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PRODUCTION AND PHYSICAL METALLURGY
OF PURE METALS --- PART I

-- USSR --

by V. S. Yemel'yanov, A. I. Yevstukhin and G.A. Leont'yev

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PRODUCTION AND PHYSICAL METALLURGY
OF PURE METALS -- PART I

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Introduction

This is a translation of an Introduction written by V. S. Yamel'yanov and A. I. Yevstyukhin, the editors of Metallurgiya i Metallovedeniye Chistykh Metallov (Production and Physical Metallurgy of Pure Metals), No.1, Moscow, 1959, pages 5-6.

In the present collection (Volume 1) all scientific works of the Chair of Metallurgy and Metallography carried out during the last 5 to 7 years are published. They concern the preparation of metals with a high degree of purity, the preparation of alloys from them, and the study of their properties. These works were not published heretofore, but the majority of them were submitted at scientific conferences of MIFI* teachers in 1955-1957. Works published in this collection are experimental studies and characterize one of the scientific research features in the work of this Chair. This trend, as will be easily seen from the works published in this collection, is dedicated to the problem of working out methods for the preparation of pure metals, which methods at the present time are of great importance in the development of a series of branches of new technology. A series of works of this Chair during 1958 which cover the same problems will be published in Volume 2 of the present collection.

Twenty-one works were included in the collection. The first two concern the preparation of thorium by the electrolysis of fused salts. They are a continuation of works already partially published by the Chair on this subject (Atomic Energy Nos. 4 and 5, 1956.)

The following four works concern the development of a new and very promising method for the preparation of pure metals by thermal dissociation.

The seventh work in the collection refers to one of the previous works concerning an iodide preparation of zirconium and relates to research on a method for the regeneration of zirconium and iodide in the process of iodide refining.

In the eighth work a review is presented covering the present state of beryllium metallurgy and the results of research carried on by the Chair with reference to a study of a magnetic thermic process for beryllium fluoride reduction, which is one of the most important methods of production

*Moscow Physics and Engineering Institute

of this metal.

The following two works are devoted to a description of the design and experimental operation of vacuum furnaces for melting and casting pure metals and alloys, MIFI-9-2 and MIFI-9-3, as designed by the laboratory of the Chair. Besides our laboratory, these furnaces have found a wide application in a series of scientific research and plant laboratories of the Soviet Union. They were found to be very convenient for a scientific research work with pure metals.

Beginning with the eleventh, the next seven works are devoted to the research on, and study of, alloy properties based on iodide zirconium. These works are of interest in connection with the selection of corrosion-resistant and refractory alloys for nuclear reactors.

One work relates to study of the corrosion properties of zirconium and its alloys. Based on kinetic and electro-graphic studies, it analyzes and discusses the mechanics of the oxidation of zirconium and its alloys, and evaluates the influence of alloying components on corrosion resistance.

A work containing a study of mechanical properties of binary and ternary alloys of zirconium with tantalum and niobium is partly a continuation of already published works of the Chair on this subject (Atomic Energy No. 1, 1957; No. 2, 1958).

A work containing a study of the state diagram in a system zirconium-niobium had already been published (Atomic Energy No. 2, 1957; No. 2, 1958), but is given here in greater detail. Works studying diffusion characteristics of zirconium and its tin-containing alloys is a continuation of a previous work of the Chair on the same subject as presented in 1957 at the All-Union Conference for use of isotopes, (Transactions of All Union-Conference for Use of Isotopes, AS USSR, 1957).

Four works of the collection are devoted to somewhat different but quite current problems of modern metallography. One of them concerns the chemistry of metallic alloys. It contains a review of published data concerning changes observed when chemical compounds are formed in metallic systems.

The other works are devoted to a study of diffusion characteristics of alloys based on iron, cobalt, and molybdenum by use of radioactive isotopes.

In its entirety, the collection will be of a considerable interest to a wide circle of Soviet readers, among them scientific workers and engineers, students and graduates, workers in the shops and plant laboratories, planning organizations and scientific research institutes.

The Editors

INVESTIGATION OF THE ELECTROLYTIC PRODUCTION OF THORIUM

This is a translation of an article written by A. I. Yevstyukhin, V. S. Yemel'yanov, and G. A. Leont'yev in Metallurgiya i Metallovedeniye Chistykh Metallov, No. 1, Moscow, 1959, pages 7-35.

Introduction

The electrolysis of fused salts is one of the basic methods for preparing metallic thorium of high purity. This method permits an additional or ultimate refining of thorium from other rare earth elements which accompany it in nature and which can be separated by other methods only with considerable difficulty. During electrolysis, their separation takes place because of the voltage difference of dissociation between thorium and metals of the lanthanide series. As an initial salt for the electrolysis of thorium, ThF₄ is taken (its preparation is simple, and it is not hygroscopic). An equimolecular mixture of sodium and potassium chlorides is taken as a solvent for depressing the fusing temperature of the electrolyte, as in analogous cases. In the initial period of electrolysis of thorium, the electrolyte is a ternary chloride-fluoride system, NaCl-KCl-ThF₄. During the process of protracted and continuous electrolysis, the system becomes more complex because of an accumulation in the electrolyte of NaF and KF, and the mechanics of the process of electrolysis change considerably. A short description of thorium preparation in the U.S.S.R. was published in 1955 (1).

State diagrams of systems entering in the multicomponent thorium electrolyte were partially published in 1956 (2, 3). The mechanics of thorium electrolysis have, until now, been scantily studied and are not to be found in the literature, although this method has been in industry for a considerable period.

The present work describes the results of a study of thorium electrolysis from a system NaCl-KCl-ThF₄, and an outline is given on the mechanics of the process.

Review of Literature

Four important metals are produced on an industrial scale by electrolysis of their fused salts; aluminum, magnesium, calcium and sodium. The process runs at a tempera-

ture of molten electrolyte somewhat higher than the melting point of the metals being produced. Therefore, these metals are deposited on a liquid cathode and are extracted from the bath in a molten state. In such cases where the melting point of the metal is higher than the temperature of the fused electrolyte (as in the case of refractory rare metals), the metal is deposited on the cathode in the shape of solid crystals. Dendritic crystals of the metal, when extracted from the bath, are covered by a film of congealed electrolyte.

After pulverization of the cathode deposits and separation of the salts from metal crystals by means of water, a powder is obtained which is directly usable in powder metallurgy.

According to data in the literature, the following powders of more than twenty metals have been obtained by this method: thorium (4) - (6), uranium (7) - (10), tantalum (11) - (14), niobium (15) - (16), titanium (17) - (18), zirconium (19) - (21), chromium (22) - (24), tungsten (25) - (28), molybdenum (29) - (30), beryllium (21) - (37), silver (38), copper (39), platinum (39), aluminum (40) - (44), cobalt (45), nickel (46) - (47), iron (48) - (50), manganese (39) - (51), bismuth (52), and other metals. Some of these metals, as for instance thorium, uranium, tantalum, and beryllium, are already being produced by this method on an industrial scale.

The electrolysis of fused salt using a solid cathode has a series of advantages as compared to electrolysis with a liquid cathode. For instance, the electrolyte temperature during electrolysis of fused salts using a solid cathode is considerably lower than that during electrolysis with a liquid cathode. This lower temperature means a saving in electric power. The deposition of metals on a solid cathode takes place at temperatures considerably lower than their melting points, and, therefore, the possibility of impurities contaminating the metal being deposited because of melting of additives, is less probable than in the case of electrolysis with a liquid cathode.

Electrolysis with a solid cathode is carried out at considerably higher current densities (because of a very large surface of crystals being deposited on a solid cathode), as compared with the electrolysis with a liquid cathode. This effect means an intensified electrolysis due to the use of high current density.

Metal powders prepared electrolytically from fused salts are characterized by high purity and are usable for powder metallurgy without being granulated or pulverized. These powders, as a rule, are coarse. They are more corrosion-resistant and oxidationproof than finely dispersed metal

powders obtained by other methods (precipitation from aqueous solution, the hydrate process and others).

All mentioned advantages of using low-temperature baths for obtaining metals in the solid state have, however, a serious drawback, owing to the fact that crystals of metal deposited on the cathode are mixed with electrolyte salts.

When processing such cathode deposits, difficulties arise during the separation of electrolyte salts from metal crystals. And although the difficulties are successfully eliminated by enriching cathode deposits on concentration tables, this method, nevertheless, has not found wide acceptance.

Although this method has been in general use for twenty-five years, it has been accepted only for the production of uranium, thorium, tantalum, and beryllium, which are produced in relatively great quantities. At the same time, electrolysis using liquid cathodes is of great industrial importance in the production of aluminum, magnesium, sodium, and other alkali and alkali earth metals.

Such a difference in the importance and acceptance of this method is explained by the fact that the electrolysis with a liquid cathode does not involve a separation of the solid powder from electrolyte salts. Fused salt electrolysis with a liquid cathode has a 95 to 98 percent metal yield, whereas electrolytic separation with a solid cathode shows direct metal yield of approximately half of the above quantity.

After long experimental work with several metals, and in particular thorium, the authors have established that the metal yield in electrolysis with a solid cathode is directly dependent on the shape of crystallization of metal on the cathode.

If finely dispersed metal is deposited on the cathode, its yield will be low, since a fine powder is oxidized more rapidly by anode gases (chlorine and oxygen), both in the bath and when leaching it with water.

If metal is deposited on the cathode in the form of large crystals, they are less oxidized by anode gases and are easier to leach with water from the electrolyte, and the metal yield is considerably higher.

The mechanics of the electrolysis of fused salts with a solid cathode, and conditions for obtaining large metal crystals have not been sufficiently studied.

In particular, a very important question has not been solved; why, during electrolysis of fused salts with a solid cathode, metals are deposited on the cathode, not in compact form as during electrolysis from water solution, but as unbonded, dendritic crystals, which, after leaching

of electrolyte salts, form a powder metal?

At first sight, one would think that the high temperature of the bath should promote cohesion of the crystals and formation on the cathode of compact deposits. However, attempts of many researchers (53) - (55), including the authors of the article (56 - (57), in forming compact deposits of metals by electrolyzing fused salts with a solid cathode, were not crowned with success.

Under all conditions tested in this case, loose dendritic crystals are deposited on the cathode, the size of which depends on the electrolytic regime and the contents of the electrolyte.

The research of electrolytic conditions under which a coarse crystalline thorium powder is obtained was one of the aims of the present work.

Experimental Part

Methods of Investigation

Experiments on thorium electrolysis from the chloride-fluoride system NaCl-KCl-ThF₄ were carried out in an installation with self-compacting cathodes, as described on page 36 of the present collection. Initially, cathodes were sunk into the electrolyte at definite and constant depths; later they were exchanged for rising cathodes, which permit the preparation of more metal during an experiment.

Together with the growing deposits, the cathodes were gradually lifted from the bath. Crystals of metallic thorium extracted from the electrolyte were coated with a film of congealed electrolyte, which prevented them from oxidizing. In the course of experiments, changes in electrolyte content during the electrolytic process were studied, as well as the influence of basic technological factors on yields with reference to current, to metal, and to the quality of metal obtained.

For a better comparison of results obtained, the following methods in carrying out the electrolysis and the processing of cathode deposits. For each experiment, a material balance was drawn up. For this purpose, before the beginning of a test and after its termination, all materials introduced into the bath and the products obtained were analyzed and weighed. The crucible was weighed so as to establish the quantity of electrolyte which was adsorbed by it after each test.

Judging from the weight difference of materials introduced and products obtained, the weight of the anode

gases was determined and also their approximate composition.

To determine the quantity of pure metal in the cathode deposit, a small portion of the latter was dried, pulverized and analyzed. The remainder of the cathode deposits was wetted with water and pulverized while wet. Simultaneously, leaching of the powder from the electrolyte salt was carried out, as well as sorting of the powder into fractions: coarse, medium and fine. Washed by water, alcohol and ether and dried, the metal powder was analyzed on a screen and tested for pure metal content. For this purpose was used a device shown schematically in Fig. 1.

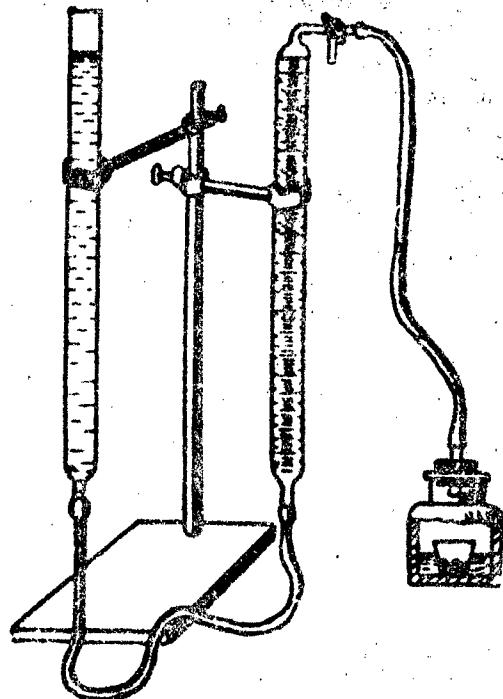


Fig. 1. Diagram of a device for the determination of metal activity, depending on the quantity of hydrogen liberated.

For the screen analysis of the relatively small quantities of powder obtained after each experiment, a special device with a collection of screens was designed (Fig. 2).

By means of the data of the material balance, the yield with reference to the current was calculated as a ration (in percent) of the quantity of pure metals in the dry cathode deposits and of the theoretical quantity of metal which should have been deposited by the quantity of electricity passed through.

The yield with reference to the metal or substance was determined as the percent of a quantity of conditioned metal powder to the quantity of metal fluoride charged in the bath, taking into consideration the difference between the metal concentration in the electrolyte and metal losses resulting from impregnation of the crucible by the electrolyte.

Electrolyte Contents

Changes in Electrolyte Contents According to data of Chemical Analyses. In the course of the electrolysis of the system $\text{NaCl}-\text{KCl}-\text{ThF}_4$, a continuous change in electrolyte content is going on. At the anode, chlorine is formed predominantly. Fluorine accumulates in the electrolyte and enriches it, converting the chloride-fluoride system into a purely fluoride system. The newly formed components, NaF and KF , bind thorium fluoride charged into the bath into complex fluoride compounds of the type $\text{Na}_x\text{Th}_y\text{F}_{x+4y}$ and

$\text{Na}_x\text{Th}_y\text{F}_{x+4y}$. After being completely tied in fluoride complexes of thorium, NaF and KF accumulate as free components.

Typical chemical analyses are given of the elementary electrolyte content at the beginning of the electrolysis and in the course of the whole process cycle of the bath in Table 1.

Data of elementary analyses, recalculated into mols of corresponding compounds, are shown in Table 2.

When calculating the quantity of chlorine found, it was conditionally distributed among sodium and potassium, whereas the remainder of the sodium and potassium was supposed to be attached by fluorine.

Thorium was assumed to be compounded with fluorine. A portion of sodium and potassium fluorides, corresponding to the quantity of soluble fluorine, is not bound into complex compounds, but one cannot determine separately the accurate quantities of sodium and potassium fluorides from the data of chemical analyses. Therefore, Table 2 shows the composition of electrolyte in molecules of simple fluorides. One must also keep in mind that a part of the simple fluorides is bound into complex compounds.

As it appears in Table 2, the results of such calculations are fairly accurate, a fact which is confirmed by a

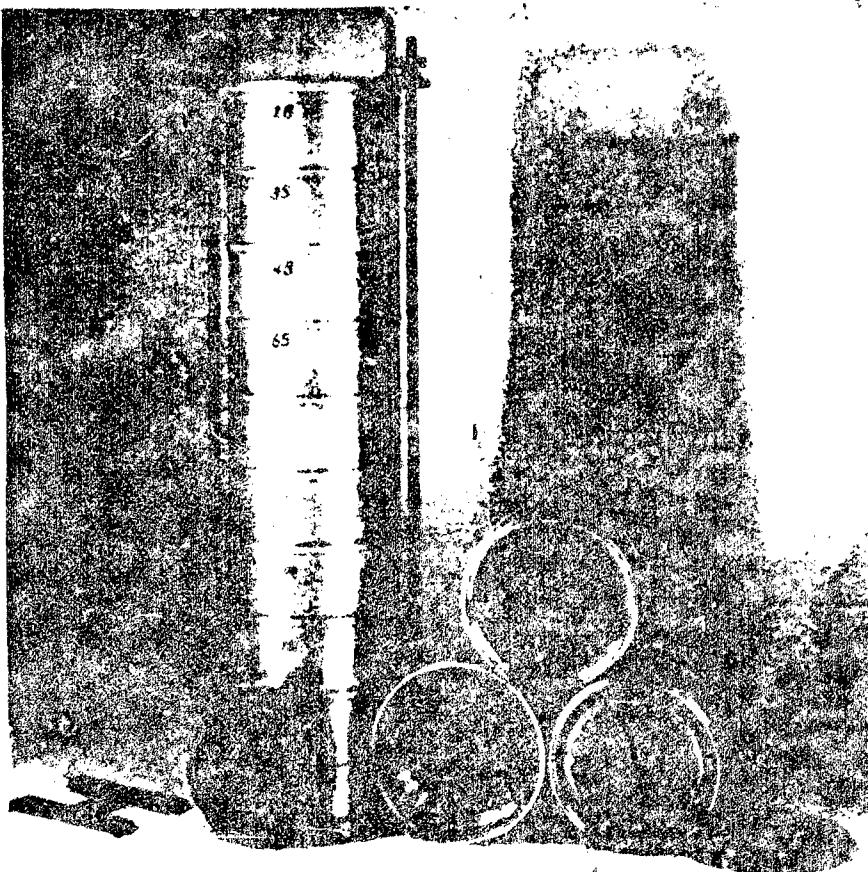


Fig. 2 External View of Device for Screen Analysis of Small Metal Powder Quantities.

nearly complete coincidence of the calculated and obtained balances of fluorine as determined by chemical analyses.

Some small discrepancies observed are to be explained by certain errors in the methods of chemical analysis.

From the above discussion, it follows that a chloride-fluoride electrolyte is gradually transformed into a purely fluoride electrolyte in the course of electrolysis. The sodium and potassium fluoride contents in the electrolyte increase. Molecular Composition of the Electrolyte During Different Periods of the Work Cycle of Electrolytic Bath.

Sodium and potassium fluoride contents increase uninterruptedly, whereas chloride contents decrease. Likewise, the concentration of thorium chloride increases from 15 weight percent at the beginning of the electrolysis

Table 1

Elementary Composition of the Electrolyte According
to Data of Chemical Analyses During Different Periods
of the Work Cycle of the Electrolytic Bath

Time from Beginning of Electrolysis	Elementary Content of Electrolyte, Percent, by Weight				
	Th	Na	K	Cl	Insoluble
Beginning of electrolysis	12,5	16,10	22,60	44,70	not
After one day	36,60	8,40	20,60	10,90	9,14
After two days	38,32	10,60	16,30	12,70	8,44
After three days	40,60	12,30	9,06	10,50	9,70
After seven days	44,70	12,44	9,15	1,28	13,56
After fourteen days	45,50	9,71	13,26	0,92	11,30
After thirty days	47,70	7,80	14,00	0,50	13,11
					14,6

Table 2

Time from Beginning of Electrolysis	Molecular Composition of Electrolyte Percent by Weight						
	ThF ₄	NaCl	KCl	NaF	KF	ΣF obtained	ΣF Calcul.
Beginning of Electrol.	16,61	40,84	43,20	uet	uet	45,34	44,6
After 1 day	48,65	8,98	11,44	8,88	21,60	23,15	23,38
After 2 days	50,80	10,47	13,32	11,83	13,88	22,38	23,07
After 3 days	53,80	8,66	11,02	16,23	5,79	22,44	22,50
After 7 days	59,32	1,06	1,35	21,93	12,55	28,69	28,76
After 14 days	60,46	0,76	0,97	12,20	18,97	28,91	30,60
After 30 days	63,21	0,41	0,52	14,23	20,4	28,20	27,71

to 60 percent after seven days, after which it remains almost at the same level.

The molecular composition of the electrolyte, as it appears from Tables 1 and 2, does not remain constant, notwithstanding its corrections in the course of electrolysis by the addition of corresponding salts.

An analysis of water-insoluble residues of the electrolyte is of great importance for the study of changes in the phase composition of the electrolyte. Insofar as the electrolyte does not react with water, it can be easily separated into two phases: water-soluble and insoluble.

Chemical, radiographic, and thermal analyses of the soluble and insoluble parts of the electrolyte facilitate considerably the deciphering of its phase content. A typical chemical analysis of the soluble and insoluble portion of the electrolyte is given in Table 3.

In accordance with the analytical data, the water-soluble portion of the electrolyte consists of sodium and potassium chlorides and fluorides; no thorium was identified. The water-insoluble part of the electrolyte contains thorium, fluorine, sodium, and potassium; no chlorine was found. Sodium and potassium contents in insoluble residues were not separately ascertained. However, as an example, full analyses of two samples are given in Table 4.

Table 3

Chemical Composition of the Insoluble and Water-soluble Phases of the Electrolyte Before and after Establishing Working Concentration.

Thorium content in electrolyte, wt %	Quantity of water-insoluble portion, wt %	Soluible portion			Insoluble portion		
		F wt %	C1 wt %	Th wt %	F wt %		
27.01	46.4	6.00	19.80			58.30	not det.
35.46	58.4	4.17	18.40			60.7	27.8
43.30	75.8	3.80	4.97			57.1	not det.
44.58	77.2	5.0	6.60			57.8	29.13
41.90	71.2	6.68	5.01			56.50	not det.
41.89	76.2	5.49	2.90			58.9	27.2
44.86	71.0	11.02	2.77			61.41	27.2
45.30	70.0	11.71	1.31			63.33	26.03
46.12	81.50	9.28	2.15			54.74	26.88
47.82	81.52	5.99	2.40			56.79	24.51

↓

Data of Table 4 also show that the residue of the water-insoluble electrolyte is not a simple thorium fluoride, but consists of complicated binary and ternary complexes. The composition of these complexes is not strictly constant, and depends on the concentration of the initial components in the electrolyte. Thorium content therein varies from 55 to 65 weight percent whereas the fluorine content varies from 25 to 30 weight percent.

Elementary and Molecular Composition of Typical Samples of Water-insoluble Residues of Electrolyte

Elementary contents wt %				Molecular composition, wt %			Molecular composition, wt %		
Tb	F	Na	K	ThF	NaF	KF	ThF ₄	NaF	KF
64.2	26.45	2.67	6.65	85.23	4.88	9.89	49.18	20.61	30.21
63.5	26.9	3.64	5.91	84.54	6.61	8.79	47.0	27.0	26.0

When the electrolyte composition is normal and the regime of the electrolyte has been stabilized, a ternary complex having the composition NaK(ThF₆) is formed, the existence of which has been confirmed by us in the system NaF-KF-ThF₄ (2).

Thermal and Radiographic Analysis of the Electrolyte. The thermal analysis of electrolyte samples and of the insoluble residue was carried out by us for the determination of the physicochemical nature of the compounds formed in the electrolyte in the process of electrolysis. The results of this analysis are given in Tables 5, 6, and 7.

During the analysis of thermograms of electrolyte samples (Table 5), it was found that most of them have only two plateaus corresponding to the initial precipitation of solid crystals and to a full solidifying of the eutectic. Temperatures of solidifying eutectics for all samples were practically the same, an average of 520 to 523°.

The greatest deviations in the temperature of the eutectic solidification points are observed in samples

Table 5

Chemical Composition and Temperatures of
Electrolyte Transformation for Thorium
Preparation

Th	Chemical Composition, % by wt				Temperature, °C	
	F _{tot}	F _{sol}	Cl	Quantity of insoluble residue	Liquidus	Solidus
41.79	27.3	5.9	4.2	not det.	538	525
44.75	26.7	12.7	0.57	not det.	539	522
45.06	30.5	7.0	2.9	not det.	546	522
43.76	29.0	7.67	3.28	not det.	535	525
27.01	33.65	6.0	19.8	46.41	627	527
27.25	29.0	4.42	33.46	23.36	629	516
35.47	32.87	4.17	18.4	58.5	620	524
42.19	33.59	5.94	7.0	71.31	560	523
43.3	29.59	3.87	4.97	75.8	532	520
44.58	34.22	5.0	6.6	77.23	553	522
44.84	31.71	5.89	13.12	76.2	536	520
43.6	36.27	7.07	3.7	78.53	558	510
41.9	26.38	6.68	5.01	71.2	562	520

Table 6

Chemical Composition and Temperatures of
Electrolyte Transformation for Thorium
Preparation

Th	F _{tot}	F _{sol}	Cl	Quantity of insoluble residue	Temperature of Transformation	
					Primary crystall- ization	Secondary crystall- ization
41,79	27,30	5,90	4,20	—	538	525
42,19	33,59	4,94	7,00	71,31	560	523
27,01	83,65	6,00	19,80	46,41	627	527
41,90	26,98	6,68	5,01	71,2	562	520
43,60	36,27	7,67	3,70	78,53	558	510
27,25	29,0	4,42	38,36	23,36	629	516
36,00	26,27	7,80	8,20	64,01	556	520
31,80	23,00	6,55	13,80	56,86	602	518
39,50	27,91	7,96	6,38	68,8	560	516
42,21	27,02	7,72	3,50	73,69	545	532

↓

with a high chlorine content and a relatively low thorium content. The temperatures of points on the surface of the liquids vary within a comparatively large range, since they probably belong to different cross-section planes of a multicomponent electrolyte system.

In the thermograms of electrolyte samples (Table 6), in addition to two plateaus of liquidus and solidus, a third effect is observed, as shown by a differential curve having an intermediate peak situated between the peaks of liquidus and solidus. This intermediate peak, corresponding to the temperature of secondary crystallization, depends on the content of chlorine in the electrolyte. At a high chlorine content in the electrolyte, the temperature of secondary crystallization, (i.e. of second solid-phase crystal precipitation) differs considerably from the temperature of primary crystallization, i.e., from precipitation of solid-phase crystals.

When the chlorine content in the electrolyte is intermediate, then the absolute quantity of second solid-phase crystal is small; and, consequently, the heat effects caused by crystallization are small, and the temperature difference between primary and secondary crystallization also decreases.

Finally, in samples with very low chlorine content, heat effects during the crystallization of the second solid phase are apparently so low that they do not influence the course of the differential curve. Cooling curves of the thermogram in this case have only two plateaus, corresponding to liquidus and solidus points.

A thermal analysis of insoluble residue gives interesting results (Table 7). These insoluble residues behave like individual chemical compounds. Their heating and cooling curves have only one plateau, corresponding to the temperature of $662 \pm 4^\circ\text{C}$.

A thermogram of a typical electrolyte sample is shown in Fig. 3 in a stable electrolytic regime, and (Fig. 4) shows a thermogram of water-insoluble residue of the same samples.

An X-ray analysis of water-insoluble and soluble portions of the electrolyte showed that the soluble part consists of sodium and potassium chlorides and fluorides.

The insoluble portion is either a mixture of both, or similar, compounds of the type $\text{Na}_x\text{Th}_y\text{F}_{4y}$, or a solid solution based on these compounds. Typical radiograms of the soluble portion of the electrolyte are shown in Fig. 5, and radiograms of the insoluble portion of electrolyte samples taken at different stages of the electrolysis are shown in Fig. 6.

↓

Table 7

Data of Thermal Analysis of Insoluble
Residues of Electrolyte for Thorium
Preparation.

No. of Sample	Chemical Composition, % by wt					Temperature Effects, °C	
	Th	F _{gen}	F _{sol}	C1	Quantity of Insoluble Residue	Curve of Heating	Curve of Heating
2351	36,0	26,17	7,8	8,20	64,01	662	662
2717	43,30	29,59	3,86	4,97	75,8	663	666
2352	31,80	23,00	6,55	13,8	56,86	663	658
2743	41,19	26,98	6,68	5,01	74,2	662	665
2353	36,6	26,8	7,7	not det.	not det.	664	660
1951	39,5	27,91	7,96	6,38	68,8	660	652
2321	42,21	27,02	7,72	3,50	73,68	663	658

Influence of Technological Factors on Yield
With Reference to Current And To Quality of
Metal

Influence of Compacting Cathode Deposits, Thorium Concentration in Electrolyte and Rate of Electrolyte Turn-over in the Bath. When cathode thorium deposits are removed from fused-salt baths, they catch and entrain hardened electrolyte. During the crushing and water treatment of cathode deposits, this entrained electrolyte is lost. This loss lowers the direct extraction of thorium during electrolysis, because the electrolyte entrained by cathode deposits is subjected to chemical treatment. This effect increases generally irreversible metal losses. The more the electrolyte is entrained by the cathode deposit and the higher its concentration, the lower will be the yield with reference to current and metal.

It was observed during our experiment that the quantity of electrolyte carried away with the noncompacted cathode deposits reached 75 percent of the entire cathode deposit, and the metal yield under these circumstances did not exceed 25 to 30 percent. The use of a self-compacting cathode decreases the quantity of electrolyte carried away with the deposit by 45 to 50 percent, and, correspondingly, the metal yield increases to 75 percent and

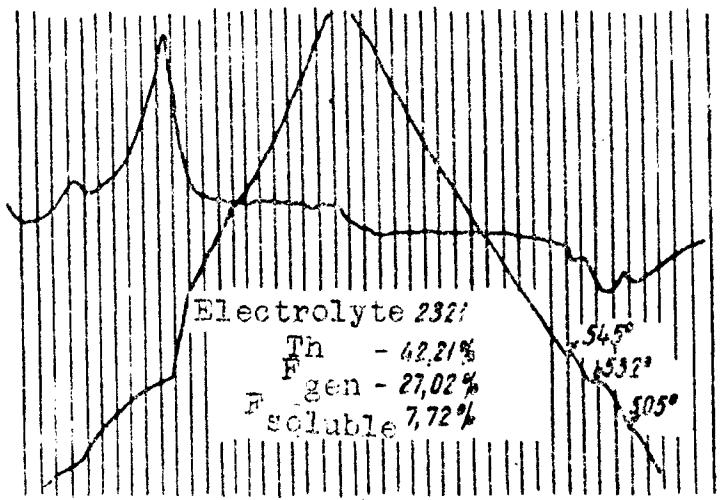


Fig. 3 Thermogram of Typical Electrolyte Sample in a Steady Electrolytic Regime

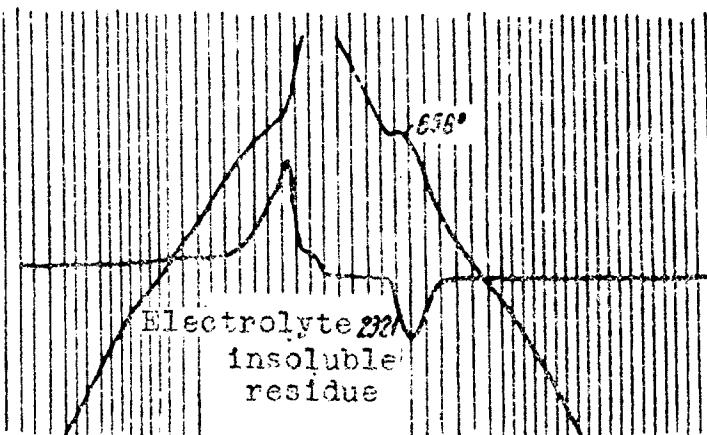


Fig. 4 Thermogram of Water-insoluble Residue of Electrolyte (Same as in Fig. 3)

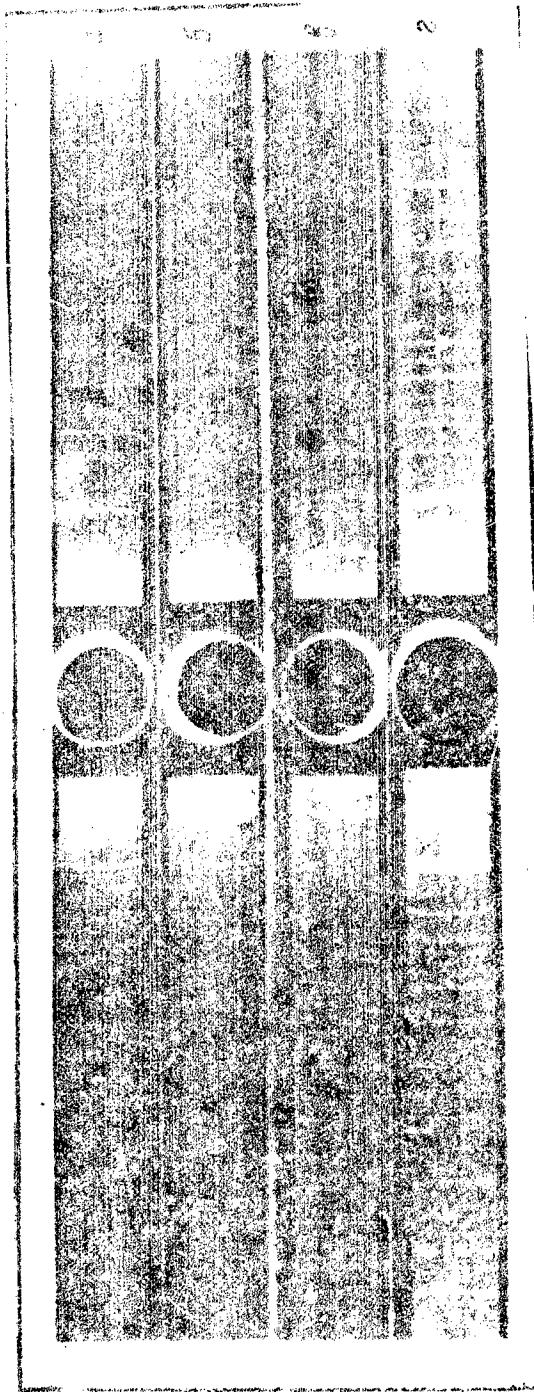


Fig. 5 Radiograms of Water-soluble Portions of Electrolyte Samples
Taken Under Different Electrolysis Conditions
Samples: a - 2754, b - 2723, c - 2706, d - 2698

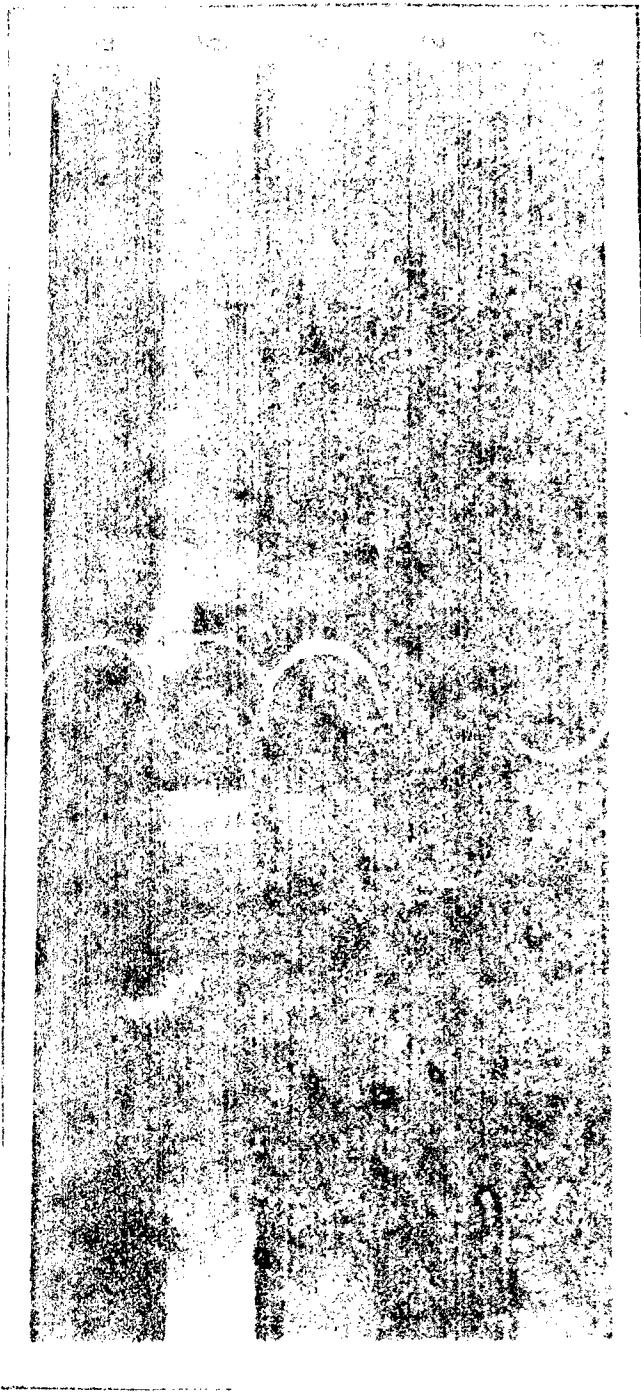


Fig. 6 Radiogram of Water-insoluble Portions of Electrolyte
Samples taken Under Different Electrolysis Conditions.
Samples: a - 2706, b - 2698, c - 2723, d - 2717

the current yield to 55 to 60 percent.

To minimize thorium losses, the entrained electrolyte must contain a minimum metal concentration. As a result of the study of this problem, it was established that during a brief electrolysis of freshly prepared electrolyte from a mixture of NaCl-KCl-ThF₄, already at relatively low concentrations of thorium - beginning with seven percent and higher, metal yields reached 70 to 75 percent, and current yields 50 to 60 percent.

Under no conditions was it possible to raise these yields. The same results are observed during a long uninterrupted electrolysis, if the turnover rate of the electrolyte in the bath reaches approximately once for each two hours and if no considerable accumulation of free NaF and KF takes place. However, attempts to work at low concentrations of thorium in the electrolyte in baths with a lower turnover factor were unsuccessful. So, for instance, in a bath with a turnover factor of the electrolyte of about once a day and a thorium concentration in the electrolyte of 10 to 40 weight percent, the current and metal yields fall to zero approximately after 20 to 24 hours from the beginning of the electrolysis. Only alkali metals begin to be eliminated at the cathode, where they rise to the surface of the electrolyte and burn in the air with small explosions. As we have shown, such a low turnover factor of the electrolyte during the bath causes an accumulation of free fluorides of potassium and sodium, which bind into complex compounds all of the ThF₄ charged into the bath. The ratio of the discharge potentials of the alkali metals cations and of those of thorium, changes under these circumstances in such a way that the alkali metals begin to be discharged predominantly at the cathode. This elimination of alkali metals ceases only when the concentration of thorium in the electrolyte becomes greater than 40 to 45 percent by weight. In its further course, the electrolysis continues undisturbed, but current yields do not exceed 50 to 60 percent. The dependence of current and metal yields on thorium concentration in the electrolyte is shown in Fig. 7.

Influence of Cathode Density and Volume Concentration of Current. Current and metal yields depend, to a great extent, on the cathode density and the volume concentration of current (Fig. 8.)

Fig. 8 shows the change in the ratio of the weight of the coarse crystalline powder fraction and the so-called slurry (a finely dispersed powder which has been oxidized to a considerable extent). As is apparent from the figure, there is an evident dependence of the current yield and the coarseness of metal powder deposited on the cathode, and

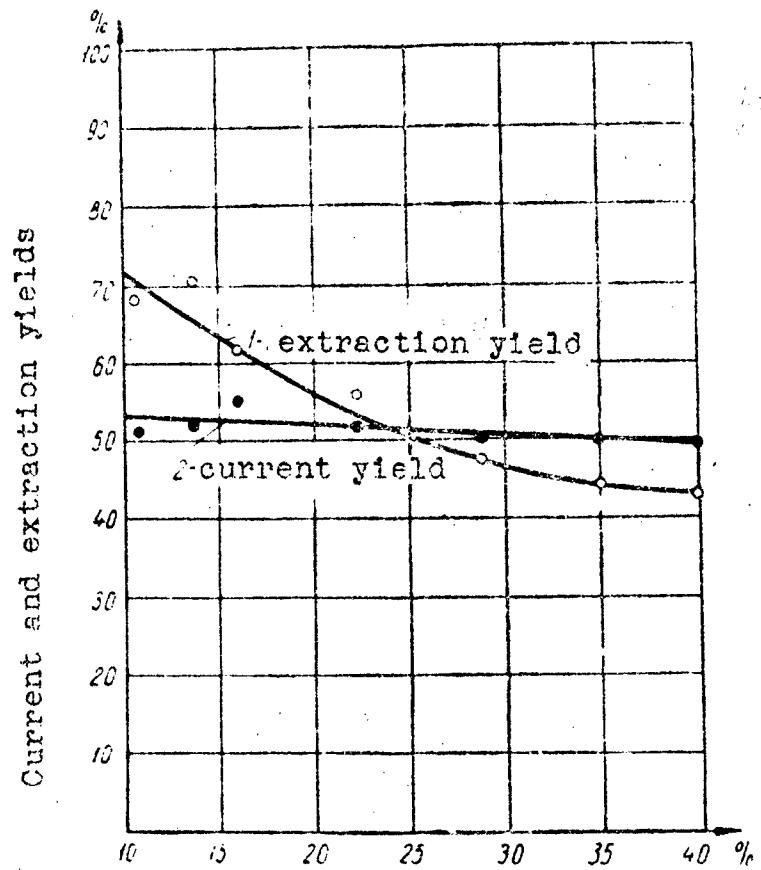


Fig. 7 Dependence of Current and Metal Yields on Concentration of Thorium in Electrolyte.

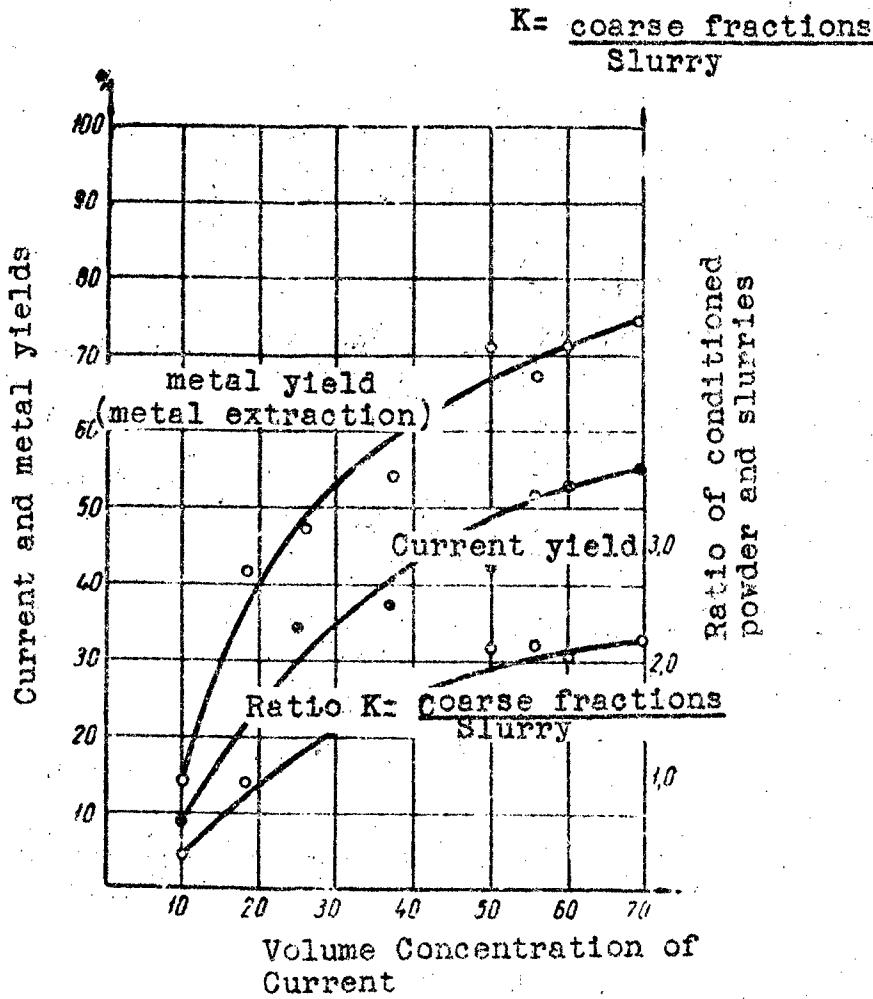


Fig. 8 Dependence of Current and Metal Yields on Cathode Density and Volume Concentration of Current.

Likewise, a dependence of the metal yield and the coarseness of the powder on cathode density and volume concentration of current. According to these data, the higher the concentration and the cathode density of current, the coarser are the crystals of thorium deposited and the greater are the current and metal yields. Current yields, however, are not high (absolutely) and, at best, reach 56 percent. This limit is apparently explained by the fact that a part of the finely crystalline metal powder is dissolved again in the electrolyte through an interaction with chlorine.

When the volume concentration of current is 50 to 70 amperes per kilogram of electrolyte, the metal yields are within the range of 70 to 75 percent and the current yield, 50 to 56 percent. At the same time, the ratio of conditioned, coarsely crystalline powder and slurries is within the range of 2.0 to 2.3.

When the volume concentration of current is 17 to 37 amperes per kilogram of electrolyte, metal yields drop to 40 to 55 percent, and the current yield to 40 percent. The ratio of conditioned coarsely crystalline powder and slurries becomes less than unity.

At still lower cathode densities and volume concentrations of current, the current yields drop even more abruptly. For instance, at a current concentration of 10 amperes per kilogram of electrolyte, and at a current density of 0.5 amp/cm², the current yield decreases to 9.3 percent; the metal yield, to 13.5 percent, and the ratio in weight of coarsely crystalline powder and slurries reaches only as high as 0.34. It is evident that under these conditions so much finely dispersed powder is deposited on the cathode that most of it reacts with chlorine and is dissolved in the electrolyte.

Influence of Electrolyte Temperature and of Volume Concentration of Current. It was established that the temperature of the electrolyte exercises substantial influence on current yield and on the shape of metal deposited. At low temperatures, when a fused electrolyte is sufficiently viscous, the current and metal yields are very low. Upon increasing temperatures to a point where the electrolyte becomes fluid, the current and metal yields increase to their maximum value. Upon a further temperature increase of the electrolyte, to a point of its overheating, current and metal yields again sharply decrease. It was noticed that from an overheated bath, thorium is deposited on the cathode in a more finely dispersed shape than from a bath with a normal temperature of the same electrolyte. Fig. 9 shows a state diagram, plotted according to our data (2) of a polythermal cross section of a system NaCl-KCl-ThF₄.

matching the thorium electrolyte. The melting point of the eutectic is 626°C, in accordance with this diagram. However, the optimum temperature of electrolyte proved to be 680 to 700°C (See curve in Fig. 10). Insofar as heat applied and temperature of electrolyte are dependent on density and volume concentration of current, the latter cannot increase above a certain value without risk of overheating the bath. On the other hand, it is necessary to use higher densities and concentration of current to obtain close crystalline deposits, as has been shown before.

In laboratory baths with external heating, volume concentration of current is not strictly limited by the intrinsic heat regime and can be carried to a considerable level. For instance, in our tests with such cells, the best current and metal yields were obtained at a volume concentration of current of 50 to 70 amperes per kilogram of electrolyte. In that case, the cathode current density was three to four amperes per square centimeter on a regular geometric surface of that part of the cathode deposit which was sunk in the electrolyte. Thorium was deposited on the cathode in the shape of large crystals, and the quantity of the slurry, after leaching the powder with water, was small.

When electrolysis is carried out in a bath without external heating, the volume concentration of current is limited by the heat regime of the bath. In this case, as our tests have shown, when electrolyzing thorium, the volume concentration of current should not exceed 15 to 20 amperes per kilogram of electrolyte. In opposite cases, the electrolyte became overheated, and a finely dispersed thorium powder was deposited on the cathode. However, the volume concentration of current is, to a great extent, a function of the size and design of the bath itself, of the distance between cathode and anode, of the electroconductivity of the electrolyte, and of some other factors. Therefore, in other cases of electrolysis, the admissible levels of volume concentration of current will be different. However, in all cases they will be limited by the heat regime of the bath.

Influence of Current Density on the Structure and Purity of Thorium Crystals. It is known that during the electrolysis of fused salts using solid cathodes, metals are deposited only in the form of loose columnar crystals. One cannot achieve electrolytically a deposition of a dense and sufficiently thick coating. This condition depends on the nature of fused electrolytes and on the low level of cathode polarization, which, anyway, almost does not depend on current density. At low current density, curves of cathode polarization in these electrolytes run nearly parallel to the ordinate axis. The graph becomes slightly sloped

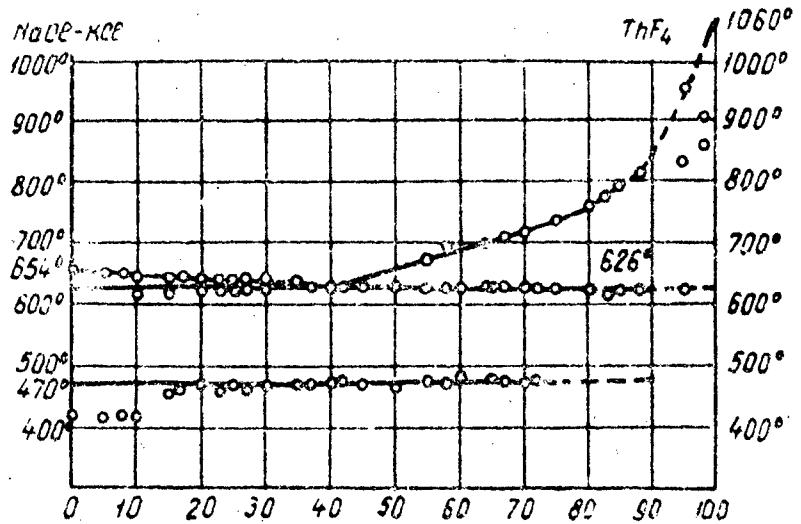


Fig. 9 Polyternic Cross Section IKCl:
INaCl-ThF₄ of a System NaCl-
KCl-ThF₄.

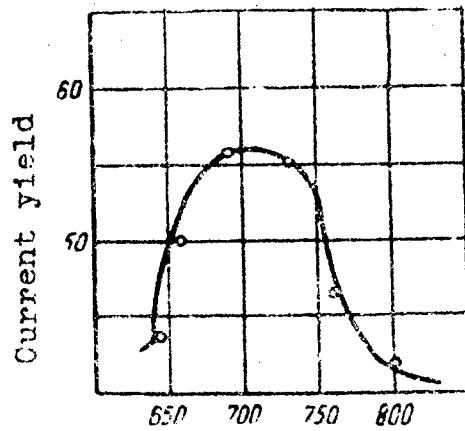


Fig. 10. Dependence of Current
Yields of Electrolyte
Temperature.

only at very high current densities, when the influence of the latter on the formation of crystals becomes decisive. The above conclusion was confirmed by electrolyzing thorium. At all current densities investigated by us -- from a tenth of an ampere to tens of amperes per square centimeter -- thorium was deposited in the form of loose crystals, recovered after leaching the electrolyte as metal powder. It was further established that the coarseness of thorium powder depends on cathode current density: the lower the density of current, the finer the thorium powder obtained, other conditions remaining unchanged.

At cathode densities lower than 0.05 a/cm^2 , only finely dispersed powders were obtained, and during leaching, they were completely changed into slurries. At higher current densities, beginning at 1.5 a/cm^2 and higher, thorium was deposited on the cathode in the shape of dendritic crystals which, after leaving the electrolyte, yielded a coarse crystalline metal powder. The cathode deposit, after removal from the laboratory bath, is shown in Fig. 11. A screen analysis of electrolytic thorium powder is given in Table 8. Thorium content in the powder is above 99.5 percent. Admixtures in the powder are approximately 0.5 percent, among which are oxygen at 0.2 percent; fluorine, 0.2 percent; carbon, 0.025 percent; nitrogen, 0.01 percent; sodium and potassium, 0.02 percent; chlorine, 0.002 percent; rare earths at a total of 0.001 percent.

A typical analysis for initial substance contents and for admixtures in [the final electrolytic] powder is shown in Table 9. In the same table, the content of initial ThF_4 is given. From a comparison of the admixture contents of rare earth metals in the initial salt and in the electrolytic thorium powder prepared, it is easy to see that, during electrolysis, a decrease of up to 60 to 80 times in the admixtures of rare earth elements in thorium is achieved.

Experiments have shown that electrolytic thorium powder as prepared is suitable for use in powder metallurgy both with regard to its granulation and its purity.

Mechanics of Electrolysis of a Fused System $\text{NaCl}-\text{KCl}-\text{ThF}_4$

By thermodynamic calculations, the results of which are partly given in Fig. 12, the authors have shown that in the initial period of electrolysis of a system $\text{NaCl}-\text{KCl}-\text{ThF}_4$ decomposition is higher by nearly one volt than that of the decomposition of the indicated alkali metal chlorides (58). Owing to this fact, one can presume that in the initial

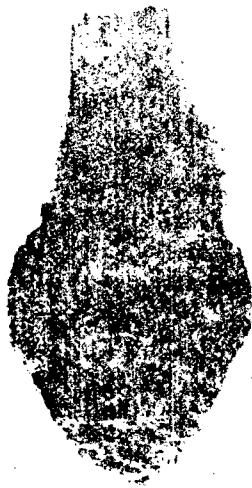


Fig. 11 Cathode Deposits
from Bath with
Manual Compacting.

Table 8
Screen Analysis of Electrolytic Thorium Powder

Fraction, Mesh	Percent by weight
+ 65	1 - 2
from - 65 to + 100	8 - 13
from - 100 to + 200	55 - 58
from - 200 to + 325	25 - 20
- 325	11 - 7

↓

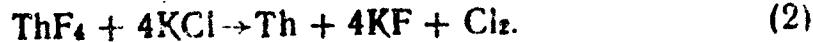
Table 9

Typical Analysis for Admixtures in Initial
Thorium Fluoride and in the Electrolytic
Thorium Powder.

Element	Content of Basic Substance and Admixture, Percent by Weight		Analytical Method
	In Initial ThF_4	In Electroly- tical Thorium Powder	
Iron	0,015	0,005	Spectral
Rare Earths, Total of Which:	0,050	0,0006	*
Nd	—	0,00050	*
Sa	—	0,000005	*
Gd	—	0,000001	*
Sodium		0,0100	*
Potassium	—	0,0100	*
Lithium	—	0,00001	*
Boron		0,00005	*
Uranium	—	0,000005	*
Chlorine	—	0,002	chemical
Phosphorus	0,010	—	*
Fluorine	23,90	0,200	*
Thorium	73,07	99,50	*
Cryst, water	2,90	—	*
Nitrogen	—	0,016	*
Sulfur	0,015	—	*
Carbon	—	0,025	*
Oxygen	—	0,220	*
Total	99,9600	99,9826	



period of electrolysis a deposition of alkali metals takes place on the cathode, which metals later enter into a secondary chemical reaction with ThF_4 . As a result of this latter reaction, displaced thorium is deposited on the cathode even at a very low concentration in the electrolyte. At the anode during this period of electrolysis, only chlorine is liberated. Fluorine is quantitatively accumulated in the electrolyte in the form of the new components NaF and KF , the presence of which can be shown analytically. Electrolysis at that period can be summarized by the following reaction:



The mechanics of electrolysis are completely changed when the new components NaF and KF , formed in its course, bond with the ThF_4 charged into the bath, forming such complex fluoride compounds as $\text{NaK}(\text{ThF}_6)$, $\text{Na}_2(\text{ThF}_6)$ and $\text{K}(\text{ThF}_5)$. These compounds dissociate with a formation of the complex anions ThF_6^{2-} and ThF_5^1 ; which are transferred by the current to the anode. Thorium deposition on the cathode in this case takes place only when the general concentration of thorium in the electrolyte is not below 42 to 43 percent by weight. At lower concentrations, only alkali metals are deposited at the cathode, which are unable to displace thorium from complex compounds and which float to the surface of the electrolyte, burning with small explosions.

The discharge of thorium cations from complex anions takes place as a result of a reversible dissociation occurring in the layer near the cathode.



Anode processes during this main stage of electrolysis and the initial stage also differ substantially from each other. In this case, together with chlorine ions, the anions ThF_6^{2-} and ThF_5^1 will also be transferred to the anode. One can assume that simultaneously with the chlorine ions, these anions will be discharged at the

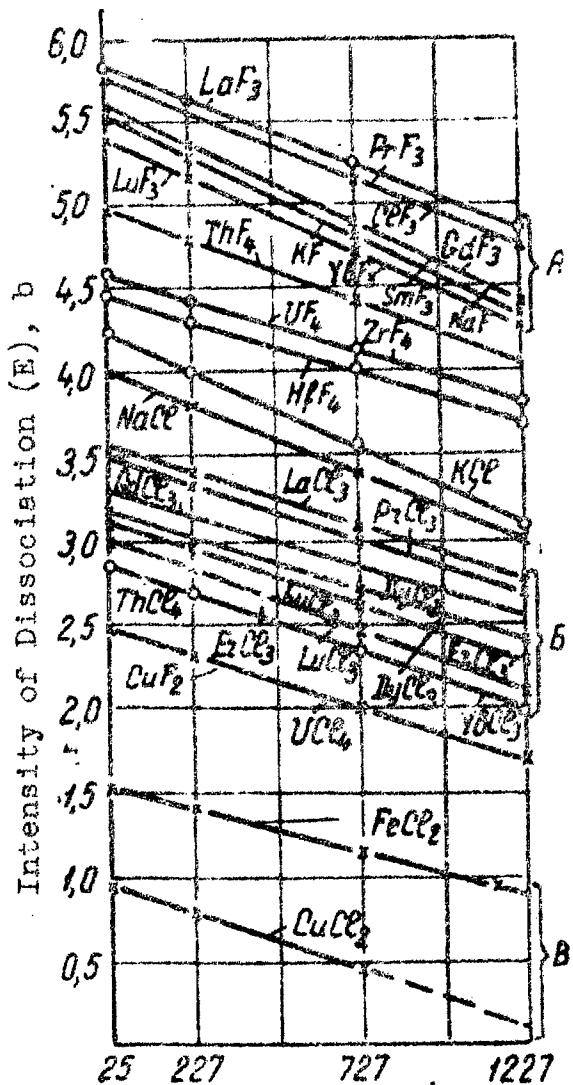
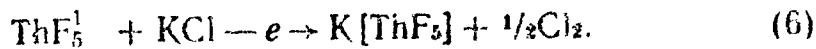


Fig. 12 Calculated Values of Dissociation Potentials for Chlorides and Fluorides of Alkali Metals, Thorium, and Rare Earth Elements. A. Area of dissociation potentials of rare earth and alkali metal fluorides; B. Area of dissociation potential of rare earth metal chlorides. C. Area of dissociation potentials of more positive metal chlorides.

↓

anode in the following reactions:



The dependence of the critical anode density of the current on the chloride content in the electrolyte, (Fig. 13) serves as experimental confirmation of the above.

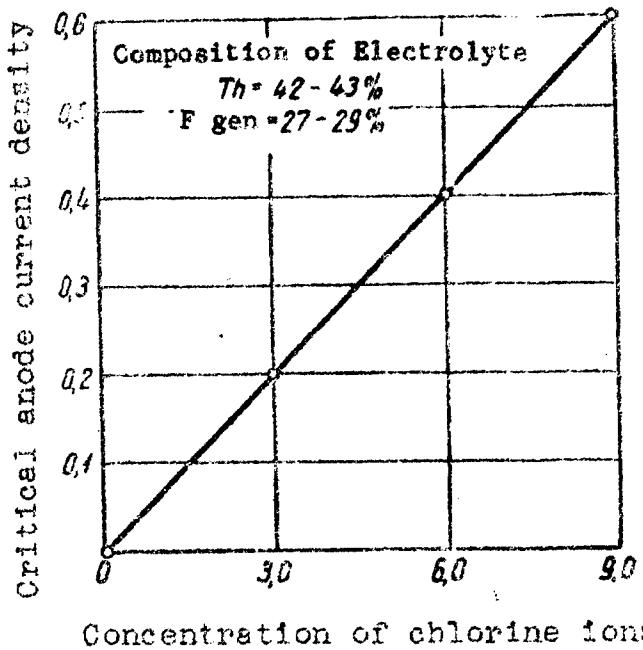
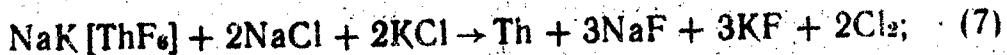


Fig. 13 Dependence of the Critical Anode Current Density on the Chlorine Content in the Electrolyte.

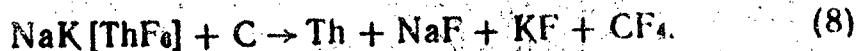
As indicated by the figures of the electrolytic balance, a discharge of fluorine, apparently forming CF_4 , takes place at the anode in an electrolyte having very low chloride content. The specific ration of the above mentioned reactions at the anode during this main period of electrolysis will depend evidently on the conservation of corresponding ions in the electrolyte. The summary

of thorium electrolysis during that main period can be represented by the following two reactions:

a) If chlorides are in sufficiently high concentration in the electrolyte:



b) If the electrolyte is very low in chlorides:



Conclusions

1. An experimental study of the electrolytic preparation of thorium from a fused mixture of sodium and potassium chlorides and thorium fluoride was carried out. It was found that:

a) During the electrolysis, an uninterrupted change in the content of the electrolyte takes place [a change] which is due predominantly to the liberation of chlorine on the anode and to the accumulation in the electrolyte of fluorine in the form of three NaF and KF components.

b) Sodium and potassium fluorides formed during the electrolysis completely tie up simple thorium fluoride, charged into the bath, into complexes of the type $\text{NaK}(\text{ThF}_6)$, $\text{K}_x(\text{ThF}_{x+4y})$ and $\text{Na}_x(\text{ThF}_{y-x+4y})$, where $x = 1$ or 2 and $y = 1$.

c) During prolonged electrolysis, maximum thorium yield at the cathodes is achieved if its concentration in the electrolyte is not lower than 40 to 43 percent by weight.

d) When the thorium concentration is less than 43 percent by weight in the electrolyte, the thorium yield drops abruptly, and alkali metals begin to be deposited at the cathode.

2. The optimum conditions for electrolysis were found, and the influence of the most important technological factors on the current and metal yields were studied. Among these factors are:

- a) Mechanical compacting of cathode deposits
- b) Concentration of thorium in electrolyte
- c) Turnover rate of electrolyte in bath
- d) Cathode density and volume concentration of current
- e) Temperature of the electrolyte

3. It was established that under the optimum conditions of electrolysis, scarcely crystalline thorium powder is obtained with a metal yield of 70 to 75 percent and a current yield of 50 to 56 percent. The ratio of coarse crystalline powder to the finely dispersed fraction (slurries) reaches 2.0 to 2.3 in this case.

It was established that as a result of the electrolytic preparation of thorium, a decrease of as much as 60 to 80 times in the content of rare earth element admixture is achieved, as compared with that in the initial thorium fluoride.

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DESIGN OF AN ELECTROLYZER WITH AUTOMATIC COMPACTING CATHODES FOR ELECTROLYSIS OF FUSED THORIUM SALTS

This is a translation of an article written by A. I. Yevstuykhin and G. A. Leont'yev in Metalurgiya i Metallovedeniye Chistykh Metallov, No. 1, Moscow, 1959, pages 36-43.

The electrolysis of fused salts is used in industry for the production of aluminum magnesium, sodium, and other alkali and alkali earth metals. In application to these metals the basic theoretical methods and the equipment are well developed. However, the methods of production of the rare and other refractory metals by the electrolysis of their fused salts, although used on an industrial scale, is only scantily studied. This situation can be explained by the relative newness of rare metal applications and by the peculiarities of the electrolysis of their fused salts by means of a solid cathode.

The electrolysis of fused salts using a solid cathode requires a special design for the electrolyzer, owing to the fact that the metal deposited on the cathode forms loosely connected crystals. Therefore, prolonged and continuous electrolysis and removal of the metal from the electrolyzer posed in this case a serious problem.

After testing many designs for carrying out laboratory experiments on electrolysis using solid cathodes, we have designed and built an installation permitting electrolysis with stationary or rising electrodes on which depositions could be compacted manually at periodic intervals, or with mechanical compacting by means of cathodes rotating toward each other. Depending on the capacity of the crucibles used, laboratory tests or tests on a semi-industrial scale could be carried out.

The installation is mounted on a metal bench, 1, and is provided with exhaust fan device, 2 (Fig. 1). A brass frame, 8, is secured to the bench or to the wall by means of brackets, and it supports a bearing-cushioned collector shaft. This shaft is mechanically and electrically connected with an iron or molybdenum rod carrying the cathode, 5.

Direct current is passed through the rotating cathode by means of four copper-graphite bushes secured to the frame and having a total contact area of 35 cm^2 . They are designed

1. The installation was built in the experimental workshops of MIFI.

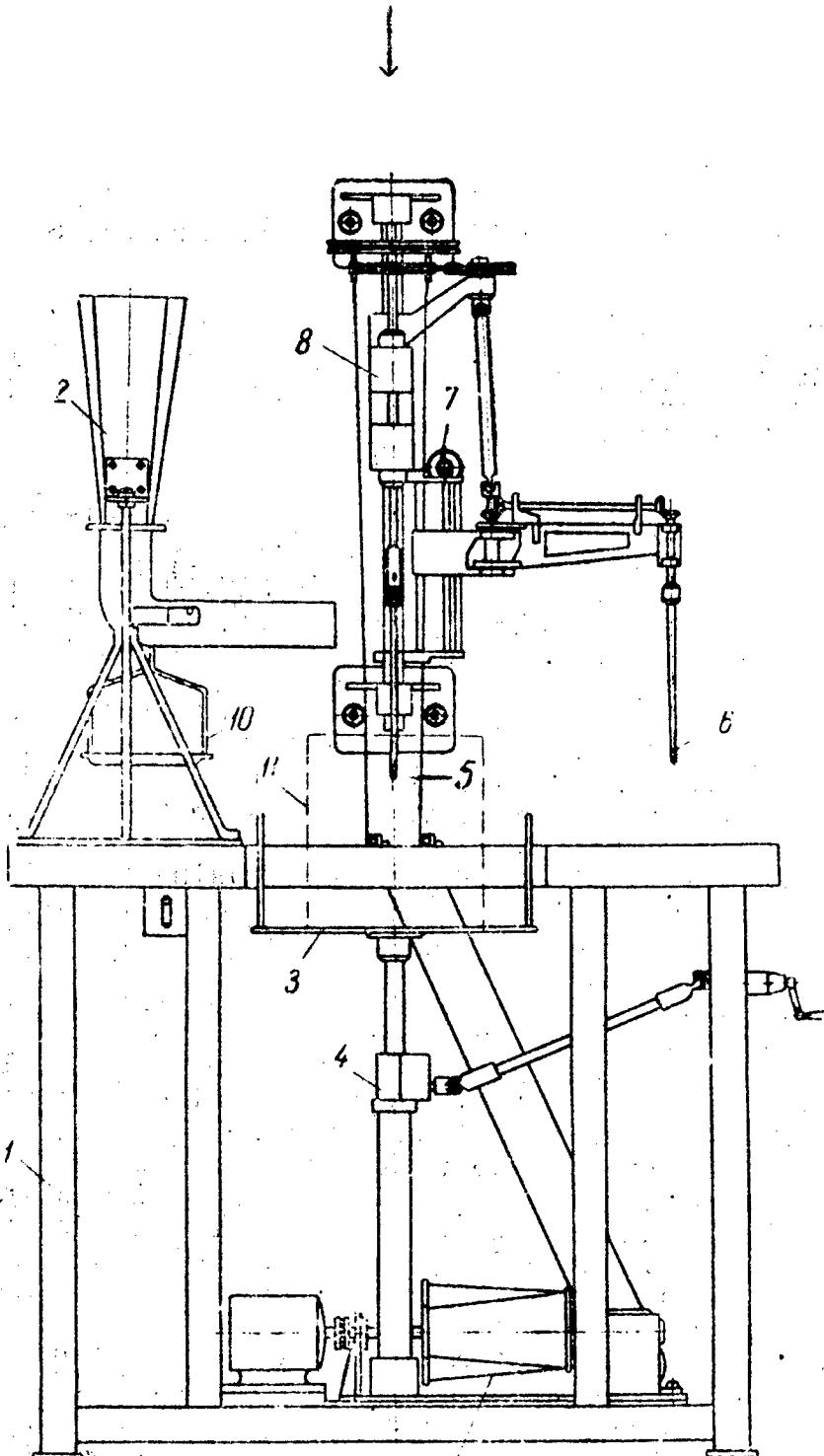


Fig. 1. General View of Electrolytic Installation with Automatic Compacting Cathodes:

1. Bench
2. Exhaust fan installation
3. Mobile platform
4. Lifting mechanism
5. Main cathode
6. Auxiliary cathode
7. Lifting mechanism of auxiliary cathode
8. Collector frame supporting main cathode
9. Motor with reduction gear
10. Platform for placing the pulling weight
11. Electrolytic cells.

to carry a current of 300 a. The frame is connected to the negative electric pole.

An electrolytic cell is installed on a movable platform, 3, under the cathode, 5. A graphite crucible is the anode. A nichrome yoke is affixed to its upper part through which the crucible is connected with the positive pole of the dynamo.

In the lower part of the table, 1, the motor, 9, is installed with reduction gear. It rotates the cathode over a series of pulleys.

Electrical measuring instruments and devices for current regulation are placed on a panel of a low-voltage dynamo 12/6 v, 250/500 a, which is the DC source. Voltage and current regulation of the electrolytic bath is effected by a shunt rheostat of the dynamo and by an additionally installed resistance rheostat.

The depth of the electrode dip into the electrolyte is controlled by shifting movable platform, 3, which is lifted vertically along the guide by a lifting device, 4, with automatically braking worm-gear transmission. A scale is provided for determining the position of the movable platform.

Automatic compacting of cathode depositions (Fig. 2) is achieved by pressing an auxiliary cathode onto the main one. They rotate in opposite directions at the same speed and rotate around each other. Dendritic crystals growing during electrolysis are firmly compacted and squeezed without dropping from the cathode.

Auxiliary cathode, 2, is connected to movable frame, 8, and can be placed under any compacting stress by means of a weight. During the whole period of growing cathode depositions, the compacting stress remains constant regardless of the changing distance between cathodes (due to the growth of depositions during electrolysis).

DC current is passed through the auxiliary cathode by means of brushes and collector, 7. Both cathodes are connected in parallel to one bus bar.

The auxiliary cathode can be moved in the vertical direction by means of worm gear transmission, 4, in relation to the main cathode, so as to equalize the growth at the end of the cathode deposition. The auxiliary cathode, permitting the growth of cathode depositions of approximately constant cross section. In the course of electrolysis, it is possible to maintain a more or less constant rolled surface, i.e., the same rate of compaction.

Graphite crucibles are used as electrolytic cells, which are firmly inserted into containers of cast silicon iron (so as to avoid the infiltration of fused electrolyte into the furnace lining). Electrolytic cells require ex-

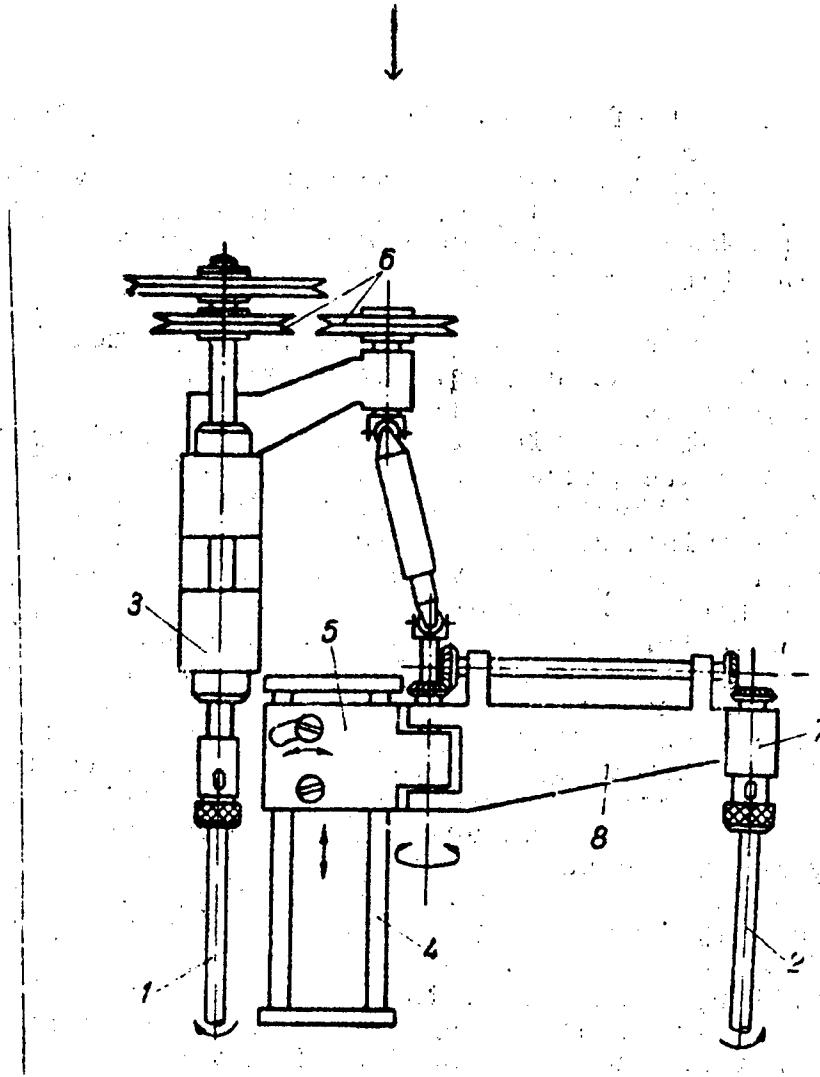


Fig. 2. General View of Compacting Device in Electrolytic Installation with Automatic Compacting Cathodes: 1. Main cathode 2. Auxiliary cathode 3. Collector frame supporting main cathode 4. Lifting mechanism 5. Mechanism for inclination of auxiliary cathode 6. Pulleys for transmission of rotation from main to auxiliary cathode 7. Collector of auxiliary cathode 8. Frame of auxiliary cathode.

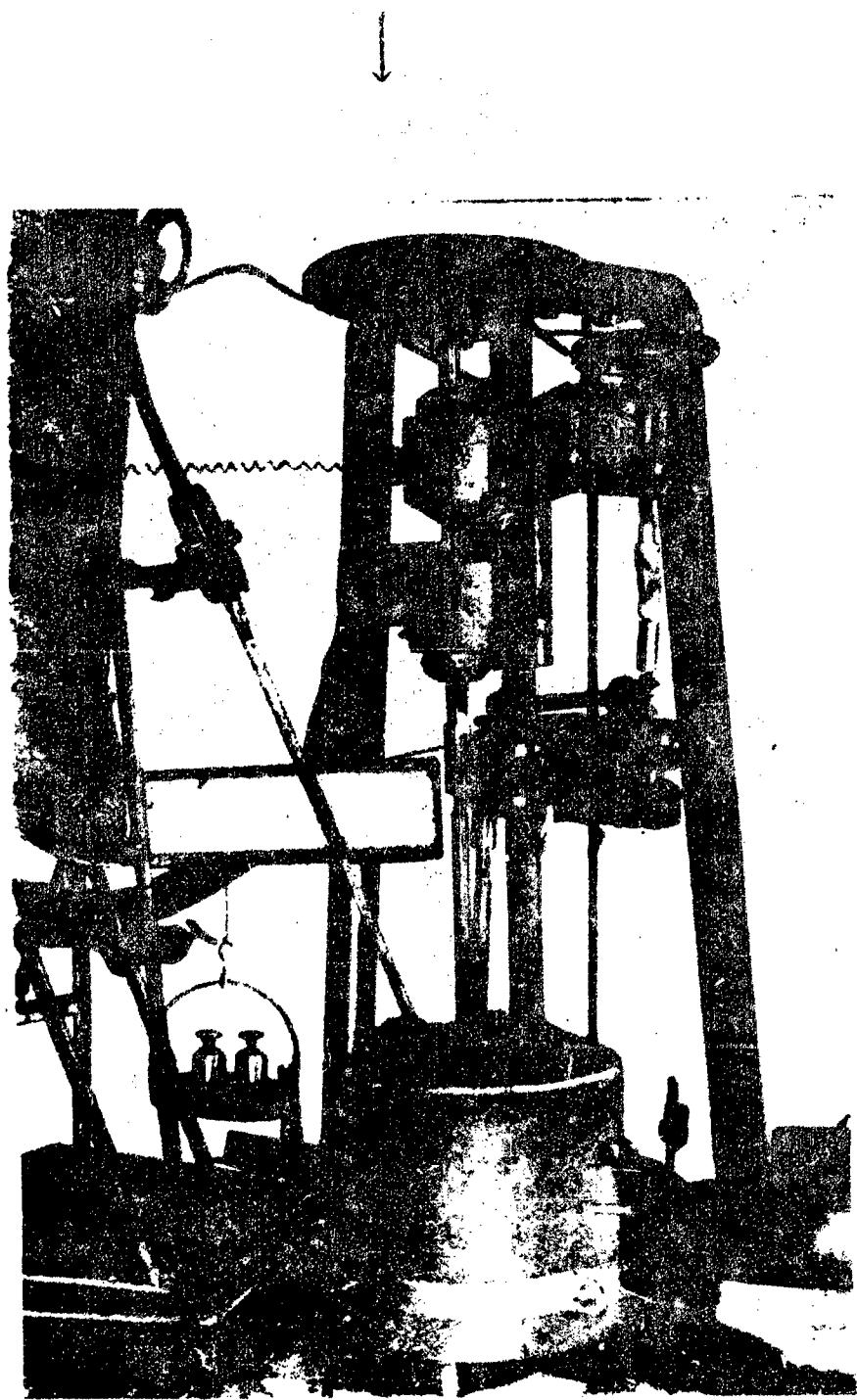


Fig. 3 External View of Electrolyzer with Automatic Compacting Cathodes Before the Test

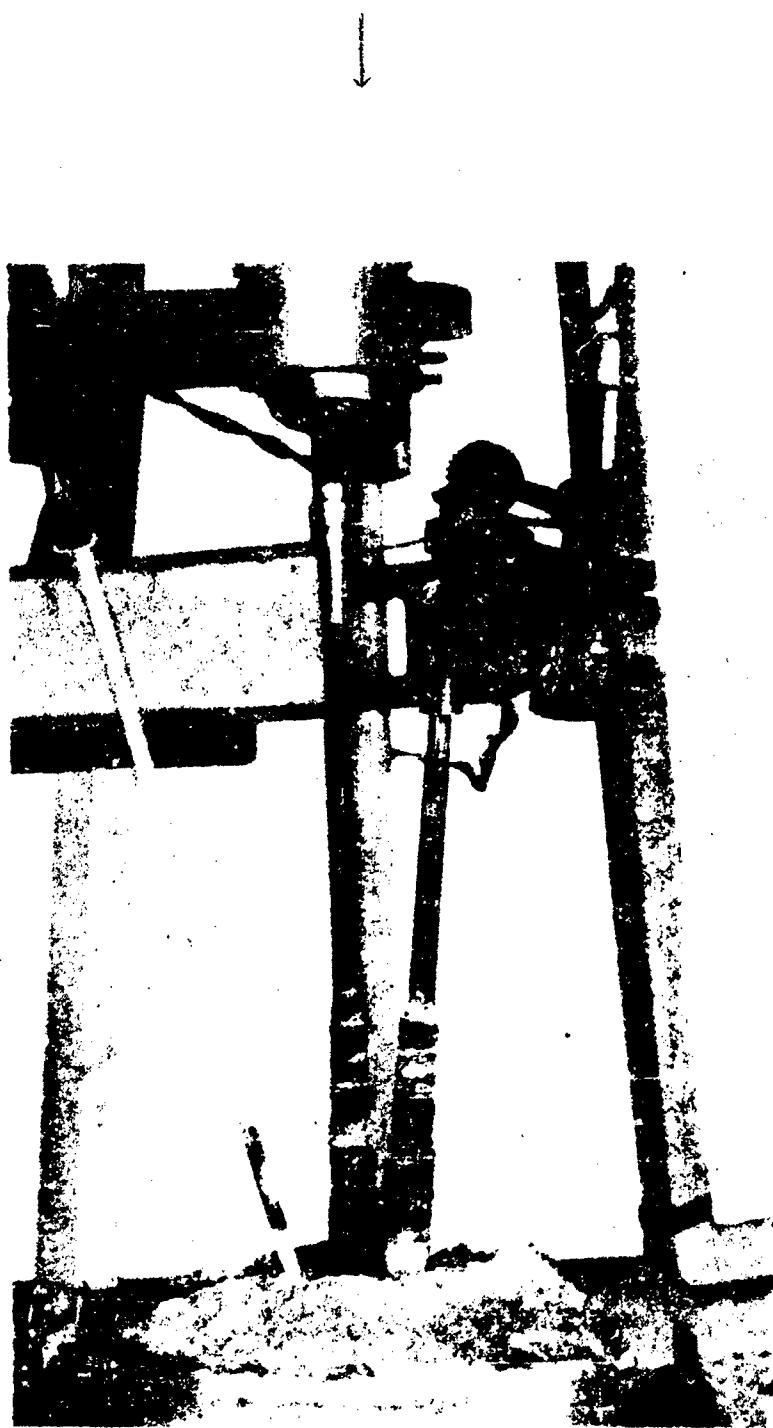


Fig. 4. External View of Electrolyzer with Automatic Compacting Cathodes During Electrolytic Operation

Fig. 5. External View of Thorium Depositions as Obtained on Automatic Compacting Cathodes.

Fig. 5. External View of Thorium Depositions as Obtained on Automatic Compacting Cathodes.

ternal heating, as Joule's heat generated by DC passing through the electrolyte is not sufficient for maintaining the required temperature of the melt. Therefore, electrolytic cells were inserted into special crucible furnaces with ni-chrome heaters. The furnace was supplied with AC over an autotransformer, permitting a smooth temperature control of the bath. Temperature measurements were made with a platinum-platinumrhodium thermocouple in a porcelain sheath.

An external view of the electrolytic installation with automatic compacting cathodes and an external view of the automatic compacting cathodes are shown in Figs. 3 and 4. An outside view of the thorium depositions from a KCl-NaCl-ThF₄ system is shown in Fig. 5.

Tests have shown that the electrolyzer design, as described, is suitable for the electrolysis of fused salts on a solid cathode only in instances where deposited, dendritic crystals are ductile and can be compacted. Thorium is typical in this respect, and this installation was designed for such deposition. It permitted a mechanization of bath operations and, at the same time, a considerable improvement of electrolytic characteristics. For instance, metal activity in unleached deposition on a non compacted cathode did not exceed 30 percent; whereas the average metal yield was 24 percent. In tests with "manual" periodic compacting, corresponding characteristics rose to 40 and 52 percent, respectively; whereas for tests with mechanized compacting and automatic compacting cathodes, from 60 and 75 percent respectively.

One can presume that the above design is also suitable for other plastic rare metals deposited on the cathode.

Although the servicing of electrolyzers with automatic compacting cathodes requires the supervision of more qualified personnel, as compared with the servicing of ordinary electrolytic baths, /the automatic compacting type/ can be unconditionally recommended for the production of rare and valuable metals.

C o n c l u s i o n s

An electrolyzer with automatic compacting cathodes was built and tested for preparing metals by the electrolysis of their fused salts, using a solid cathode. The electrolyzer permits: a) mechanization of compacting cathode depositions; b) maintenance of such conditions of metal deposition on the cathode that the current density remains constant (a continuous compacting of dendritic crystals prevents their growth); c) increased metal activity in the cathode deposit

and improvement of technical and economical characteristics
of electrolysis.

END

FOR REASONS OF SPEED AND ECONOMY
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