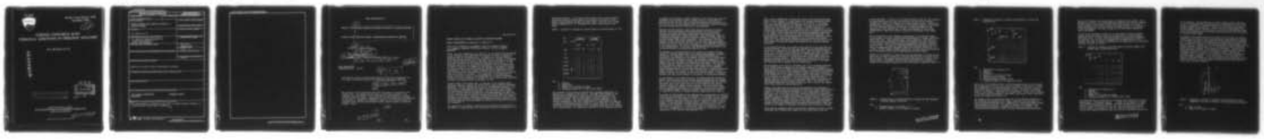
AD-A034 238 COLD REGIONS RESEARCH AND ENGINEERING LAB HANOVER N H F/G 13/3
CURING CONCRETE WITH CHEMICAL ADDITIVES IN FREEZING WEATHER (TV--ETC(U)
OCT 76 S A MIRONOV, A V LAGOYDA, Y N UKHOV

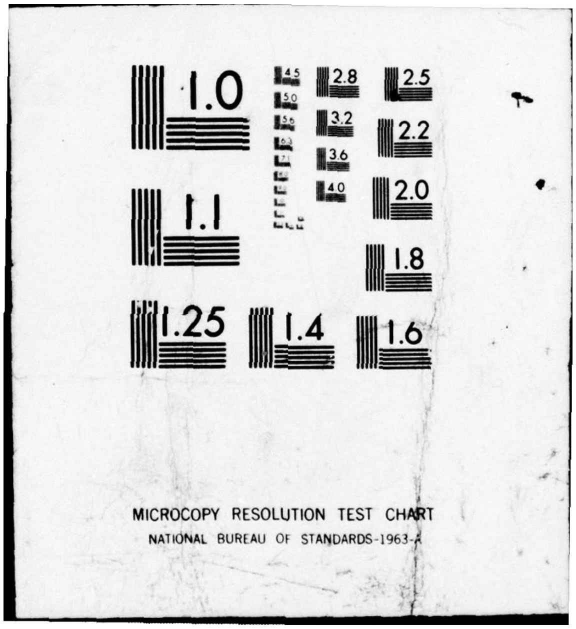
UNCLASSIFIED CRREL-TL-545 NL

1 OF 1
AD
A034238



END

DATE
FILMED
2-77



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TL 545

Draft Translation 545
October 1976

12

B. S

CURING CONCRETE WITH CHEMICAL ADDITIVES IN FREEZING WEATHER

S.A. Mironov et al

CORPS OF ENGINEERS, U.S. ARMY
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER Draft Translation 545	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CURING CONCRETE WITH CHEMICAL ADDITIVES IN FREEZING WEATHER		5. TYPE OF REPORT & PERIOD COVERED 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) S.A. Mironov et al		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE October 1976 13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

COLD WEATHER CONSTRUCTION
ADMIXTURES
CONCRETE SETTING

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This paper reports on advances in the field of adding chemical additives to curing concrete during winter conditions.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SECURITY CLASSIFICATION OF THIS PAGE(*When Data Entered*)

SECURITY CLASSIFICATION OF THIS PAGE(*When Data Entered*)

DRAFT TRANSLATION 545

⑥

ENGLISH TITLE: CURING CONCRETE WITH CHEMICAL ADDITIVES IN FREEZING WEATHER

FOREIGN TITLE: (TVERDENIE BETONA S KHIMICHESKIMI DOBAVKAMI NA MOROZE)

⑩

AUTHOR: S.A. Mironov, et al
A. V. Lagoyda
Ye. N. Ukhov

㉑ Trans. of ~~SOURCE:~~ Beton i zhelezobeton March 1968, no. 3, p.1-4.
(USSR) n3 p1-4 Mar 68.

⑫ 12p.

CRREL BIBLIOGRAPHY
ACCESSIONING NO.: 23-2557

⑪ Oct 76

Translated by Office of the Assistant Chief of Staff for Intelligence for U.S. Army Cold Regions Research and Engineering Laboratory, 1976, 9p.

⑭ CRREL-TL-545

NOTICE

The contents of this publication have been translated as presented in the original text. No attempt has been made to verify the accuracy of any statement contained herein. This translation is published with a minimum of copy editing and graphics preparation in order to expedite the dissemination of information. Requests for additional copies of this document should be addressed to the Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314.

D

1473
037100
LB

UDC 693.547.32

CURING CONCRETE WITH CHEMICAL ADDITIVES IN FREEZING WEATHER

BETON I ZHELEZOBETON in Russian No 3, 1968 pp 1-4

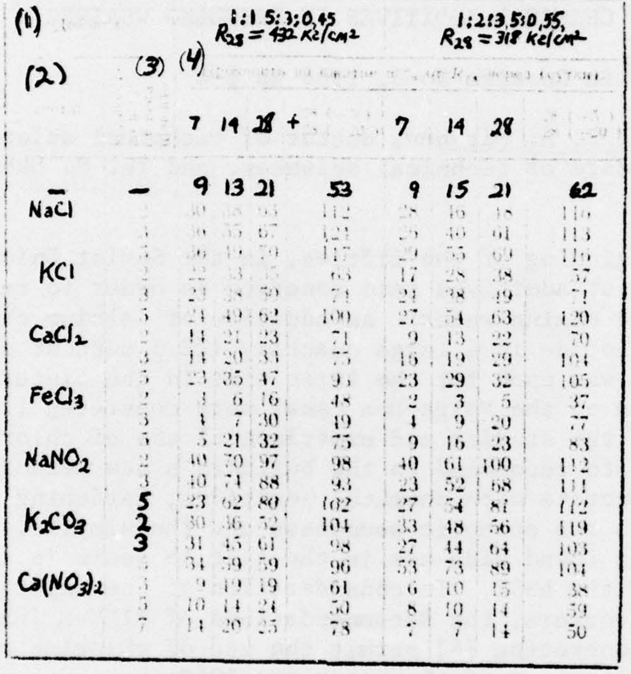
[Article by Professor S. A. Mironov, doctor of technical sciences, A. V. Lagoyda, candidate of technical sciences, and Ye. N. Ukhov, engineer]

[Text] Up to the beginning of the fifties, in the Soviet Union and abroad, it was forbidden to put additives into concrete in order to reduce the freezing point of the mixing water. An additive of calcium chloride, along with sodium chloride in a large quantity (22.5 percent of the weight of the mixing water) was used for the first time in the winter of 1951-1952, when the aprons of the Volga-Don Canal were concreted [1, 2]. The favorable results of the studies and experimental use of chlorine salts [3] made it possible to recommend to the builders a new method of winter concreting--using concrete with chemical additives, *hardening at subzero temperatures*. Due to its economic soundness and the simplicity of the work, this method has found wide use in the last 15 years in the practical construction work of the USSR. In consideration of the experience of Soviet construction workers, the Recommendations of RILYeM [expansion unknown] *on winter concreting* [4] permit the use of chlorine salt additives to reduce the freezing point of the water to -10°C.

Further studies [5-8] showed that, in addition to the chlorine salts, potassium carbonate (potash) and sodium nitrite may be used as antifreeze additives. Any new compound may be used as an antifreeze additive, if it contributes to obtaining concrete which is not inferior with respect to its construction-technical properties to concrete with potash, sodium nitrite or sodium and calcium chloride, with approximately the same cost for the concrete, which is formed from the cost of the additives per m^3 of concrete, the process of adding it, additional measures for labor safety techniques when working with dangerous substances and the intensity of the concrete hardening, which determines the period for putting the structures into operation.

The capacity of the chemical compound for lowering the freezing point of the water is a necessary but not a sufficient condition for using it as an antifreeze additive. As the data given in Table 1 show, ferric chloride and calcium nitrate provide almost no acceleration of curing concrete based on high-aluminate Spasskiy portland cement, even with such a slight subzero tempeyature as -5°, although they create a nonfreezing liquid phase.

Table 1. Increase in Strength of Concrete Based on Portland Cement at -5°C



(1)		1:1,5:3:0,45 $R_{28} = 432$ kg/cm²				1:2:3,5:0,55 $R_{28} = 318$ kg/cm²			
(2)	(3)	(4)							
		7	14	28	+	7	14	28	
—	—	9	13	21	53	9	15	21	62
NaCl	2	30	38	53	112	28	46	48	110
	3	30	35	67	121	25	40	61	113
	5	36	49	79	117	29	55	69	116
KCl	2	22	33	35	63	17	28	38	57
	3	23	38	59	71	24	38	49	71
	5	24	49	62	100	27	54	63	120
$CaCl_2$	2	11	21	23	71	9	13	22	70
	3	11	20	33	75	16	19	29	104
	5	23	35	47	93	23	29	32	105
$FeCl_3$	2	3	6	16	48	2	3	5	37
	3	4	7	30	19	4	9	20	77
	5	5	21	32	75	9	16	23	83
$NaNO_2$	2	40	70	97	98	40	61	100	112
	3	40	74	88	93	23	52	68	111
	5	23	62	80	102	27	54	81	112
K_2CO_3	2	30	36	52	104	33	48	56	119
	3	31	45	61	98	27	44	64	103
	5	34	59	59	96	53	73	89	104
$Ca(NO_3)_2$	3	9	19	19	61	6	10	15	38
	5	10	14	24	50	8	10	14	59
	7	11	20	25	78	7	7	14	50

Key:

1. Additive
2. Composition
3. Amount in % of weight of cement
4. Crushing strength in % of R_{25}, after (days)

The intensity of the curing of concrete with antifreeze additives, it appears to us, depends on two factors: the number and strength of the bond between the molecules of water and the ions (molecules) of the compound introduced, and the participation of these compounds in the hydration processes. The latter acquires decisive importance at low subzero temperatures, when the introduction of a large amount of additive to obtain a nonfreezing solution leads to a sharp reduction in the "free" molecules of water as the result of an increasing large part of it passing into a solvate state. In connection with this it is of undoubted interest to examine the processes of cement hydration, since their course and the properties of new hydrate phases, provided there is no influence of physical factors (in this case of freezing) determine the properties of the concrete mix and the hardened block, and along with them--the boundary and area of using concrete with each of the additives.

When the concrete mixtrue is mixed with aqueous solutions of calsium chloride, the lime released with the hydrolysis of the tricalcium silicate reacts with the salt, forming calcium oxychloride with an approximate composition of $3CaO \cdot CaCl_2 \cdot 15H_2O$. The oxychloride, which is a crystalline compound, fulfills a function similar to $Ca(OH)_2$ when the concrete hardens under normal conditions. The formation of the low-soluble calcium oxychloride contributes to the more rapid and complete hydration of the tricalcium silicate, since the lime immediately goes out of the liquid phase. The latter circumstance, along with the reduction in the freezing point of the water also determines the efficiency of the calcium choloride as an antifreeze additive [9, 10].

The presence in the liquid phase of the concrete of calcium chloride, capable of yielding complex salts with calcium hydroaluminate, somewhat accelerates the formation of the calcium hydrosulfoaluminate and consequently the formation of the primary structure of the cement block. After the gypsum is completely bound, the aluminate components of the cement react with the $CaCl_2$, forming calcium hydrochloraluminates most probably with the composition of $3CaO \cdot Al_2O_3 \cdot CaCl_2\ 10H_2O$. The occurrence of this compound, however, apparently causes practically no change in the kinetics of the concrete curing, since instead of the hexagonal calcium hydroaluminates, calcium hydroaluminate with a similar crystalline shape is formed. As a result of this, the intensity of the concrete curing rises with an increase in the content in the cement of tricalcium silicate, and has little relation to the amount of tricalcium aluminate.

In the presence of the sodium chloride, the above-described new hydrate phases--calcium oxychloride and calcium hydrochloraluminate--are formed. But in view of the slow reaction of the sodium chloride with the calcium hydroxide, which takes place only due to the bonding of the calcium chloride formed into complex crystal hydrates, the nonfreezing liquid phase is permanently retained in the concrete. This is also the reason for the higher strength indices of concrete with an additive of NaCl, as compared with $CaCl_2$, at slightly subzero temperatures (see Table 1).

To create the liquid phase at low temperatures, a large amount of chlorine salts must be introduced into the concrete. If only NaCl is used, because of the bonding of a large amount of water in the solvates and the absence of an intensive reaction of the salt with the hydration products of the cement, the concrete gains strength slowly. Adding only $CaCl_2$, however, because of the formation of calcium oxychloride, soon leads to the freezing of the concrete. To avoid this, when the temperature is below -5°, it is recommended that both chlorine salts be introduced into the composition of the concrete simultaneously [11].

With a rise in temperature to above-zero values, and even with prolonged curing of the concrete, in frosty weather the calcium oxychloride breaks down. If this compound is predominant in the structure of the cement block which has been formed, its breakdown will lead to a considerable reduction in the strength of the concrete. A stable structure, as studies show, may be obtained by introducing into the composition of the concrete mix chlorine salts in an amount not over 7.5 percent of the weight of the cement, which also determines the minimal permissable temperature of the concrete (-15°) when they are used as antifreeze additives. The metastability of the calcium oxychloride, as well as the presence of free sodium chloride, restrict the sphere of use of concrete with chlorine salts [11], since the unbound chlorides contribute to the corrosion of the reinforcement and migrate towards the surface of the concrete, forming salt-outs.

In the potash solutions, as a result of the reaction of the salt with the calcium hydroxide, low-soluble calcium carbonates and hydrocarbonates are formed with a composition of $CaCO_3 \cdot 6H_2O$ [12]. When the doses of potash are up to 5-7 percent of the weight of the cement, this leads to excessive acceleration of the hydration processes of the bonding agent, and as a result--to the formation of a porous structure of the cement block with the use of certain cements. The formation of a defective structure is manifested externally in the almost instantaneous setting of the cement and the rapid loss of mobility of the concrete mix.

When the amount of the salt is increased, due to the increased alkalinity of the liquid phase, formation of the calcium carbonate is delayed. A dense structure of the cement block is formed. The calcium hydrocarbonate, appearing in the form of large prismatic crystals, reinforces the structure being formed, and in the first period of curing, along with the products of the hydration of the aluminate constituents of the cement, the strength of the concrete is determined. Then this crystal hydrate fulfills a similar function to that of the calcium oxychloride when the concrete mix sets by means of the chlorine salt solutions. But in its absence, the $CaCO_3 \cdot 6H_2O$ breaks down into $CaCO_3$ and H_2O only with a rise in the temperature of the concrete to values above zero.

Formed at the same time as the calcium hydrocarbonate and carbonate is calcium hydroxide, the aqueous solution of which has a lower freezing point (Figure 1). The increase in alkalinity of the liquid phase, due to the passing of part of the K_2CO_3 into KOH, delays the hydration processes of the cement, but at the same time leads to a reduction in the dose of potash needed to create an aqueous solution which does not freeze at a certain subzero temperature. Since the rate of KOH formation in the early periods of the curing is determined primarily by the amount of rapidly hydrated minerals--tricalcium aluminate and tetracalcium aluminoferrite--when their content in the cement is increased the optimal dose of potash is reduced.

Since they are compounds which are practically insoluble in water, calcium carbonates may be formed until almost all the potash reacts with the calcium hydroxide. If there is not enough hydrolitic lime for this reaction, the expectation should be that the principle carriers of the concrete strength will begin to be removed--the calcium hydrosilicates. Taking into consideration the degree of hydration of the portland cement and the content in it of tricalcium silicate, the amount of potash introduced in the composition of the concrete mix, to avoid the breakdown of the calcium hydrosilicates, should not exceed 15 percent of the weight of the cement [13].

With the hydration of the aluminate constituents of the portland cement, in the present of potash, calcium hydrocarboaluminate is formed, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ [14]. This compound plays a more significant role than the calcium hydrochloroaluminate in forming the strength and other properties of the concrete, since calcium hydrosulfoaluminate is unstable in potash solutions [15]. In addition, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ may coalesce with the $CaCl_3$, strengthening the crystalline frame of the cement block [16]. As a result of this, higher strength indices for concrete with potash additives may be obtained with the use of high-aluminate portland cement.

Studies of the kinetics of curing concrete with additives of sodium nitrite show that its rates of curing as a rule are delayed with an increase in the dose of salts. The highest strength indices are obtained, contrary to the potash, with the inclusion in the concrete composition of the amount of sodium nitrite minimally possible at the given subzero temperature (Table 2).

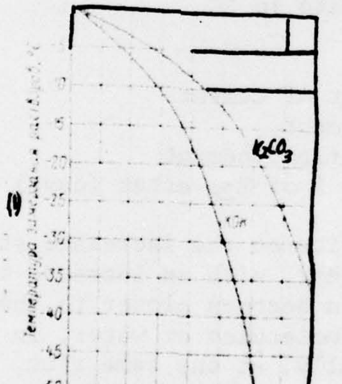
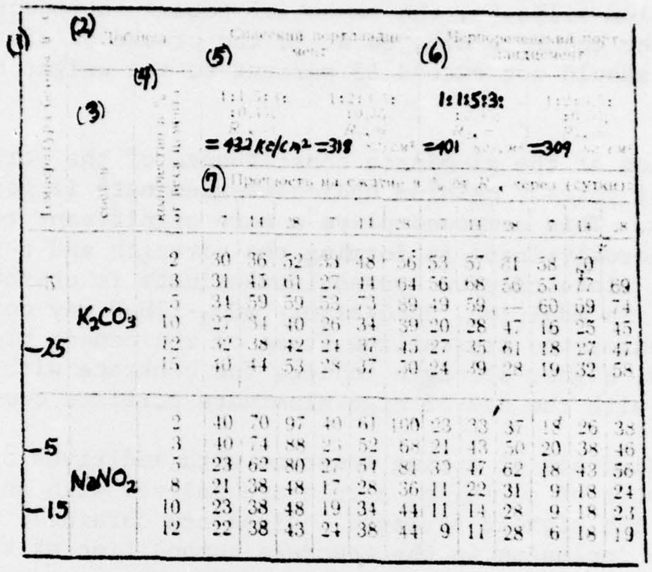


Figure 1. Freezing Point of Aqueous Solutions of K_2CO_3 and KOH, Depending on Potash Content in Solution

Key:

1. Freezing points of solutions, in °C
2. Content of K_2CO_3, in % of weight of solution

Table 2. Increase in Strength of Concrete With Additives of Potash and Sodium Nitrite



(1)	(2) (3)	(4)	(5)						(6)					
			=432 кг/см²			=318			1:1:5:3: =401			=309		
			(7)											
			7	14	28	7	14	28	7	14	28	7	14	28
		2	30	36	52	33	48	56	53	57	81	58	70	
-5		3	31	45	61	27	44	64	56	68	56	55	77	69
		5	34	59	59	53	73	89	49	59	—	60	69	74
	K_2CO_3	10	27	34	40	26	34	39	20	28	47	16	25	45
-25		12	32	38	42	24	37	45	27	35	61	18	27	47
		15	40	44	53	28	37	50	24	49	28	19	32	58
		2	40	70	97	40	61	100	23	33	37	18	26	38
-5		3	40	74	88	23	52	68	21	43	50	20	38	46
		5	23	62	80	27	51	81	39	47	62	18	43	56
	$NaNO_2$	8	21	38	48	17	28	36	11	22	31	9	18	24
-15		10	23	38	48	19	34	44	11	14	28	9	18	23
		12	22	38	43	24	38	44	9	11	28	6	18	19

Key:

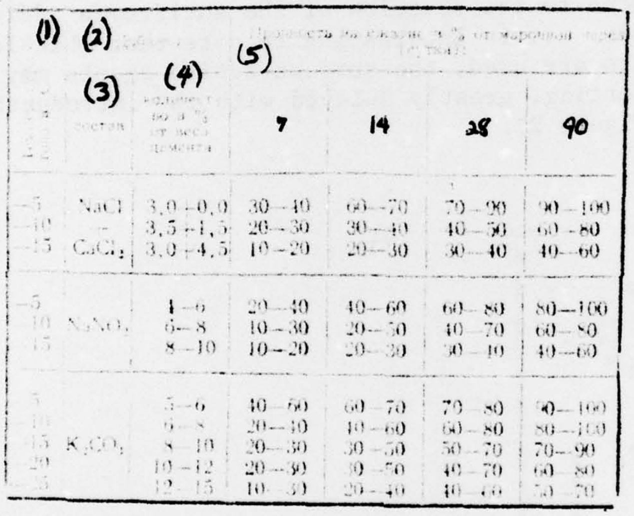
1. Temperature of concrete in °C
2. Additive
3. Compositon
4. Amount in % of weight of cement
5. Spasskiy portland cement
6. Chernorechenskiy portland cement
7. Crushing strength in % of R_{28} after (days)

This effect of the sodium nitrite on the increased strength of the concrete may be explained by the fact that, with an increase in the amount of salts, the composition of the solution becomes closer to the eutectic, characterized by the absence of "free" molecules of water, in view of their being bound in the solvates. Naturally, at the same time, a delay in the reaction of the water with the minerals in the cement takes place, which practically ceases with temperatures below -15°.

The sodium nitrite can apparently take part in the hydration processes of the aluminate constituents of the cement, leading to the occurrence of calcium hydronitroaluminate with a composition of $3CaO \cdot Al_2O_3 \cdot Ca(NO_2)_2 \cdot 10H_2O$. This compound may form after the complete bonding of the gypsum in the calcium hydrosulfoaluminate, somewhat accelerating this process. The calcium hydronitroaluminate itself, like the calcium hydrochloroaluminate, has little influence over the increase in strength of the concrete. But, probably as a result of the NaOH appearing simultaneously with it, adsorbed by the surface of the silicic filler better than the salt, to obtain a higher strength of the concrete with an increased content in the cement of tricalcium aluminate, the dose of $NaNO_2$ at the same subzero temperature must be increased.

A study of the increased strength of concrete based on portland cements made by seven plants made it possible to establish the optimal doses of antifreeze salts. The salt doses established in this way and recommended for practical use, as well as the generalized strength indices of the concrete when they are present, depending on the temperature of the hardening concrete, are given in Table 3.

Table 3. Increase in Strength of Concrete Based on Portland Cements With Optimal Doses of Antifreeze Salts



(1)	(2)		(5)			
	(3)	(4)	7	14	28	90
−5 −10 −15	NaCl + $CaCl_2$	3,0+0,0 3,5+1,5 3,0+4,5	30—40 20—30 10—20	60—70 30—40 20—30	70—90 40—50 30—40	90—100 60—80 40—60
−5 −10 −15	$NaNO_2$	4—6 6—8 8—10	20—40 10—30 10—20	40—60 20—50 20—30	60—80 40—70 30—40	80—100 60—80 40—60
−5 −10 −15 −20 −25	K_2CO_3	5—6 6—8 8—10 10—12 12—15	40—60 20—40 20—30 20—30 10—30	60—70 40—60 30—50 30—50 20—40	70—80 60—80 50—70 40—70 40—60	90—100 80—100 70—90 60—80 50—70

Key:

1. Temperature of concrete in °C
2. Additive
3. Composition
4. Amount in % of weight of cement
5. Crushing strength in % of branded after (days)

The sodium nitrite and potash do not accelerate the corrosion of the steel reinforcement. The caustic akalies, formed in the process of curing cement with these additives, however, eliminate the possibility of their use with active silicon fillers [17, 18]. When fillers are used which are not capable of reacting, one may rely upon the sufficient life of concrete with potash additives, since the silicon is uniformly distributed in the concrete. The introduction of finely crushed pozzolan additives, i.e., as if lessening the nonuniformity in the distribution of the active silicon, eliminates the alkaline corrosion of the concrete even based on fillers capable of reacting [19]. Still, the lack of experimental data on this problem leads to prohibiting the use of potash as antifreeze additives for the manufacture of structures destined for service in an aqueous or extremely moist medium.

As opposed to the sodium chloride and sodium nitrite, potash and calcium chloride, as the result of active participation in the hydration processes of the cement, may lead to the rapid loss of the mobility of the concrete mix. An effective means of slowing down excessively rapid setting of the concrete mix is to include in its composition surface-active agents (sulfite-alcohol residues, naphtha soap, etc.). The amount of setting retarding agents may reach 2 percent of the weight of the cement. In contrast to concrete without additives, such large doses of sulfite-alcohol residues of naphtha soap will not lead to an excessive delay in setting and hardening, which is related to the reaction of the antifreeze additives with the organic compounds. It is interesting to note that when low aluminate portland cements are used, the surface-active agents may also be used to accelerate the setting, greatly delayed with the introduction of large doses of potash (Figure 2).

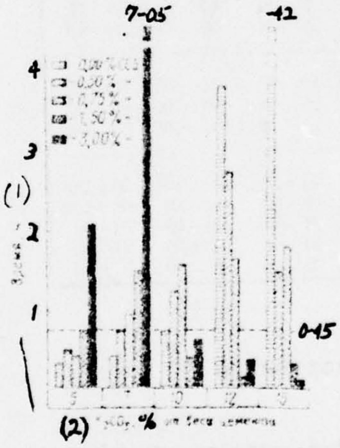


Figure 2. Beginning of Setting of Bryanskiy Portland Cement at +20°C, Depending on the Dose of Potash in the Sulfite-Alcohol Residues

Key:

1. Time, in hours
2. K_2CO_3 in % of weight of cement

The hydration processes discussed above, of course, do not present an exhaustive explanation of the effect of antifreeze additives on concrete curing processes. When salts are present, there is a change in the solubility of the initial minerals and hydrate phases, the stability of the latter and practically all the physical-chemical processes taking place in concrete curing. Large amounts of salt introduced into the composition of the concrete mix and an appreciable relation of the effectiveness of the additives to the mineralogical composition of the cement, however, give reason to feel that the intensity of concrete curing in many ways depends upon the ability of the additives to participate in the hydration processes of the cement, with the formation of new phases favorably influencing the formation of the structure of the cement in the concrete.