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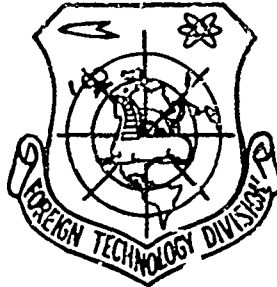
# FOREIGN TECHNOLOGY DIVISION



FULL-SCALE AND LABORATORY TESTS OF THE CORROSION  
RESISTANCE OF PRESTRESSED REINFORCEMENT  
IN CONCRETE WITH ADDITIVES

by

S. G. Yenisherlova, O. I. Dovzhik,  
and V. B. Ratinov



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## EDITED TRANSLATION

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13. ABSTRACT In dense concrete without cracks or with cracks where the width of exposure does not exceed approximately 0.1 mm, stressing of the reinforcement results in virtually no change in its chemical resistance in atmospheric conditions even when the concrete contains 2% chlorine salts. The nature of the control over the corrosion process is unchanged. Five-year full-scale tests have shown the possibility of protecting unstressed and prestressed reinforcement in solid concrete with 2% calcium chloride by introducing an addition of 2% sodium nitrite. Sodium nitrite is retained longer in the liquid phase of the concrete than the calcium chloride; the latter converts to the low-solubility hydrate of calcium chloroaluminate. This leads to a systematic increase in the properties of nitrite additives as corrosion protection.			

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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, ь; e elsewhere.  
 When written as ѣ in Russian, transliterate as yě or ě.  
 The use of diacritical marks is preferred, but such marks  
 may be omitted when expediency dictates.

FULL-SCALE AND LABORATORY TESTS OF THE  
CORROSION RESISTANCE OF PRESTRESSED  
REINFORCEMENT IN CONCRETE  
WITH ADDITIVES

S. G. Yenisherlova, O. I. Dovzhik,  
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The addition of 2% and more of calcium chloride intensifies the corrosion of unstressed and stressed reinforcement in concrete, especially when defects are present. According to laboratory data [1] sodium nitrite effectively inhibits corrosion of unstressed steel reinforcement in concrete with additions of calcium chloride. However, these conclusions required confirmation by prolonged full-scale tests. Besides this, no data were available on the corrosion of stressed reinforcement under these conditions. These problems were the object of study in this work.

The experiments were conducted with models of prestressed reinforcement and prestressed reinforced concrete prisms 120 cm long, reinforced with high-strength cold-drawn deformed steel wire, 0.3 mm, made from carbon steel with the following composition: C, 0.78%; P, 0.048%; S, 0.031%, and traces of Mn, Ni, and Si. The stress was 50% of destructive. During manufacture of the prisms the concrete composition (mark 300) was 1:1.2:2; cement consumption

was 520 kg/m<sup>3</sup>; and the water-to-cement ratio (W/C) was 0.4. Three lots of prisms were concreted on one line with identical reinforcement stress: without additives, with addition of 2% sodium chloride, and with additions of 2% CaCl<sub>2</sub> and 2% NaNO<sub>2</sub>, introduced with the mix water. After two months had passed the prisms were subjected to "rooftop" tests - i.e., they were exposed to the atmosphere.

The degree of corrosion damage was evaluated quantitatively in terms of the maximum depth of corrosion pits and by the change in the magnitude of the resistance of the armature to tensile failure. After the armature was covered it was found that after five years damage with a depth up to 1.3 mm occurs only on the reinforcement located in concrete with an addition of sodium chloride. In the concrete with a complex additive (CaCl<sub>2</sub> + NaNO<sub>2</sub>) no visible traces of corrosion were found on the reinforcement; its tensile strength was no lower than that for reinforcement located in concrete without additives (Table 1).

Table 1. Results of corrosion testing of pre-stressed reinforcement after 5-year storage of prisms in the open air.

(1) Добавка в бетон	Максимальная глубина коррозии, $\mu\text{м}$ (2)	Разрывное напряжение арматуры диаметром 3 мм, кг (3)
(4) Без добавки 2% CaCl <sub>2</sub> 2% CaCl <sub>2</sub> + +2% NaNO <sub>2</sub>	(5) Коррозии нет (6) От 650 до 1300 (5) Коррозии нет	1260 (6) от 1000 до 635 1270

KEY: (1) Additive in concrete; (2) Maximum depth of corrosion,  $\mu\text{m}$ ; (3) Breaking stress of reinforcement 3 mm in diameter, kg; (4) Without additive; (5) No corrosion; (6) From 650 to 1300 (1000-635).

From Fig. 1 it is clear that the complex additive, like the addition of CaCl<sub>2</sub>, improves adhesion of the armature to the concrete. These tests were carried out by M. M. Kholmyanskiy and V. M. Kol'ner according to existing procedures [2].

Analyses were conducted on the solid and liquid phases of the concrete to detect ions of chlorine and nitrite.

Chlorine ions were determined in the liquid phase by titration of a water-alcohol extract of the concrete by a solution of silver nitrate, while the total content was determined by titrating a concrete sample previously dissolved in nitric acid, using the same silver nitrate solution.

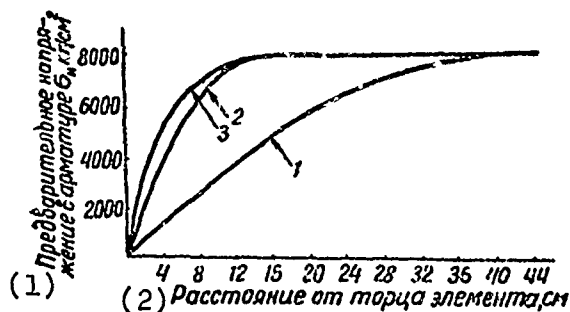


Fig. 1. Distribution curve for preliminary stresses in the reinforcement: 1 - concrete without additives; 2 - concrete with 2%  $\text{CaCl}_2$ ; 3 - concrete with 2%  $\text{CaCl}_2$  and 2%  $\text{NaNO}_2$ .

KEY: (1) Preliminary stress in the armature,  $\sigma_H$ ,  $\text{kg/cm}^2$ ; (2) Distance from the face of the element, cm.

The content of nitrite ions ( $\text{NO}_2^{-1}$ ) was determined as follows:  $\text{NO}_2^{-1}$  ions were oxidized in a solution of potassium permanganate ( $\text{KMnO}_4$ ) in an acid medium to  $\text{NO}_3^{-1}$  ions, while the excess  $\text{KMnO}_4$  was titrated off by the iodometric method. To determine the free nitrite ions, an aqueous extract of concrete with addition of  $\text{Ca}(\text{OH})_2$  was titrated, while the total content was determined by dissolving concrete in dilute hydrochloric acid. The results of these tests are shown in Table 2.



Table 2. Results of quantitative determinations of  $\text{Cl}^{-1}$  and  $\text{NO}_2^{-1}$  ions in concrete.

	(1)			
	Количество $\text{CaCl}_2$		Количество $\text{NaNO}_2$ (2)	
	(3) в кг $\text{CaCl}_2$ на м <sup>3</sup> бе- тона	(4) в г-ион $\text{Cl}^{-1}$ на м <sup>3</sup> бе- тона	(5) в кг $\text{NaNO}_2$ на м <sup>3</sup> бе- тона	(6) в г-ион $\text{NO}_2^{-1}$ на м <sup>3</sup> бетона
(7) Исходное количество добавок				
(8) В бетоне с $\text{CaCl}_2$	10,2	183,1	—	—
(9) В бетоне с комплексной добавкой ( $\text{CaCl}_2 + \text{NaNO}_2$ )	10,4	187,5	10,4	132,0
(10) Общее количество добавок через 5 лет				
(8) В бетоне с $\text{CaCl}_2$	6,3	114,4	—	—
В бетоне с комплексной добавкой (9)	6,3	114,4	6,4	83,0
(11) Количество свободных добавок				
В бетоне с $\text{CaCl}_2$ (8)	1,1	20,1	—	—
(9) В бетоне с комплексной добавкой	1,4	24,8	5,8	73,6

KEY: (1) Quantity of  $\text{CaCl}_2$ ; (2) Quantity of  $\text{NaNO}_2$ ; (3) as kg  $\text{CaCl}_2$  per m<sup>3</sup> concrete; (4) in g-ions  $\text{Cl}^{-1}$  per m<sup>3</sup> concrete; (5) in kg  $\text{NaNO}_2$  per m<sup>3</sup> concrete; (6) in g-ions  $\text{NO}_2^{-1}$  per m<sup>3</sup> concrete; (7) Initial quantity of additive; (8) In concrete with  $\text{CaCl}_2$ ; (9) In concrete with the complex additive; (10) Total quantity of additives after 5 years; (11) Quantity of free additives.

From Table 2 it follows that after five years of storage in open air 80% of the residual calcium chloride has gone into reaction with the components of the cement and has been removed from the liquid phase, where the calcium chloride appears as an aggressive substance with respect to the reinforcement, into the solid phase, where it no longer behaves as an aggressive agent.<sup>1</sup>

In contrast to this, the sodium nitrite reacted with the components of the cement with the formation of poorly soluble

<sup>1</sup>In individual cases the content of calcium chloride and sodium nitrite in the cement was reduced due to washing out.

hydrated calcium nitroaluminate in a quantity of only 8%, with the principal amount found in the liquid phase, and passivated the metal.

Thus, sodium nitrite is retained in the liquid phase of the concrete for a substantially longer period and in a larger quantity than calcium chloride; this, naturally, should lead to an increase in the protective properties of the sodium nitrite with passage of time.

To clarify the mechanism by which an addition of sodium nitrite acts on the corrosion of prestressed reinforcement, electrochemical tests which involved taking polarization curves from a model of prestressed reinforcement were carried out.

The installation whose diagram is shown on Fig. 2 was used for the electrochemical tests. Steel plates were pulled on the installation up to a given stress (usually 60% of destructive) and held in the stressed state during the entire test. A cement-sand solution was placed in a small mold  $80 \times 40 \times 30$  mm.

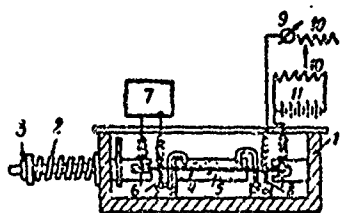


Fig. 2. Diagram of installation for testing stressed reinforcement: 1 - channel; 2 - cylindrical spring; 3 - nut; 4 - steel specimen; 5 - concrete; 6 - calomel electrode; 7 - potentiometer; 8 - auxiliary platinum electrode; 9 - galvanometer; 10 -  $120 \text{ M}\Omega$  resistor; 11 - DC source.

The specimen was connected to an auxiliary and a saturated calomel electrode by means of glass tubes filled with the cement solution. Potentials were measured with an LP-5 potentiometer. The electric circuit permitted taking polarization curves at growing current densities without a break in the circuit. All electrochemical measurements were carried out at a relative humidity of 80%, which ensured the possibility of simultaneous

penetration of moisture and air into the reinforcement through the pores in the concrete [1, 3]. Such conditions are considered very aggressive.

To accelerate the tests we took cement-sand solutions with additions of 10% calcium chloride and 6% sodium nitrite. This amount of sodium nitrite does not give a complete guarantee of protection from corrosion [1, 4].

As is evident from the data in Fig. 3 and Table 3, the armature stress state finds no reflection whatever in the polarizability of the steel or in the magnitude of its corrosion in the concrete.

Table 3.

(1) Добавка в бетон	Максимальная глубина (2) коррозии, мк	
	ненпря- женная арматура	напряжен- ная арма- тура
(5)	(3)	(4)
Без добавки	30	35
10% CaCl <sub>2</sub>	422	405
10% CaCl <sub>2</sub> + +6% NaNO <sub>2</sub>	235	223

KEY: (1) Concrete additive; (2) Maximum depth of corrosion, μm; (3) unstressed reinforcement; (4) stressed reinforcement; (5) Without additive.

The tests (Fig. 3) showed that as in solutions of electrolytes, sodium nitrite in concrete operates as an inhibitor of steel reinforcement corrosion by an anode effect but, in contrast to the behavior in electrolyte solutions, in concretes sodium nitrite has no influence on the rate of the cathode process. This is explained by the fact that corrosion of the reinforcement in concrete is basically determined by diffusion processes [1-5], whose rate depends in the presence of moisture on the quality of the protective layer of concrete and is virtually independent of

of the area of the cathode segments. The addition of sodium nitrite does not lower the quality of the protective layer and, consequently, does not increase the rate of diffusion of corrosion agents; this is supported by the cathode polarization curves.

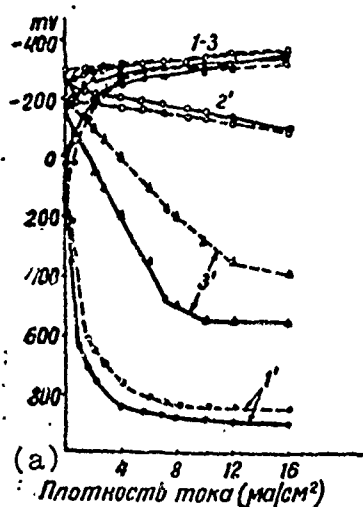


Fig. 3. Effect of stress on polarization of steel in concrete: 1, 1' - concrete without additives; 2, 2' - 10% CaCl<sub>2</sub>; 3, 3' - 10% CaCl<sub>2</sub> + 6% NaNO<sub>2</sub>.

— unstressed reinforcement;  
 - - - - stressed reinforcement.

KEY: (a) Current density  
 (mA/cm<sup>2</sup>).

Thus, in dense concrete, where corrosion proceeds with diffusion control, sodium nitrite slows the anode process through the creation of a protective film on the surface of the metal; it does not influence the cathode process and, consequently, it should be a safe corrosion inhibitor at any concentrations of the NO<sub>2</sub><sup>-1</sup> ion. This is confirmed by the results from our earlier laboratory investigation.

### Conclusions

1. In dense concrete without cracks or with cracks where the width of exposure does not exceed approximately 0.1 mm, stressing of the reinforcement results in virtually no change in its chemical resistance in atmospheric conditions even when the concrete contains 2% chlorine salts. The nature of the control over the corrosion process is unchanged.

2. Five-year full-scale tests have shown the possibility of protecting unstressed and prestressed reinforcement in solid concrete with 2% calcium chloride by introducing an addition of 2% sodium nitrite.

3. Sodium nitrite is retained longer in the liquid phase of the concrete than the calcium chloride; the latter converts to the low-solubility hydrate of calcium chloroaluminate. This leads to a systematic increase in the properties of nitrite additives as corrosion protection.

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