i_0^2 dt_0 = \frac{1}{2a+1}$$

From which:

$$\tau_0 = \frac{T_0}{2 - T_0}$$

The absolute value of the number of hours of maximum losses in the year

$$\tau = \frac{T}{2 - \frac{T}{8760}}$$

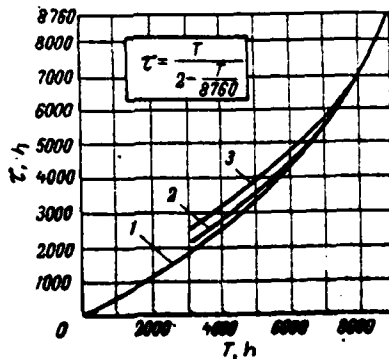


Figure IV-1. Dependence of the Number of Hours of the Maximum Losses τ on the Number of Hours of Use of the Maximum Load with Different Values of $\cos \phi$

1. $\cos \phi = 1$
2. $\cos \phi = 0.8$
3. $\cos \phi = 0.7$

Figure IV-1 shows the dependence of the number of hours of maximum losses on the number of hours of use of the maximum load.

Classification of the Production Rooms and Outer Units for Fire- and Explosion Danger

The nitrogen industry productions reprocess different gases and liquids that are distinguished both in physical-chemical and fire-explosion-dangerous properties. The set of electrical equipment is therefore also diverse, both of general industrial design and of explosion-protection.

Classification of production rooms for general characteristics of the environment is presented in chapter I-1 of the PUE.⁷

The gases and gas mixtures with relative density for air lower than one, (for example, hydrogen, natural gas, nitrogen-hydrogen mixture) are mainly collected at the top, therefore, in the hydrogen units, compressor stations of natural, water and semi-water gases, nitrogen-hydrogen mixture and others, the upper zone of the room is the most dangerous. The installation of extension shafts and bay windows considerably reduces or completely eliminates the probability of dangerous concentrations of the indicated gases forming in the rooms.^{9,12}

Vapors of easily igniting liquids and gases with relative density more than one, especially with density in limits over 1.5-2 are mainly accumulated at the bottom. Thus, for example, in pumping units of gasoline, benzene, and cyclohexane, the lower zone is the most dangerous. In addition to general exchange ventilation, it is very important to install local suction fans from the equipment.

Mixtures of air with vapors of easily igniting liquids (EIL) belong to the explosion-dangerous if the flash point of the vapors is 45°C and lower*. The more dangerous are the EIL with flash point of the vapors below 28°C and the most dangerous are those with flash point of the vapors below 15°C.

Depending on the temperature of spontaneous combustion, the gas- and vapor-air mixtures are divided into four groups. They correspondingly stipulate the permissible temperatures for the elements of the explosion-protection electrical equipment that comes into contact with the explosion-dangerous medium:⁸

Group of explosion-dangerous mixture	Temperature of spontaneous combustion of mixture, °C	Temperature of elements of electrical equipment, °C
A	over 450°	360
B	300-450	240
G	175-300	140
D	120-175	100

*There is currently a suggestion to classify as explosion-dangerous the EIL with flash point of vapors 61°C and lower.

One of the most popular explosion-protection devices of electrical equipment is flange (slit) protection. Four categories of explosion-dangerous mixtures have been set depending on the size of the flange gaps in shells with volume 2.5 l with flange width of 25 mm in which the frequency of transmission of the explosions is 50% from the number of explosions made:⁸

Category of explosion-dangerous mixture	Size of gap between surfaces of flanges, mm
1	Over 1.0
2	0.65-1.0
3	0.35-0.65
4	Less than 0.35

The actually adopted sizes of the gaps in the explosion-impermeable electrical equipment have correspondingly lower values that can be defined by calculations and experiments. Data on the gaps and junctions in the shell are presented in the PIVE (§86-92 and table 16).⁸

Table IV-14 shows the distribution of certain explosion-dangerous mixtures according to categories and groups.⁸

Thus, among the most dangerous we can classify the media that contain heavy gases and vapors (density 1.5-2.0) which have a low limit of explosiveness (to 2.5%) and low temperature of spontaneous combustion (and for EIL vapors an even lower flash point of less than 15°C).

In determining the degree of danger of the media that contain explosion-dangerous gases and gas mixtures, as well as EIL vapors, it is necessary to take into consideration not only the final product of production, but also the initial products that participate in the technological process, and for each room separately. Most often the initial and final products of production have a varying degree of explosion danger.

Below is a classification of the explosion-dangerous rooms and outer units depending on the production factors and the physical-

chemical properties of the vapor-gas-air mixtures.

According to chapter VII-3 of PUE⁷, class V-I includes the rooms in which the explosion-dangerous mixtures of gases and vapors with air or with other oxidizers can be formed during normal short operating regimes.

Class V-Ia includes the rooms in which during normal operation, the explosion-dangerous mixtures of combustible vapors or gases with air or other oxidizers are not formed, but are only possible as a result of accidents or malfunctions.

Taking into consideration the physical-chemical properties of mixtures, the explosion-dangerous rooms can be divided into the following classes:

class V-1A-T includes rooms of class V-Ia, but with more dangerous combustible gases or vapors (with relative density over 1.5; the lower limit of explosiveness to 2.5% and flash point of vapors of the EIL is lower than 15°C);

class V-Ia-S includes rooms of class V-Ia, but with very dangerous combustible gases or vapors (with relative density less than 1.5; the lower limit of explosiveness is from 2.5 to 10%, the flash point of the EIL vapors is from 15 to 28°C);

class V-Ia-L includes rooms of class V-Ia, but with dangerous combustible gases or vapors (relative density less than 0.8; the lower limit of explosiveness is over 10%, flash point of the vapors from 28 to 45°C).

Note. The rooms in which combustible liquids with flash point over 45°C are used or stored (for example, warehouses of mineral oils, units for their regeneration, etc.) refer to fire-dangerous of class P-I.

Class V-Ib refers to the same rooms as class V-Ia, but is distinguished by one of the following features:

a) in these rooms it is possible to have release of combustible gases with high lower limit of explosiveness (15% and more) and sharp smell with maximum permissible concentrations according to the sanitary norms (for example, machine halls of ammonia compressors and cooling absorption units with operating personnel, constantly or strictly periodically servicing them; with complete absence of the service personnel, additional preventive measures must be stipulated);

b) in emergencies, the formation in rooms of general explosion dangerous concentration is excluded according to the conditions of the production process, and local explosion-dangerous concentration is only possible (for example, rooms of water electrolysis when they do not have tanks with combustible gases);

c) combustible gases that easily ignite and combustible liquids are in rooms in small quantities that do not create a general explosion-dangerous concentration, and working with them is done without the use of open flame. These units are classified as nonexplosion-dangerous, if work is done in them in exhaust shafts or under exhaust hoods.

Class V-Ib also includes rooms of pumping units for circulating incombustible liquids through the apparatus with explosion-dangerous gases, if these units are installed outside the rooms of the pumping or are isolated from them, and reliable protective devices are provided to prevent penetration of the combustible gases from the apparatus through the liquid pipelines into the pumping units.

Note. The separation of the explosion-dangerous rooms into classes V-Ia-T, V-Ia-S and V-Ia-L is still not stipulated by the PUE, however, it is permitted to classify the explosion-dangerous rooms as class V-Ib instead of V-Ia for gases and vapors lighter than air (density 0.8 and less in relation to air). In this case, the frequency and seriousness of the emergencies observed during operation of the production must be taken into account, as well as the degree of reliability of the stipulated protective measures (ventilation, signalling). One can expect that in this case, the rooms of a number of explosion-dangerous productions for gases and vapors lighter than air will be categorized as class V-Ib.

TABLE IV-14. DISTRIBUTION OF CERTAIN COMBUSTIBLE SUBSTANCES ACCORDING TO CATEGORIES AND GROUPS

Category of explosion dangerous mixture	Group of explosion-dangerous mixture			
	A	B	C	D
1	Ammonia, methane dichloroethane, acetic acid, isobutylene, cyclohexanol, α -methylstyrene, coal solvent, methyl chloride, acetonitrile	Acetic anhydride butyl alcohol (tertiary), isopropylene alcohol, isoprene, isobutanol, vinyl acetate, amyl acetate	White spirit, turpentine, cyclohexane	-
2	Ethane, propane, acetone, ethyl chloride, diethylamine, benzene, toluene, xylene, ethylbenzene, chlorobenzene, diisopropylene ether, isopropylbenzene, styrene, pyridine, blast furnace gas, gasoline B-100, carbon monoxide, isobutane, naphthalin	Butane, pentane, propylene, methyl alcohol, ethyl alcohol, ethyl acetate, isopentane, butyl alcohol (normal), butyl acetate, dioxane, furfural, divinyl, nitrile of acrylic acid, nitrocyclohexane	Hexane, acetaldehyde, ethylcellulosols, fuel T-1, gasolines (A-66, B-70), heptyl samin	Diethylene ether of ethylene glycol
3	Ethylene, lamp gas, coking gas (approximately 30% methane, 60% hydrogen remaining CO, N, C H.)	Ethylene oxide, propylene oxide	Diethyl (black) ether, ethyl-dichlorosilan, vinyltrichlorosilan	-
4	Hydrogen, water gas, mixture of gases: * 1. 93.15% H ₂ ; 4.8% CO; 0.55% CH ₄ 1.5% N ₂ + Ar 2. 66.5% H ₂ ; 24.4% CO; 0.5% CH ₄ 7.2% CO ₂ ; 1.4% N ₂ + Ar 3. 72-75% H ₂ ; 21-18% CO; 1% HCO ₃ ; 6% CH ₄ +N ₂ 4. Gases of pyrolysis for acetylene production:	Acetylene**	Hydrogen sulfide, trichlorosilan	Carbon disulfide

56% H₂; 25% CO; 5%
CH₄; 8-10% C₂H₂; 3%
CO₂
5.2 Nitrogen-hydro-
gen mixture:
75% H₂; 25% N₂

*The category and group of the indicated gas mixtures must be experimentally confirmed.

** Acetylene cannot be classified with the fourth category since the gaps in the explosion-impermeable shells for acetylene are much smaller than the permissible for the fourth category. Acetylene belongs to group B according to the temperature of spontaneous combustion.

However, one should consider that the most reliable electrical equipment must be selected for these rooms. The production rooms of this type should be classified with the explosion-dangerous class V-Ia-L. The requirements for the electrical equipment of these rooms are reduced as compared to the requirements for the electrical equipment of class V-Ia, but are considerably increased as compared to those for class V-Ib.

Class V-Ig includes explosion-dangerous outer units (VN). They can be divided into 3 classes according to a diminishing scale of danger (classification of GIAP):

VN-I--the most dangerous units with compressed gases;

VN-Ia--technological units and containers with easily igniting liquids;

VN-Ib--technological units and apparatus with combustible gases lighter than air.

The following zones should be considered explosion-dangerous:

for the class VN-I--in limits of 30 m from the technological apparatus on the horizontal and the vertical (at the suggestion of GIAP);

for classes VN-Ia and VN-Ib--respectively in limits of 20 m and no less than 3 m on the horizontal and vertical from the technological apparatus, and 5 m from the breather and safety valves of the apparatus and gas holders (according to PUE data).

The nonexplosion-dangerous rooms include:

a) rooms in which solid, liquid or gaseous fuel is burned (for example, furnace divisions of gas generator stations, gas boilers, etc.); productions in which the technological process is associated with the use of an open flame or incandescent particles (for example, opening electric and other furnaces); rooms in which the heating temperature of the outer surfaces of the apparatus exceeds the temperature of spontaneous combustion of the vapors and gases of the environment;

b) individual gas analyzers insulated from explosion-dangerous rooms for analyzing explosion-dangerous gases, vapors and gas mixtures can be categorized as nonexplosion-dangerous, if the size of the room is such that if there is a complete break in the gas-conducting pipe of one gas analyzer (regardless of the number of them in this room) and when the gas pressure in it is no more than 8 mm wat. col., the lower limit of explosiveness of the gas in the mixture with air may not be reached in 1 h. The size of room that is computed according to the following equation will satisfy this condition:

$$V_n > \frac{1.252 D^2 \sqrt{h}}{nk \sqrt{\rho}}$$

where D--inner diameter of gas conducting pipe of the gas analyzer, mm (but not more than 7 mm);

h--gas pressure in the gas conducting pipe, mm wat. col.;

n--lower limit of explosiveness of gas, %

k--frequency of air exchange;

ρ --density of gas, kg/m³.

The recommended area of vitrification in the rooms of the gas analyzers is 0.05 m² per 1 m³ of room size.

The most important preventive measures which improve the reliable operation of the plants are sanitary-technical ventilation which is stipulated in all the rooms, and automatic signalling when an explosion-dangerous concentration develops. It is permitted to reduce the classes of explosion-dangerous rooms of V-I, V-Ia and V-II by one degree, if the following measures have been taken

or one of them:

a) several continually operating ventilation units have been installed, and if there is an emergency stopping of one of them, the others guarantee the maximum effectiveness of ventilation in the room;

b) a reserve ventilation unit has been installed which is automatically turned on when there is an emergency stopping of the working unit;

c) when an explosion-dangerous concentration develops which does not exceed 20-50% of the least explosion-dangerous (and for toxic substances--when the concentration approaches the sanitary norms), automatic signalling is triggered.

Table IV-15 presents a classification of the production rooms and outer units of the nitrogen industry for fire- and explosion-danger which was compiled according to chapters VII-3 and VII-4 of the PUE.

Below are the requirements for the substations, distribution devices and electric rooms which can be built into the explosion-dangerous rooms or built onto them.¹²

1. Direct arrangement of the distribution devices with voltage of 1000 V and higher in explosion-dangerous rooms of all classes is generally not permitted; it is forbidden in rooms of classes V-I, V-II, V-Ia-T and V-Ia-C; in rooms of classes V-Ia-L, V-Ib and V-IIa it is permitted in the corresponding explosion-protection design.

It is permitted to install control knobs, columns, panels and boards of control over the electric motors in the explosion-protection design or panels with apparatus and electrical-measuring instruments installed on them or built into them in a design permissible for the appropriate class of explosion-dangerous rooms. This equipment may be installed in rooms of all classes.

2. It is not permitted to build in distribution devices in rooms of classes V-I, V-II, V-Ia-T and V-Ia-S.

It is permitted to build in transformer substations, distribution devices with voltage to 1000 V and higher and electric rooms into rooms of classes V-Ia-L, V-Ib and V-IIa. The latter must be insulated from the explosion-dangerous rooms by walls and roofing with limit of flame-resistance of no less than 1 h and must have one exit to the outside with length to 7 m and two exits with length of 7 m and more. It is permitted to place one of the exits in the adjacent nonexplosion-dangerous room or in the explosion-dangerous, but with installation of a double door with fire-proof self-closing door with limits of fire-resistance no less than 0.75 h.

The distance on the horizontal from the edge of the windows and the doors of explosion-dangerous rooms of class V-Ia-L to the edge of the doors of the adjacent distribution devices and electric rooms must be no less than 6 m. The openings in the walls and in the floor for laying cables and pipes must be solidly made of incombustible materials.

When the distribution devices and the electric rooms are placed on the upper stories, the exits from them can be made in non-explosion-dangerous adjacent rooms (onto the stairwell, into the corridor).

Rooms of class V-Ib can be separated from the distribution devices and electric rooms by fireproof walls or partitions with fireproof self-closing doors (without double doors).

3. It is permitted to add on substations with transformers to the rooms of all classes (it is desirable to have dry or incombustible filler), distribution devices and electric rooms, and to rooms of classes V-I, V-II; V-Ia-T and V-Ia-S--only in those cases where it is impossible or difficult to remove them because of the limitedness of the territory, encumbered with underground or surface piping.

The transformer chambers must not have windows, doors or any other openings that communicate with explosion-dangerous rooms.

The walls which separate the substation from the explosion-dangerous rooms must be incombustible with limit of fire-resistance no less than 1.5 h.

Explosion-dangerous gases must not penetrate through the ventilation openings. This is achieved, for example, by installing individual ventilation systems or by the appropriate arrangement of the balanced air ducts.

The distribution devices and electrical rooms are made analogously to point 2. In addition, gage pressure of pure air equal to 5 mm wat. col. must be provided for in the substations that are attached to the rooms of classes V-I, V-II, V-Ia-T and V-Ia-S.

The walls which separate the rooms of the substations from the explosion-dangerous rooms must be plastered on both sides. Exits from them into the explosion-dangerous rooms are forbidden. Input of cables and pipes from the electrical rooms and from the distribution device into the explosion-dangerous rooms is only permitted through the outer walls or through the buffer rooms (stairwells, corridors, etc.). Openings in the walls after laying of the cables and pipes must be packed and reliably made of incombustible materials (according to decision No. E-3/67 of the Technical Administration of the USSR Ministry of Power and Electrification of 18 March 1967).

When the electrical rooms and distribution devices are placed on the upper stories of the rooms of classes V-I, V-II, V-Ia-T and V-Ia-S, one exit must be made on the outer balcony with the possibility of descending on the built-in staircase (fire escape is permitted).

If the distribution devices are arranged on the upper stories of the room of classes V-Ia-L, V-Ib and V-IIa, both exits may be

TABLE IV-15. CLASSIFICATION OF ROOMS AND OUTER UNITS FOR FIRE AND EXPLOSION-DANGER

Section, shop or structure	Architectural construction forms of structure	General characteristics of environment	Characteristics of environment for fire- and explosion-danger	Class of room (units)
Conversion of methane and carbon monoxide (technological apparatus outside building)	Outer platform forms	Atmospheric conditions	Production of ammonia 4A (for converted gas: 66.5% H ₂ ; 24.4% CO; 0.5% CH ₄ ; 7.2% CO ₂ ; 1.4% N ₂ +Ar)	V-Ig(VN-Ib)
Separate room for trigger gas blowers	Single-story building	Normal	1A (for methane)	V-Ia-L (V-Ia for gases and vapors lighter than air)
The same for pumps	The same	Wet	4A	Electrical equipment selected as for class V-Ib
The same for acid blowers	"	Normal	Explosion-safe	-
Monoethanolamine purification (technological apparatus outside building)	Outer platform forms	Atmospheric conditions	4A (for purified converter gas: 93.2% H ₂ ; 4.8% CO; 0.5% CH ₄ ; 1.5% N ₂ +Ar)	V-Ig(VH-Ib)
Separate room for pumps	Single-story building	Wet	4A	Electrical equipment selected as for V-Ib class
Water and copper-ammonia purification	The same	The same	4A (for purified converter gas: 70% H ₂ ; 4.9% CO; 0.5% CH ₄ ; 1.6% CO ₂ ; 23% N ₂)	V-Ia-L
Regeneration of copper-ammonia solution	"	Wet chemically active	1A (for ammonia vapors)	V-Ib
Compression and synthesis of ammonia	High two-story building with platform forms	Chemically low-active	4A (for nitrogen-hydrogen mixture: 75% H ₂ ; 25% N ₂)	V-Ia-L
Synthesis (technological apparatus)	Outer platform forms	Atmospheric	the same	V-Ig(VN-Ib)

tus outside building)		(conditions		
Methane conversion	Outer platforms	Production of methanol Atmospheric conditions	4A (for converted gas: 65% H ₂ , 28% CO; 6% CO ₂ ; 1% CH ₄ +N ₂)	V-Ig (VN-Ib)
Monoethanolamine purification (technological apparatus outside building)	The same	The same	4A (for gas mixture: 68-69% H ₂ , 30-29% CO; 1% CH ₄ +N ₂ ; 1% CO ₂)	The same
Compression and synthesis	High two-story building	Normal	4A (for gas mixture: 72-75% H ₂ ; 24-21% CO; 1% CH ₄ +N ₂ ; 1% CO ₂)	V-Ia-L
Synthesis (technological apparatus outside building)	Outer platforms	Atmospheric conditions	The same	V-Ig (VN-Ib)
De-etherization, distillation of methanol, permanganate purification and warehouses	Building with platforms	Wet	2B (for methanol)	V-Ia-S (V-Ia for gases and vapors with relative density less than 1.5)
		Production of nitric acid under pressure		
Turbocompression	Two-story building with platforms	Chemically active	-	-
Conversion (contact section)	The same	The same	1A (for ammonia vapors)	V-Ib
The same, but with technological apparatus outside building	Outer platforms	"	The same	V-Ig (VN-Ib)
		Production of ammonium nitrate		
Neutralization	Multistory building with platforms	Chemically active (Vapors of nitric acid)	1A (for ammonia vapors)	V-Ib
Evaporation, drying and cooling	The same	Wet and dust	For dust of ammonium nitrate	V-IIa
Granulation	Towers with superstructure	Dust	1A (for dust of ammonium nitrate and ammonia vapors)	V-IIa and V-Ib
Packing with loading and warehouse	One-story building	The same	The same	V-IIa

Gas holders

Gas holder of converted gas, gases of pyrolysis or water gas	Metal structure	Atmospheric conditions	4A (for converted gas, gases of pyrolysis or for water gas)	V-Ig(VN-Ib)
Chamber of gas input	Single-story deepened building	Damp	The same	V-I
Gas holder of semi-water or coking gas	Metal structure	Atmospheric conditions	3A (for semi-water or coking gas)	V-Ig (VN-Ib)
Chamber of gas input	Single-story deepened building	Damp	The same	V-I
Auxiliary production units (according to decision No. E-17-62 of Soyuzglavenergo of 17 October 1962)				
Boiler(ash, bunker section; rooms of electrical filters, ventilators and mills)	Structure with plat-forms	High air temperature	-	-
Section of coal supply. Preparation and transporting of coal	Structure with plat-forms	Dust	Fire-dangerous	P-II
Preparation of coal dust	The same	"	Explosion-dangerous	V-IIa
Machine hall with gas turbines*	Two-story structure	-	-	-
Pump mazut	One-story structure	Flash point of vapors above +45°C	Fire-dangerous	P-I
Oil point (warehouses and distributing lubricants)	The same	The same	The same	P-I
Room of storage batteries**	"	Normal	4A (for hydrogen)	V-Ia (V-Ia-L)
Double door into storage battery room	"	"	"	V-Ib
Chamber of exhaust ventilation from storage battery room	"	"	"	V-Ib
Open warehouses of	-	Atmospheric	Fire-dangerous	P-III

fuel (coal and peat) Open unit of tanks with oil and mazut	- conditions The same	Fire-dangerous	P-III
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*The machine hall with gas turbines is a room with normal environment. It is necessary to stipulate the following measures in it to guarantee fire safety: intensified ventilation during normal operation; emergency ventilation; installation at the gas pipe inlet into the machine hall of a cut-off valve which is automatically triggered when the gas pipeline breaks; installation of a relay which turns off the gas supply into the combustion chamber if the pilot light goes out; installation in the area of location of the gas pipeline and gas valves of automatic gas analyzers which are connected to the cut-off valve and with the relay for turning off the gas; minimum number of flange connections on the section of the gas pipeline in limits of the machine hall.

**The sites of location of the storage batteries that are connected to the charging units and ventilation units which guarantee reliable ventilation before the beginning of charging, during it and after its completion are not standardized. Requirements for installation of windows, lamps and the use of individual easily-expendable covering panels do not cover these storage battery rooms (see SNIP P -I. 8-62, table 1).

into nonexplosion-dangerous adjacent rooms (into the stairwell, corridor, etc.).

The distance on the horizontal from the edge of the windows and doors of the explosion-dangerous rooms to the edge of the doors of the connected rooms of the substations and the distribution devices must be: for rooms of classes V-I, V-Ia-T, V-Ia-S no less than 10 m; for rooms of class V-Ia-L no less than 6 m. The doors of the connected rooms should be moved to the other side if possible.

4. It is permitted to connect to rooms of all classes complete transformer substations (KTP) with transformers (desirably dry or with incombustible filler), and in rooms of classes V-Ia and V-Ib it is permitted to build in a KTP room. In the KTP rooms that are added onto the rooms of classes V-I, V-Ia-T and V-Ia-S, gage air pressure must be provided which is equal to 5 mm wat. col. (according to the decision No. E-3/67 of the Technical Administration of the USSR Ministry of Power and Electrification).

The walls which separate the KTP rooms from the explosion-dangerous must be fireproof with limit of fire-resistance no less than 1.5 h, for KTP with oil transformers, and no less than 0.75 h for KTP with dry transformers or filled with incombustible substances.

The exit from the KTP room must be to the outside. For rooms of classes V-Ia-L, V-Ib and V-IIa, one of the exits may be into the nonexplosion-dangerous adjacent room. The distance on the horizontal from the edge of the windows and doors of the explosion-dangerous rooms to the edge of the doors of the KTP room must be: for rooms of classes V-I, V-II, V-Ia-T, V-Ia-S 10 m; for rooms of class V-Ia-L 6 m. The doors of the KTP should be on the other side if possible.

The complete transformer substations with oil transformers which can be connected to rooms of classes V-I, V-II, V-Ia-T and V-Ia-S should not have more than two transformers with rated power of

over 1000 kW each. Only auxiliary or general nonexplosion-dangerous rooms with a few personnel may be located above the KTP rooms.

The floors and bottoms of the passages or areaways of the substations, distribution devices, electrical rooms and KTP must be higher than the floors of the adjacent explosion-dangerous rooms of classes V-I, V-Ia-T and V-Ia-S by no less than 0.25 m. An exception is permissible for cable passages of distribution devices of the substations when the passages are located at a distance of no less than 3 m from the explosion-dangerous rooms of the indicated classes.

The minimum gaps from the built-in transformer substations (TP), distribution devices (RU) and distribution points (RP) to other explosion-dangerous rooms, explosion-dangerous outer units and vessels should be adopted in accordance with the decision presented in the protocol of the technical conference with the chief engineer of the State Power Inspection of 6 May 1968.

Electrical Equipment

One of the most reliable designs of explosion-protected electrical equipment is explosion-impermeable which is popular in explosion-dangerous productions of the nitrogen industry.¹⁰ This equipment is currently manufactured for media 1A with marking V1A (RV), 2B with marking V2B and 3G with marking V3G. The electrical equipment that is made for a more dangerous medium can be used in less dangerous one if the appropriate explosion-protected electrical equipment is lacking, as well as in those cases where this is expedient. For example, electric motors with marking V2B can be used in media 1A, 1B, 2A and 2B, and with marking V3G--in media 1A, 1B, 1G, 2A, 2B, 2G, 3B and 3G.

The explosion-impermeable electrical equipment that is manufactured to operate in an explosive medium of a certain category or group can be used in an explosion-dangerous medium of the same

category of another group if the maximum possible temperature of the outer parts of the shell in the working regime does not exceed the permissible for this group (see p.590). Practical measurements have shown that for the currently manufactured explosion-impermeable electric motors, this temperature is less than 95°C with rated load. However, it must be confirmed by the manufacturing plants or the appropriate organizations.

According to GOST 183-66, the temperature of the winding of the alternating current machines with class V insulation must not exceed 125°C. According to plant data¹², depending on the cooling system and the polarity of the electric motors, the temperature drop between the stator winding and the outer surface of the electric motor fluctuates in limits of 10-60°C. The nitrogen industry uses air-cooled electric motors for which the temperature drop is (roughly) 40°C. In this case, the temperature on the surface of the electric motors is roughly 85°C. Under these conditions, the explosion-impermeable electric motors with marking VI A(RV) can be used in explosion-dangerous media of category not only 1A, but also 1B and 1G (in this case their marking VI B or VI G, and electric motors with marking V2B--in media not only 2A and 2B, but also 2G (in this case their marking is V2G).

With a temperature drop of 45°C and temperature on the surface of 80°C, the electric motors with the indicated markings can be used respectively in media 1D and 2D, and with marking V3G in the medium 3D. If it is necessary to reduce the temperature on the surface, it is possible to correspondingly decrease the rated output of the electric motors.

The dependence of overheating of the surface of the electric motor mounting on the load current is approximately determined by the following equation:

$$\theta = \left(\frac{I}{I_r}\right)^2 \theta_r$$

where I_{μ} and θ_{μ} --rated current and overheating;
 I and θ --current and overheating for given load.

Table IV-16 gives the marking of explosion-protected equipment of various designs.

TABLE IV-16. CONVENTIONAL DESIGNATIONS OF EXPLOSION-PROTECTED ELECTRICAL EQUIPMENT

Design of electrical equipment	Explosion-dangerous medium	Designation of medium	Marking of electrical equipment
1. Explosion-impermeable	Coking gas	3A	V3A
2. Blown-through under gage pressure			
with explosion-impermeable elements	Ethers	3G	P3G
without explosion-impermeable elements	Hydrogen	4A	P0A
3. Increased reliability against explosion			
without explosion-impermeable elements	Coking gas	3A	N0A
with explosion-impermeable elements	Acetaldehyde	2G	N2G
with elements blown through under gage pressure	Carbon disulfide	4D	NPD
with oil-filled elements	Carbon disulfide	4G	NMG
4. Spark-dangerous without explosion impermeable elements	Ethylene	3A	I0A/ethylene
5. With oil filling			
without explosion-impermeable elements	Cyclohexane	1G	M0G
with explosion-impermeable elements	Methyl alcohol	2B	M2B
6. Special			
with elements of increased reliability against explosion	Nitrocyclohexane	2B	SNB
with explosion-impermeable elements	Cyclohexanon	1A	S1A

The currently manufactured explosion-impermeable apparatus with marking RV is mainly designed for shafts, but can be also be used under similar conditions in shops of the nitrogen industry. The start-up-distributor electrical apparatus is mainly used in general industrial designs. It is removed from the

explosion-dangerous rooms to individual rooms isolated from production. This is the most reliable. The electrical equipment in the design of increased reliability against explosion can be installed in explosion-dangerous rooms of classes V-Ia-L; V-Ia-S and less dangerous ones. It is permitted to use explosion-impermeable electric motors with squirrel-cage rotor under conditions of explosion-dangerous media of a higher category than that for which it was made, but in the quality of closed air-cooled electric motors in the design of increased reliability against explosion. In this case, the corresponding temperature conditions must be observed (see tables 21 and 22 of PIVE).

Table IV-17 presents the conditions under which a certain type of explosion-protected electrical equipment is used.

TABLE IV-17. AREA OF APPLICATION OF EXPLOSION-PROTECTED ELECTRICAL EQUIPMENT

Class of room and characteristics of explosion-dangerous medium	Design
<p style="text-align: center;">With marking RV and V1G</p> <p>Explosion-dangerous rooms of all classes with medium 1A, 1B, 1G and 1D Explosion-dangerous rooms of classes V-Ia and less dangerous with medium 2A-4A and 2B-4B</p>	<p>Explosion-impermeable Closed¹ air-cooled of increased reliability against explosion</p>
<p style="text-align: center;">With marking V2B(V2G)</p> <p>Explosion-dangerous rooms of all classes with medium 1A, 1B, 1G, 1D, 2A, 2B, 2G, 2D Explosion-dangerous rooms of class V-1A and less dangerous with medium 3A, 3B, 4A and 4B</p>	<p>Explosion-impermeable Closed² air-cooled of increased reliability against explosion</p>
<p style="text-align: center;">With marking V3G</p> <p>Explosion-dangerous rooms of all classes with medium 1A-3A, 1B-3B, 1G-3G, 1D-3D Rooms of class V-Ia and less dangerous with medium 4A and 4B</p>	<p>Explosion impermeable Closed air-cooled of increased reliability against explosion</p>

Note: 1. The possibility of using explosion-impermeable electric motors with rated or reduced power in rooms of the more dangerous group than that for which it was made (but of the same category) must be agreed upon with the manufacturing plant and the institute "Giproniselektroshakht."

2. The conditions of increased reliability against explosion

are set by the institute "Giproniselektroshakht."

The currently manufactured oil magnetic starters of the series PM-700 with elements in the design of increased reliability against explosion have marking MND and are suitable for all explosion-dangerous media of rooms in classes V-Ia and less dangerous ones. However, because of the insufficient reliability of the PM-700 starters, they should be avoided. The explosion-protected universal switches in the series UP-5800 in the oil design with marking MOD are suitable for explosion-dangerous rooms of all classes and for all media.

Lamps of increased reliability against explosion are made in types NOB-300 and NOB-150 with incandescent lamps respectively to 300 and 150 W for media 1A-4A and 1B-4B. It is permitted to use lamps NOB-300 and NOB-150 with lamps respectively to 200 and 100 W for media 1G-4G if the temperature of spontaneous combustion of them is not below 300°C. Manufacture has been started of lamps of increased reliability against explosion with incandescent lamps to 500 W, with DRL lamps to 500 W, for group B, and to 250 W for groups G and D; with luminescent lamps 80 W for groups B and G, and 40 W for group D.

One of the most reliable designs of explosion-protected electrical equipment^{11,12} is blown-through under gage pressure. Asynchronous and synchronous electric motors of high power are mainly used in this design, from 250-300 kW to 4000-6000 kW and more, with velocities from 125 to 3000 rpm. In the design blown through under gage pressure, electric motors can be used of general industrial series. They include asynchronous motors of the AP series (modification of series A), DAZ, ATD, etc.; synchronous motors of the series SDNZ, SDNP, SDS, SDKP, STM, STMP and others.

The electric motors can be cooled according to an open or closed system. In the first case, the cooling clean air (usually outside) is sent into the machine, while the heated is discharged

from the explosion-dangerous room. With this method of cooling, it is necessary to have a filter for cleaning the air of dust. The outer air can be contaminated by gases or vapors which cause corrosion, therefore, it is more convenient to install a closed system of cooling with the use of built-in or separately installed water air-cooler. The Novosibirsk turbogenerator plant manufactures electric motors in the series ATD 3000/6000 V for 3000 rpm in a closed blown-through design with closed system of ventilation, with two sections of air-cooler located in the stator housing. In this design, there is no need for separately installed air-cooler and air-lines.

The plant "Elektrosila" has updated the series of asynchronous squirrel-cage closed air-cooled electric motors DAZO. They are air cooled on a closed system through a tubular air-cooler installed above the stator.

Synchronous motors in the series SDNZ in a closed blown-through design with closed or open cooling cycle are made with power from 320 to 10,000 kW for voltage of 6000 V with leading $\cos\phi=0.9$ and for velocities from 100 to 1000 rpm. Direct connection of the electric motors to the circuit for full voltage is permitted. The motors of the series SDNZ also have explosion-protected modification, motors in a design blown-through under gage pressure. In this case, the series is designated SDNP. The types of motors are correspondingly designated. The adjustment dimensions and technical data of the motors of both series are the same.

A series of synchronous motors SDKP in design with blow-through under gage pressure with closed or open cooling cycle has been developed for piston compressors of increased velocities with opposite movement of the pistons. They are made with power from 320 to 6300 kW for voltage 6000 V with leading $\cos\phi=0.9$ and for velocities from 250 to 600 rpm. Direct connection of the electric motors of this series to the circuit for full voltage is permitted. A modification of these motors is currently being developed for voltage of 10,000 V.

The turbocompressors mainly use high-speed synchronous motors of the series STM for 3000 rpm in a closed blow-through design with power from 1500 to 6000 kW for 6000 V and power of 4000 kW for 10,000 V. They are started through jet resistance (reactor) which reduces the voltage to 50-70% of the rated (the motor for 1500 kW by agreement with the manufacturing plant can have direct start). According to a report of the Lys'va turbogenerator plant, the STM motors can be made with power from 800 to 9000 kW for voltage of 6000 or 10,000 V. There is an explosion-protected modification of the STM series motors in a blow-through design under gage pressure (STMP) with power of 1500, 2000 and 4000 kW for 6000 V with leading $\cos\phi=0.9$.

Panels and cases with control and measuring equipment in a closed blow-through design at gage pressure with open ventilation system, as well as in a special design have become popular.

Table IV-18 and IV-19 present the instructions on selecting designs and types of electrical equipment for outer and inner units of the nitrogen industry.

It is expedient for enterprises of the nitrogen industry to stipulate the following categories of electrical receivers in relation to their reliable electrical supply.

Category 0. This includes especially important electrical receivers of continuous production and electrical receivers necessary for safe stopping of the production process. Power supply of these electric receivers must come from two independent power sources with installation of an AVR (automatic reserve turn-on). In addition, a third independent power source of the electric receivers of the indicated category must be provided. The third power source may be mobile power plants, the nearest municipal power plants, as well as storage batteries.

It is recommended that a connector be installed with the nearest points that have independent power, with automatic turn-on

TABLE IV-18. INSTRUCTIONS FOR SELECTING ELECTRICAL EQUIPMENT FOR

Section or structure	Medium	For internal production units	
		Class of room	Three-phase current electric motor to 600 V to 6000 V and more
Production of ammonia and methanol			
1. Conversion of methane and carbon monoxide	4A	V-Ia-L	Explosion-impermeable series MA-36, KO, KOM, VAO and other marking V4A and V3G. Permitted in design of increased reliability against explosion with markings V1A(RV) and V2B
2. Water and copper ammonia purification	4A	V-Ia-L	Closed blow-through series AO2, DAZO. Preferable explosion-impermeable series KO, KOM, VAO etc. with marking V1A(RV) (mandatory for emergency fans)
3. Separate room of start-up methane gas-blowers	3A	V-Ia-L	
4. Regeneration of copper-ammonia solution in separate room	1A	V-Ib	
5. Mono-ethanol-amine purification (MEA)	4A	V-Ia-L	Explosion-impermeable with marking V4A. Permitted in design of increased reliability against explosion with markings V1A(RV), V2B and V3G of series Ma-36, KO-KOM
6. Compression, as well as synthesis (if synthesis columns are in the same room)	4A	V-Ia-L	The same
7. Separate room for oxygen blow-thru (with extension vessels)	Normal	-	Protected or explosion-protected series A, DAZ, ATD etc..
Production of diluted nitric acid under pressure			
8. Turbo-	Chemi-	-	As for point 4 and Closed blow-through

INTERNAL ELECTRICAL UNITS OF NITROGEN INDUSTRY PRODUCTION

For internal production units		For ventilation units of sanitary-technical purpose in isolated chambers		
Start-up apparatus	Instruments of control and measurement	Class of room	Electrical equipment for exhaust systems	for intake systems
Production of ammonia and methanol				
1Magnetic starters and control units	Knob posts oil-filled series KU-700 with marking MOD	V-Ib	Explosion-impermeable electric motors with markings RV, V2B, V4A and V3G of series	Closed blow-through electric motors of series AO-AO2
2in open or protected design, extended from production rooms, with remote control	Control cases with KU-700 knobs and hermetic ampere meter D-180 or E-309	V-Ib	Closed blow-through series AO-AO2 permit.	Magnetic starters, dust-water protected (their removal from chamber desirable)
		V-Ib	Magnetic starters and control blocks removed from chamber	Knob posts, water-protected series KU-123
			Knob posts, explosion-impermeable KUV series with VZG marking or oil-filled series KU-700 with MOD mark.	
4Magnetic starters, oil-filled series PM-700 with marking MNA	As for points 1-3	Non-explosion dangerous	Magnetic starters in dust-protected or protected design	Protected electric motors series A2
Preferable magnetic starters and blocks removed from production rooms, with remote control				Magnetic starters in protected design
5As for points 1-3	As for points 1-3	V-Ib	Knob posts in water-protected design series KU-123	Knob-posts in protected design series KU-122
6The same	The same	V-Ib	Explosion-impermeable electric motors with marking VIA(RV), V2B or V3G series KO, KOM etc.	As for points 1-3 The same
			Close blow-through series AO2 permitted	
			Magnetic starters and Control blocks, removed from chambers	
			Knob posts, explosion-protected oil-filled KU-700 with MOD marking	

[continuation of table IV-18 from p. 612]

compressor	cally active		if possible with chemically stable insulation	Closed blow-through with close or open cooling cycle series A, ATD, SDNZ, STM and others.
9. Conversion (contact section)	The same as 1A	V-Ib		
Production of ammonium nitrate				
10. Neutralization	Chemically active as well as 1A	V-Ib	As for point 4 and if possible with chemically stable insulation	As for point 9
11. Evaporation, drying and cooling	Dust of ammonium nitrate	V-IIa	The same	The same
12. Granulation	The same	"	"	"
13. Packing from platform and warehouse	"	"	"	"
Gasholders				
14. Gas-holders of converted gas, gases of pyrolysis or water gas; gas input chamber	4A	V-I	Electric motors must be removed beyond the limits of the gas input chamber	
15. The same, but semiwater or coking gas	3A	V-I	The same	

[continuation of table IV-18 from p. 613]

Magnetic starters or control blocks in: protected design	Knob posts protected, series KU-122 Cases with Knobs KU-122 and ampere meter E-30	Normal		Normal
Production of diluted nitric acid under pressure				
8.As for point 4	Knob posts oil-filled series KU-700;water-protected series KU-123 permitted	Non-ex- ploseive danger-ous	Closed blow-through electric motors series A02. Protec- ted series A2 per- mitted	Magnetic starters in protected design
9.The same	Cases of control with men- tioned knobs and hermetic ampere me- ter D-180 or E-309		Magnetic starters, oil-filled PM-700 or dust-protected (desirably removed from chambers) Knob posts,oil- filled or water- protected	Knob posts in in protected design series KU-122
Production of ammonium nitrate				
10.As for point 4	As for point 9	Non-ex- plosion danger.	As for point 9	As for points 1-3
11.The same	The same	The same	The same	The same
12.	"	"	"	"
13.	"	"	"	"
Gasholders				
14.Must be removed be- yond limits of gas in- put chamber	Expedient to remove from gas input chamber. Knob posts may be ex- plosion- protected, oil-filled, series KU-700 with MOD mark,	V-Ia-L	Explosion-impermeable electric motors of series KO,KOM, etc. with V3G marking. Start-up apparatus must be removed from chamber	As for points 1-3
15.The same	The same	V-Ia-L	The same	The same

TABLE IV-19. INSTRUCTIONS FOR SELECTING ELECTRICAL EQUIPMENT FOR

Section or structure	Category and medium group	Class of rooms	Electric motors of three-phase current
1. Conversion of methane and carbon monoxide 2. Water and copper-ammonia purification 3. Monoethanol-ammonia purification. Compression and synthesis (if synthesis apparatus is placed in the same room) 4. Regeneration of copper-ammonia solution in separate room	4A 1A	V-Ig (VN-Ib) V-Ig (Vn-Ib)	Explosion-impermeable series KO, KOM, VAO, etc. with marking V1A(RV), V4A, V2B or V3G Closed blow-through DAZO with heaters. Closed blow-through series A, DAZ, AP, ATD, SDNP, SDKP etc. with supply of clean air at temp. of 5-35°C As for points 1-3
Production of diluted nitric acid under pressure			
Turbocompressor	Chemically active	Nonexplosion-dangerous	As for points 1-3
Conversion (contact section)	The same and 1A	The same	The same
Production of ammonium nitrate			
Neutralization	Chemically active and 1A	Nonexplosion-dangerous	As for points 1-3
Evaporation, drying, cooling Granulation Packing from platform and warehouse	Dust of ammonium nitrate	The same	The same
Gasholders			
Gasholders of converted gas, gases of pyrolysis or water gas; gas input chamber	4A	V-Ig (VN-Ib)	As for points 1-3 (for zone to 5 m)
The same, of semi-water or coking gas	3A	V-Ig (VN-Ib)	

Note: Electric motors and electrical apparatus installed in the open air must be protected from atmospheric effects.

EXTERNAL UNITS OF NITROGEN INDUSTRY PRODUCTION¹⁰

Start-up apparatus

Control instruments

Production of ammonia and methanol

1. Magnetic starters and control blocks installed in separate electric rooms or in dust-impermeable cases

Knob posts, explosion-impermeable series KUV with marking V3G

3. Oil starters of series PM-700 (with definite temperature)

Cases with indicated knob posts; and hermetic ampere meter D-180 or E-309
Control columns K-3G with marking V3G

As for points 1-3

As for points 1-3. In addition, the knob posts also with marking RV

Production of nitric acid under pressure

As for points 1-3

Knob posts of control, oil-filled KU-700 (with definite temperature) or water-protected KU-123

The same

Control cases with indicated knobs and hermetic ampere meter D-180 or E-309

Production of ammonium nitrate

According to points 1-3

As for points 1-3

The same

The same

Gasholders

As for points 1-3

As for points 1-3
(for zones in limits of 5 m)

TABLE IV-20. CATEGORIES OF ELECTRIC RECEIVERS BY RELIABILITY OF THEIR ELECTRICITY SUPPLY

Production, section or unit	Characteristics of medium for explosion danger	Class of unit	Type and purpose of electric receiver	Permissible category of electric receivers	Grounds for classification with indicated category
Production as a whole	Explosion-dangerous for converted gas(4A) and nitrogen-hydrogen mixture(4A)	V-Ia-L	Synchronous electric motors of compressors and asynchronous centrifugal pumps, fans and other mechanisms	1	To avoid disruption of complicated technological process and reduction in output of product
Conversion of methane and carbon monoxide	Explosion-dangerous for methane (1A) and converted gas	V-Ia-L	Asynchronous electric motors of centrifugal pumps and fans	1	The same
Purification from carbon dioxide(external unit)	Explosion-dangerous for converted gas	V-Ig (VN-1b)	Electric motors of cut-off fittings	1	The same and disorders in control of production process For individual units, category 0 is recommended
Rooms of pumping units with removed production apparatus	The same	V-1b	Electric motors of pumps and fans	1	As for production as a whole
Purification from carbon monoxide(washing with liquid nitrogen)	The same	V-Ia-L	The same and synchronous electric motors of compressors	1	The same
Precatalysis and section of synthesis	Explosion-dangerous for converted gas and	V-Ig	Induction regulators; electric heaters	1	The same

(usually external units)	nitrogen-hydrogen mixture (4A)	(VN-1b)			
Electric drives of cut-off apparatus and pneumatic units for regulated and cut-off apparatus	Depending on site of installation	-	Asynchronous electric motors of gate valves and compressors	1	To avoid disorders in control of production process For individual units, category 0 is recommended
Ventilation units of sanitary-technical purpose (located in isolated rooms) exhaust ventilat. intake ventilat.	-	-	Asynchronous electric motors of fans	1	To avoid formation of dangerous concentrations of combustible gases
Units to obtain and distribute nitrogen with gas holders for blowing through production equipment	Depending on site of installation	-	V-1b Nonexplosion dangerous Primarily asynchronous electric motors of compressors and gas blowers	1	To avoid danger of damage to equipment and accidents In the absence of gas holders, category 0 is recommended
Pumping units of water lines (mainly located in individual rooms) production antifire	-	-	Nonexplosion dangerous Primarily asynchronous electric motors of centrifugal pumps	1	As for production as a whole, as well as to guarantee elimination of fires and explosions For antifire water line in individual cases, category 0 is recommended
Electric lamp units working lighting emergency lighting	Depending on site of installation	-	Lighting instruments	1 0	As for production as a whole To avoid disorders in control of production process

Production of diluted nitric acid

Production as a whole	Explosion-dangerous for ammonia in conversion section (IA) Chemically active	-	Synchronous or asynchronous electric motors of compressors; asynchronous electric motors of pumps, fans, etc.	2	To avoid reduction in production output
Section of ammonia conversion	Explosion-dangerous for ammonia Chemically active	V-IB	Asynchronous electric motors of fans	2	The same
Compression section	Chemically active	-	Synchronous or asynchronous electric motors of compressors	2	"
Absorption section	The same	-	Asynchronous electric motors of pumps and fans	2	The same
Warehouse of nitric acid	The same	-	The same	3	To avoid reduction in quantity of manufactured product
Sanitary-technical fan units (located mainly in isolated chambers)	-	-	The same	2	To avoid development of dangerous concentration of toxic gases and vapors the first category is recommended in individual cases
Pumping stations of water lines (usually located in separate rooms) production antifire	-	-	The same	2	As for production as a whole, as well as to guarantee elimination of fires and explosions For anti-fire water line in individual cases, first category is recommended
Electric lighting units working lighting emergency lighting	Depending on installation site	-	Lighting instruments	2 1	As for production as a whole To avoid disorders in production process

Production of Ammonium Nitrate

Production as a whole	Explosion-dangerous for ammonia (IA) and for dust	V-Ib	Asynchronous electric motors of pumps and fans	2	To avoid reduction in production output
Neutralization section	Explosion-dangerous for ammonia and chemically active	V-Ib	The same	2	the same
Granulation section	Explosion-dangerous for ammonia	"	"	2	"
Packing and warehouse	Explosion-dangerous for dust	V-IIa	Electric motors of fans and conveyers	2	"
Sanitary-technical fan units	Mainly located in isolated rooms	-	Electric motors of fans	2	In order to avoid strong dust accumulation
Pumping stations Electric lighting units	As for pumping stations and electric lighting units for production of diluted nitric acid				

of reserve power.

Category 1. It includes important electric receivers operating round-the-clock. Interruption in their power supply can result in a disorder in the complex production process and damage to the equipment with possible danger for human life. These electric receivers should be powered from two independent power sources with two or more lines (air or cable) when the AVR is installed.

It is recommended that a connection be installed to the nearest points that have independent power.

Category 2. It includes electric receivers whose interrupted power supply results in a decrease in the manufactured product, idling of workers, equipment and mechanisms, as well as industrial transport. These electric receivers should be powered from two independent power sources with two or more lines (air or cable) with AVR installation. The use of one two-circuit line is permitted.

It is recommended that a connection be installed to the nearest points that have independent power.

Category 3. It includes electric receivers of auxiliary shops, repair-mechanical workshops, warehouses of auxiliary materials, etc., for which interruptions in the electricity supply lasting no more than 24 h are permitted. It is permitted to power these electric receivers by one air or cable line.

Categorization of the electric receivers for the nitrogen industry depending on the reliability of power supply is presented in table IV-20.

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V. Accident Prevention

The majority of nitrogen industry productions reprocess combustible and toxic substances. When there is a disorder in the operating regime, as well as in various types of emergencies, a danger develops of considerable quantities of these substances entering the work rooms in the form of gases, vapors and dust. This may result in explosions, fires and poisoning.

Table V-1 presents a classification of the production buildings according to the degree of fire danger.

As follows from table V-1, the most dangerous productions of the nitrogen industry correspondingly belong to categories A (for hydrogen) or B (for ammonia). Since these productions are fire and explosion dangerous, the fire-resistance of the construction materials here must be no lower than the II degree.

Higher requirements are made for the arrangement and operation of the productions that are classified by degree of fire danger to categories A and B. These requirements are stated in detail in the construction, fire and sector regulations and standards.

The production of ammonia, methanol and nitric acid are the most dangerous in the nitrogen industry since it is possible that ammonia, hydrogen sulfide, nitric oxides, carbon monoxide and other combustible and toxic gases could be released into the working area. When these gases are emitted into the atmosphere, when there is insufficient sealing of the apparatus and pipelines, and especially when there are accidents, strong gas content generally develops in the working rooms and the adjacent territory. Therefore, hermetic sealing of the apparatus and purification of the production wastes are given a lot of attention.

The quantity of emissions of harmful substances into the atmosphere must not exceed the norms indicated in table V-3. If it is not possible to guarantee the required degree of purification of

the gases of harmful admixtures, the height of their discharge should be selected so that the hazards are scattered to the maximum permissible concentrations. In order to protect the air of the populated areas from harmful production emissions, the agencies of the State Sanitary Inspection have set up sanitary protected zones (minimum permissible distances from the populated areas to the industrial enterprises). The sizes of the sanitary-protected zones for the nitrogen enterprises are presented in table V-3.

In order to guarantee the normal working conditions at the nitrogen enterprises, correct classification of the productions to the appropriate group of production processes according to sanitary characteristics is very important. In order to facilitate this work and to exclude possible errors, table V-1 presents a unified classification of the groups of production processes for enterprises of the nitrogen industry.

Table V-3 also presents the maximum permissible concentrations of harmful substances in the waste waters and basic indicators which characterize the toxicity of the productions of the nitrogen industry.

The explosion danger of the nitrogen industry enterprises is mainly determined by the use in these productions of hydrogen which has a low lower level and a broad range of explosiveness (4-75% vol.).

It is also necessary to take into consideration that the minimum energy of ignition of hydrogen-air mixtures is very low, only 0.019 mJ (i.e., 10-fold lower than the energy needed to ignite acetylene. This is 14-fold less energy than that required to ignite methane, 30-fold less energy than ignition of methanol, and 400-fold less than carbon monoxide). Practically any spark is capable of igniting the hydrogen-air mixture. Oxygen-hydrogen mixtures are even more dangerous.

Almost all the combustible gases used in the nitrogen industry are good dielectrics which create high static electricity potentials when they move in pipes and flow from pipes. A danger of gas

ignition develops as a result.

TABLE V-1. CLASSIFICATION OF PRODUCTION BUILDINGS AND STRUCTURES ACCORDING TO DEGREE OF FIRE DANGER^{1,3,4,5,7-10}

Object	Category of fire danger	Degree of fire-resistance of buildings (no lower)
Production of synthetic ammonia and methanol		
Crushing unit for coke preparation	B	II
Section of preparation, drying and supply of coal	B	II
Gas generator station	D	II
Section of purification from dust of gases from gas generator section	A	II
Gas blowing station of coking, natural, semiwater and water gases	A	II
Section of purification of coking gas from naphthalin	A	II
Pumping station with arsenic-soda wet sulfur purification (on the condition that the absorber is on the street)	E	II
Section of regeneration of arsenic-soda solution	E	II
Warehouse of sulfur in section of sulfur purification	B	II
Section of dry sulfur purification of coking, semiwater and water gases	A	II
Section of preparation of purification mass for dry sulfur purification of gases	C	II
Section of purification of coking gas from heavy hydrocarbons by coal and "organic" sulfur purification	A	II
Section of preparation and regeneration of ammonium sulfide and production of sulfur	B	II
Section of conversion of natural gas	A	II
Section of CO conversion	A	II
Oxygen-blowing section	B	II
Air-blowing section	E	II
Section of air compression	E	II
Sections of compression of water, semiwater, coking, natural gases and nitrogen-hydrogen mixture	A	II
Pumping sections of purification of coking, water, semiwater and converted gases of CO, (water, water-ammonia, alkali, ethanol-amine purification with regeneration of ethanol-amine solutions) when there are scrubbers in the room	A	II
The same, but with scrubbers outside the room on the condition of the installation of reliable cut-offs	E	II
Section of alkali regeneration room of tanks for spent alkali	A	II

remaining rooms, including unit for preparation of milk of lime	E	II
Expander and unit of degasification water	B	II
Section of coking gas separation	A	II
Section of washing converted gas of CO by liquid nitrogen	A	II
Section of nitrogen compression	E	II
Section of air separation	B	II
Section of air purification from CO ₂	E	III
Ammonia-cooling unit	B	II
Pumping section of copper-ammonia purification when scrubbers are in the room	A	II
The same, but with scrubbers outside room (on the condition of installation of reliable cut-offs)	E	II
Section of regeneration of copper-ammonia solutions	B	II
Unit for preparation of copper-ammonia solution	B	II
Pumping section of fine purification of gas from CO ₂ when scrubbers are in the room	A	II
The same, but with scrubbers outside the room (on the condition that reliable cut-offs are installed)	E	II
Section of ammonia synthesis	A	II
Section of methanol (raw material) synthesis	A	II
Warehouse for liquid ammonia storage	B	II
Unit for preparation of aqueous ammonia from blowing gases of ammonia production from ammonia	A	II
	B	II
Warehouse of aqueous ammonia	B	II
Warehouse of methyl alcohol	A	I
Shop of methanol rectification (sections of de-etherization, permanganate purification, distillation, etc.)	A	II
Room for filling cylinders with ammonia	B	II
Room for filling cylinders with hydrogen and nitrogen-hydrogen mixture	A	II
Room for filling cylinders with oxygen	C	II
Warehouse of oils and their regeneration	C	II

Production of diluted nitric acid at atmospheric pressure

Station for collecting and filtering air	E	III
Contact section	B	II
Section of acid absorption	E	II
Section of alkali absorption	E	II
Section of inversion	E	II
Section of preparation for milk of lime or dissolving of soda	E	III
Warehouse of lime or soda	E	III

Production of diluted nitric acid under pressure

Station for collecting and filtering air	E	III
Section of air compression	E	II
Section of conversion and absorption	B	II

Weighing room of liquid ammonia	B	II
Section of turbocompression of nitrous gases	E	II
Section of absorption located outside building	E	II
Section of acid bottling	E	II
Warehouses of diluted nitric acid	C	II
Production of concentrated nitric acid by method of direct synthesis		
Contact section	B	II
Oxidation section	E	II
Section of nitro-oleum absorption	C	II
Autoclave section	C	II
Warehouse of concentrated nitric acid	C	II
Section of preparation of blend and warehouse for its storage	C	II
Concentration of diluted nitric acid with help of 92-94% H ₂ SO ₄		
Production structure	C	II
Section of absorption of exhaust nitrous gases	C	II
Section of preparation of blend	C	II
Warehouse of blend and loading-unloading station	C	II
Shop of sulfuric acid concentration		
Air-blowing section	E	III
Section of concentrators and electric filters	B	II
Mazut section	B	I
Warehouse of diluted sulfuric acid	E	III
Warehouse of oil of vitriol	E	II
Substation of electric filters	E	III
Production of ammonium nitrate		
Section of neutralization	B	II
Evaporation section	C	II
Section of crystallization, granulation (excluding room of evaporation equipment), drying and cooling	C	II
Packing station with platform	C	II
Warehouse of ammonium nitrate	C	II
Section of preparation and warehouse of inorganic additives	E	III
Production of carbamide		
Section of synthesis and distillation	B	II
Section of compression of carbon dioxide	E	II
Section of pumps for pumping liquid ammonia and ammonium carbonate solutions	B	II
Oil point	C	II
Section of reprocessing carbamide solutions	E	II
Granulation towers	E	II

Section of packaging	C	II
Warehouse of finished product	C	II
Gas holder of carbon dioxide	E	II
Central control point	E	II
Warehouse of empty packages	C	II

Auxiliary and utility rooms for all productions

Mechanical workshop	E	II
Transformer box	C	II
Water pumping station	E	II
Electric substations	C	II
Shop laboratories	C	II
Central control panels	E	II
Room for distribution points and automatics	E	II
Ventilation exhaust chambers	By categories as for production room	

Note: The category of fire danger is presented according to SNIIP II-M-2-62; the degree of fire-resistance of the buildings is according to SNIIP II-A.5-62.

Table V-2 presents the limits of explosiveness of gases, vapors and dust, and table V-4 presents the limits of explosiveness of gas mixtures.

One should also bear in mind that explosions of solids are possible at the nitrogen industry enterprises. Thus, the settling of ammonium nitrate on the blades of the rotors or walls of the nitrous fans (most often when there is too long of a time of firing the contact apparatus or when there is a break in the contact grids) can result in an explosion if the fans are not washed with water in time.

Accumulation of ammonium nitrite in the towers for absorption of nitrous gases by solutions of ammonium carbonate or ammonia water is especially dangerous. Explosions occur if sprinkling stops.

Ignition and explosions are possible in other productions of the nitrogen industry, in particular, in the shops of ammonium nitrate (see section on ammonium nitrate for more detail). It should be taken into consideration that mixing of liquid nitric oxides with ammonia can also result in an explosion.

TABLE V-2. BASIC PHYSICAL-CHEMICAL AND FIRE-EXPLOSION-DANGEROUS PROPERTIES OF RAW MATERIALS, AUXILIARY SUBSTANCES AND PRODUCTS OF THE NITROGEN INDUSTRY^{1,2,5,11}

Substance	Use and role in nitrogen industry	Characteristics	Limit of explosiveness, vol. %		Temperature, °C		
			in mixture with air	in mixture with oxygen	flash point	ignition	spontaneous combustion
Ammonia NH ₃	Final product; raw material for production of nitric acid and nitrogen fertilizers	Colorless combustible gas with sharp smell; with air and oxygen forms explosive mixtures	15-28	15-69	-	-	650
Nitric acid HNO ₃	Final product; diluted acid raw material for production of concentrated nitric acid nitrogen and complex fertilizers	Colorless liquid with caustic smell; incombustible, strong oxidizer	Does not form explosive mixtures with air and oxygen		Not burn		
Sodium nitrate NaNO ₃	Side product of production of diluted nitric acid; produced as commercial-grade product (fertilizer)	Colorless, incombustible powder; promotes spontaneous combustion of combustible materials	-	-	-	-	-
Nitrogen N ₂	Included in gases for production of ammonia and methanol	Colorless gas without smell (incombustible) (see also vol. I, p. 29, 48, 54, 61, and following)	-	-	-	-	-
Ammonia water (25% aqueous solution of ammonia)	For purification of production gases from CO ₂ ; produced as commercial-grade product	Colorless, transparent incombustible liquid with sharp smell of ammonia; fire-danger accepted for ammonia (see above)	15-28 (for ammonia)	15-79 (for ammonia)	-	-	650
Ammonium nitrate NH ₄ NO ₃	Final product (fertilizer and technical-grade salt)	Solid crystalline substance of white color	Not set		Temperature of breakdown depends on		

						heating con- ditions of nitrate and presence of admixture	
Acetylene C_2H_2	Product of methane pyrolysis; admixture in coking gas	Colorless explosive gas with characteristic sharp smell; with copper silver, mercury and their salts forms very explosive acetylides. At 1.4 atm. and more and 500°C (and higher) breakdown with explosion possible	2.1 (all mixtures with acetylene content above the indica- ted quantities are explosive)	2.8			335
Benzene C_6H_6	Vapors-admixture in coking gas	Colorless transparent easily igniting liquid; with air and oxygen the vapors form explosive mixtures	1.1-9.5	-	-11	-	540
Hydrogen H_2	Raw material for production of ammonia, methanol; admix- ture in original gas for pro- duction of carbamide	Colorless combustible gas without smell. With air and oxygen forms ex- plosive mixtures. Mix- ture with chlorine(1:1) explodes in light; with fluorine, H ₂ is connected with explosion even in darkness; mixture with oxygen (2:1)detonating gas	40-75	40-94	-	320	510
Carbon dioxide CO_2	Raw material for production of carbamide; included in composition of gases of dis- tillation and production gases; obtained during their purification from CO_2	Colorless odorless gas	-	-	-	-	-
Sodium hydro- xide NaOH	In alkali purification of gases for production of ammonia and methanol	White transparent very hygroscopic mass; also 42% and 50% aqueous so- lutions are produced	-	-	-	-	-

Oxygen O ₂	Obtained by separating air by method of deep cooling. Use in conversion of hydrocarbon gases, gasification of solid fuel, in direct synthesis of nitric acid, in production of carbamide (introduced into carbon dioxide to prevent corrosion)	Colorless incombustible, gas which actively maintains combustion. With combustible gases, vapors of combustible liquids and dust forms explosive mixtures in broad range of concentrations. When O ₂ contacts oil in compressor cylinders and other equipment, rapid increase in temperature occurs, intensive oxidation and evaporation of oil, formation of explosive mixtures of oil vapors with oxygen, and explosion occur. Clothing saturated with gaseous oxygen ignites from any flame source (match, cigarette). Liquid oxygen is extremely dangerous: in contact with organic substances it forms explosive mixtures (when oxygen contacts asbestos packings and fillings made of cotton, paraffin and other organic substances, fires and explosions are possible). Oils and fats in a medium of compressed oxygen ignite spontaneously with an explosion. Oily clothing in a medium of oxygen ignites in the absence of a flame source						
Mono-ethanol-amine NH ₂ CH ₂ -CH ₂ OH Carbamide (NH ₂) ₂ CO Methane CH ₄	20% solution--selective absorber of CO ₂ in purification of gases for production of ammonia and methanol Final product (fertilizer, feed additive, original substance for syntheses) Admixture in gases for production of ammonia, methanol, carbamide (to 1%)	Colorless oily combustible liquid with smell of ammonia; vapors form with air and oxygen explosive mixtures Solid combustible crystalline substance Colorless combustible explosive gas without smell (see also Vol. 1, p. 33 and following, 50, 71 and following)	Not set		95	-	450	
					182	223	640	
			4.9-1.54	5.1-6.1	-	600	537	
Methanol CH ₃ OH	Final product	Colorless easily igniting liquid; in contact with Na ₂ O or Cr ₂ O ₃ ignites; with air and oxygen, vapors form explosive mixtures	5.5-36.5	-	8	-	464	
Arsenous acid anhydride As ₂ O ₃	In arsenic-soda sulfur purification of gases in production of ammonia and methanol	Crystalline or amorphous substance of white color	-	-	-	-	-	

Carbon monoxide CO	Contained in gases for production of ammonia and methanol and in carbon dioxide	Colorless combustible gas; with air and oxygen forms explosive mixtures	12.5-74	15.5-94	-	590	610
Nitric oxides	Intermediate products in production of nitric acid	Gases, mainly oxide and dioxide of nitrogen	-	-	-	-	-
Carbon disulfide CS ₂	Admixture in gases for production of ammonia and methanol	Colorless easily igniting liquid; with air and oxygen vapors form explosive mixtures	1-50	-	-43	-	90
Carbon oxysulfide COS	The same	Colorless combustible gas; forms explosive mixtures with air and oxygen	11.9-28.5	-	-	-	-
Hydrogen sulfide H ₂ S	"	The same	4.3-46	-	-	-	246
Sulfuric acid H ₂ SO ₄	Water-removing substance for concentrating nitric acid	Caustic incombustible liquid; concentrated H ₂ SO ₄ causes spontaneous combustion of combustible substances	-	-	-	-	-
Hydrogen cyanide HCN	Admixture in coking gas	Colorless mobile easily igniting liquid	5.6-40	-	-18	-	538

TABLE V-3. TOXIC PROPERTIES OF RAW MATERIAL, AUXILIARY SUBSTANCES AND PRODUCTS OF NITROGEN INDUSTRY 1,2,6,11

Substance	Toxic properties (effect on human body)	Maximum permissible concentrations			Brand of protective gas mask	Group of product. process (from SN 245-63)	Width of sanitary protective zone, m	
		In air of working zone of production rooms mg/m ³	In atmospheric air of populated areas mg/m ³	In water of reservoirs of sanitary general water use mg/l				
Ammonia NH ₃	Causes acute irritation of mucous membranes, lachrymation, burns of mucous membranes, dyspnea. Liquid ammonia burns the skin	20	0.2	0.2	2.0 (for nitrogen)	Filtering type KD or M	IIe	500
Nitric acid HNO ₃	Toxic, causes severe burns of skin, mucous membranes; vapors irritate respiratory passages	5 (in conversion for N ₂ O ₅)	0.4	-	Not permitted	Filtering brand V	IIIf	1000
Ammonium nitrate NaNO ₃	Solution acts as irritant and as caustic on integument	-	-	-	-	Antidust respirator	IIe	500
Hydrogen sulfide H ₂ S	Strong poison, with high concentration causes loss of consciousness and death	10	0.008	0.008	-	Filtering brand V	IIIf	1000
Sulfuric acid H ₂ SO ₄	Causes skin burns, vapors irritate and sear mucous membranes	2	0.3	0.1	Not permitted	The same	IIIf	1000
Hydrogen cyanide HCN	Strong poison, causes rapid dyspnea (paralysis)	0.3	-	-	-	Filtering brand V	IIIf	1000

Arsenous anhydride	of respiratory passages) Strong poison, causes acute and chronic poisoning	0.3	Not set	0.003	0.05 (for arsenic)	Filtering Brand A	IIIa	1000
As ₂ O ₃								
Carbon monoxide	Poisoning substance, causes oxygen deficiency resulting in dyspnea	30	3.0	1.0	-	Filtering Brand SO	IIf	-
CO								
Nitric oxides	Causes general aethenia, vertigo, numbness of legs. In strong poisoning--nausea. Delayed action; lethal outcome possible	5 (in conversion for N ₂ O ₅)	0.085	(in conversion for NO ₂)	-	Filtering mark V	IIf	1000
Carbon disulfide	In large concentrations acts like narcotic; in small concentrations causes sickness of the nervous system	10	0.03	0.01	1.0	Filtering Brand A	IIf	1000
CS ₂								
Carbon oxysulfide	Acts on central nervous system	10	-	-	-	Filtering Brand V	IIf	1000
COS								
Monoethanolamine	Causes skin irritation	3	-	-	1.0	-	-	-
NH ₂ CH ₂ CH ₂ OH								
Caffeine	The same	-	-	-	-	Antidust respirator	IIf	500
(NH ₂) ₂ CO								
Methane	Narcotic in large concentrations	300	-	-	-	Insulating (oxygen) or hose	Ia	
CH ₄								
Methanol	Strong poison; when taken internally causes blindness and death. Lethal dose 30 g	50	-	-	In limits permissible	Hose	IIf	1000
CH ₃ OH								

Sodium hydroxide NaOH	Causes burns; dissolves protein substances with formation of scabs and scars; especially dangerous when sodium hydroxide falls into the eyes	0.5	-	-	-	by calculation for content of organic substances, and for BPK indicators and dissolved oxygen	Antidust respirator	IIf	1000
Oxygen O ₂	Nontoxic; shortage of O ₂ results in decrease in intensity of oxidation processes in cerebral tissue and disorder in central nervous system. With lengthy inhalation of pure O ₂ , death occurs because of development of massive pleural edema	-	-	-	-	-	-	Ia	50
Acetylene C ₂ H ₂	Narcotic; during inhalation causes dyspnea because of reduction in oxygen content in air	300 (in conversion for C)	-	-	-	-	Filtering Brand A	IIf	500
Benzene C ₆ H ₆	Narcotic; with acute poisoning loss of consciousness possible. Liquid benzene irritates skin	20	1.5	0.8	0.5	-	the same	IIf	1000
Hydrogen H ₂	Inert; with high concentrations causes dyspnea Narcotic effect manifest at high pressures	-	-	-	-	-	Insulating (oxygen or hose)	Ia	50
Carbon dioxide	Narcotic and suffocating (displaces oxygen from	-	-	-	-	-	the same	Ia	50

CO ₂	respiratory zone); in small concentrations stimulates, in large concentrations inhibits respiratory center	-	-	-	-			
Nitrogen N ₂	Physiologically inert; with shortage of oxygen in air causes dyspnea	-	-	-	-	Insulating (hose or oxygen) Filtering brand KD or M	Ia	50
Ammonia water (25% aqueous so- lution of ammonia)	Causes acute irritation of mucous membranes, lachrymation, dyspnea	20 (for ammonia)	0.2	0.2	2.0 (for nitrogen)		IIe	300
Ammonium nitrate NH ₄ NO ₃	Causes burns and irritation of skin, especially when there are cracks and small wounds	-	-	-	-	Antidust	IIe	500

Note: The current width of the sanitary protective zone is pinpointed for certain substances.

TABLE V-4. FIRE-, EXPLOSION-DANGEROUS AND TOXIC PROPERTIES OF GAS MIXTURES USED IN THE NITROGEN INDUSTRY^{3,12}

Gas	Composition Components	Content vol. %	Use in nitrogen industry	Limits of explosiveness in air, vol. %	Fire-, explosion-dangerous and toxic properties	Brand of protective gas mask
Natural (in composition corresponds to gas of Stavropol' field) Coking gas for synthesis	CH ₄	97.6	Basic raw material in production of gases for synthesis of ammonia and methanol	5.0-16.0	In large concentrations has narcotic effect Forms explosive mixtures with air and oxygen Has general toxic and narcotic effect Forms explosive mixtures with air and oxygen	Insulating hose, oxygen (with O ₂ content less than 16 vol. %)
	C ₂ H ₆	0.25				
	C ₂ H ₈	0.15				
	CO ₂	0.5	Raw material for production of gas for ammonia synthesis	4.1-73.0		
	N ₂	1.5				
	H ₂	57-61				
	N ₂	No more than 5.0				
	O ₂	No more than 0.8				
	CO	5.0-8.0				
	CH ₄	24-27				
	C _n H _{2n}	1.8-3.2				
	C ₂ H ₂	0.1-0.5				
	H ₂ S	0.3-1.4				
CO ₂	No more than 3.0					
C ₆ H ₆	No more than 4 g/m ³					
C ₁₀ H ₈	0.2 g/m ³					
NO	0.4-0.8 cm ³ /m ³					
Coking enriched fuel (rich gas) (GOST 8331-57)	(by permanganate method)		Waste in separation of coking gas by method of deep cooling; returned to coking-chemical plant for burning	5.25-19.5	The same	CO
	CO ₂	0.98				
	O ₂	1.01				
	C ₂ H ₆	1.74				
	CO _n	18.48				
	H ₂	5.59				
CH ₄	57.48					
N ₂	14.72					

Converted gas (after steam-oxygen conversion of natural gas and CO conversion under pressure 1.7 atm)	CO ₂	22.59	For synthesis of ammonia after purification and doxing of nitrogen	4.1-5.1	Has general toxic effect	CO
	CO	3.75				
	H ₂	72.08				
	N ₂	0.48				
	Ar	0.68				
Converted gas (after steam-oxygen conversion of natural gas CO conversion under pressure 20 atm)	CH ₄	0.42	The same	4.15-68	The same	CO
	CO ₂	24.30				
	CO	2.46				
	H ₂	70.18				
	N ₂	0.52				
Converted gas (after high-temperature conversion of casing-head gas by oxygen and CO conversion under pressure of 30 atm)	Ar	0.80	"	4.1-73	"	CO
	CH ₄	1.74				
	CO ₂	25.90				
	CO	3.75				
	H ₂	65.76				
Converted gas (after second stage of CO conversion at 20 atm. on low-temperature catalyst)	N ₂	3.40	"	4-73.5	"	CO
	Ar	0.81				
	CH ₄	0.38				
	CO ₂	17.75				
	CO	0.28				
Nitrogen-hydrogen mixture	H ₂	61.34	For ammonia synthesis	Not set	Has narcotic effect Forms explosive mixtures with air and oxygen	Insulating (oxygen or hose)
	N ₂	20.19				
	Ar	0.26				
	CH ₄	0.18				
	H ₂	-				
Fresh synthesis--gas	N ₂	74-75	For methanol synthesis	the same	Has general toxic effect	CO
	N ₂	24.5-25				
	CH ₄	0.3-1.2				
	Ar	to 0.3				
	H ₂	67-69				
	CO	28-30				

CO ₂	0.5-1.5
Ar	0.3-0.4
CH ₄	0.4-0.7
N ₂	0.5-1.0

Forms explosive mixtures with air and oxygen

In designing, building and operating nitrogen industry processes, one should be guided by the data presented in tables V-1-V-4, the standardized materials indicated, as well as other active regulations, norms and instructions for accident prevention.

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