

Technical Review of Calcium Nitrite Corrosion Inhibitor in Concrete

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Calcium nitrite has been used as a corrosion inhibitor against chloride attack and as a set accelerator in concrete for more than 20 years. Considerable data are available concerning its effects on corrosion inhibition, setting times, freeze-thaw resistance, strength, and other properties. Although much of the data have been published in the open literature, a full-scale review is not available. This paper reviews past and present research on the properties of calcium nitrite in concrete. While the bulk of the data have been generated by W.R. Grace & Co., considerable information is available from outside sources, including the U.S. Federal Highway Administration (FHWA), departments of transportation, universities, and independent test laboratories. It is shown that calcium nitrite is an effective corrosion inhibitor for steel in concrete, based upon extensive corrosion testing in laboratory and field concrete specimens. The effects of mix design and concrete cover on corrosion resistance with calcium nitrite are also discussed. Furthermore, in most cases, calcium nitrite improves the compressive strength of the concrete mix and, with proper air entrainment, is freeze-thaw durable. In conclusion, the data generated in the last 20 years show that calcium nitrite is a proven corrosion-inhibiting admixture to be used to protect concrete structures in a chloride environment.

Steel-reinforced concrete is a widely used construction material. The concrete provides a protective environment for the steel, and the steel provides the concrete with tensile strength. When reinforced concrete is subjected to chloride-containing salt, however, corrosion of the steel reinforcement can occur. The corrosion of the steel eventually leads to significant deterioration of the reinforced concrete.

The effects of corrosion are staggering. Approximately half of the 500,000-plus bridges in the U.S. highway system are in need of repair (1). The Strategic Highway Research Program pointed out that \$450 to \$500 million per year can be saved by correcting corrosion problems in extant bridges (2).

Most bridge failures are due to deicing salts. However, bridges in marine environments are also susceptible to severe corrosion due to chloride ingress. The severity of the marine environment is such that damage may be evident in as little as 5 years (3).

This paper reviews the development of calcium nitrite as a corrosion inhibitor to protect steel in concrete from chloride-induced corrosion. Additionally, the beneficial effects of calcium nitrite on concrete, such as improved properties of mechanics and durability, are discussed.

HISTORY OF DEVELOPMENT

In 1961 the need for a noncorrosive accelerator for concrete became apparent. The main impetus was the definitive paper by Monfore and Verbeck (4) in which they showed that admixed calcium chloride caused the Regina, Saskatchewan, waterpipe failure. This followed closely a similar study by Evans (5), in which he found that chloride caused corrosion of steel in prestressed concrete.

The most obvious approach seemed to be a salt that would accelerate concrete's setting time but also act as a corrosion inhibitor. Treadaway and Russell (6) studied sodium nitrite and sodium benzoate. Craig and Wood (7) studied potassium chromate, sodium benzoate, and sodium nitrite. These papers and others agreed that sodium nitrite offered the best protection for concrete from chloride-induced corrosion but that the strength of the concrete was reduced when any of these materials were used. Figure 1 shows the reduction of strength with various inhibitors (7). Further, the risk of the alkali-aggregate reaction was worsened by the addition of a sodium salt.

Further studies revealed that to maintain or improve the strength of the concrete, the cation system of concrete, namely calcium, could not be changed. Thus, in 1964 a noncorrosive accelerator based on calcium formate and a small amount of sodium nitrite was introduced; it did not result in loss of strength (8). The calcium formate/10 percent sodium nitrite

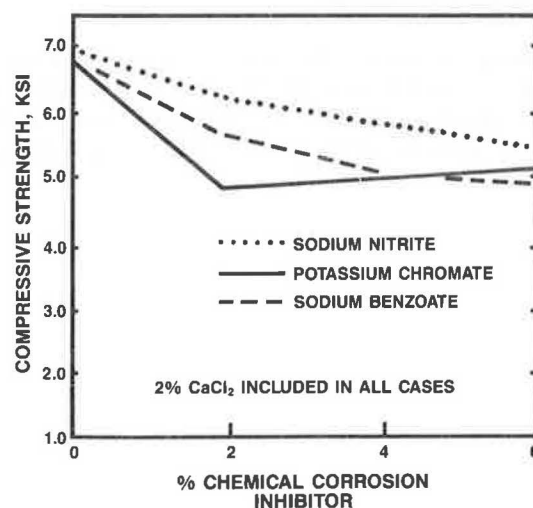


FIGURE 1 Effects of some corrosion inhibitors on compressive strength (7).

accelerator gave good setting time acceleration with no loss in compressive strength (9). The product had to be handled as a dry powder, however. Ten years later the corrosion of steel in concrete became a serious problem in the United States, and a process for the manufacture of calcium nitrite became available in Japan. The new corrosion threats to concrete placed in marine environments and the use of marine sand, along with the fact that calcium nitrite could be prepared as a 40 percent stable solution, encouraged further study of calcium nitrite for use as an admixture in concrete.

First the mechanism of calcium nitrite's protection of steel in concrete was determined. Several experts were consulted, and laboratory experiments were conducted to confirm the mechanism. If corrosion was the dissolution of iron or

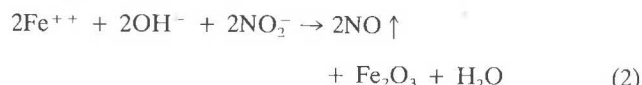


a solid ferrous hydroxide (white) corrosion product would form in concrete (pH = 12.5), preventing further dissolution of iron, in the absence of chloride. In the absence of chloride, the iron will convert to the ferric state. The resultant protective ferric oxide is less than 100 Å thick.

When not protected by concrete, iron continues to corrode because of available oxygen, carbon dioxide, moisture, and changing temperatures. The initial ferrous ions change to the more stable $\text{Fe}_2\text{O}_3 \times \text{H}_2\text{O}$ going through different intermediate stages, such as Fe_3O_4 . In well-rusted iron, layers of the various oxides of red and black rust are observed. The layers of oxides prevent a strong, continuous passive film from protecting the iron from further corrosion.

Foley (10) has shown that iron forms soluble, light green complexes with chloride ion. These have been observed in concrete. These soluble forms of ferrous ions are able to migrate away from the reinforcing bar, encouraging more iron to dissolve. This prevents the passive layer from forming. Thus, the corrosion process in concrete depends on chloride ion, water, and oxygen content, as borne out by Hartt and Rosenberg (11) who found the worst corrosion of marine-exposed concrete at the intertidal zone.

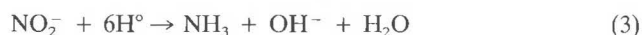
It was determined that calcium nitrite does not react with Fe^0 or Fe^{+++} . It does react with Fe^{++} according to the following:



Thus, if ferrous ions are produced in concrete, calcium nitrite changes them to a stable passive layer, avoiding all the metastable intermediate forms. Chloride ions and nitrite ions compete for ferrous ions produced in concrete. The relative concentrations of chloride and nitrite determine the type of reaction that takes place. If the nitrite ion concentration is large, then nitrite reacts with ferrous ions to form a passive layer that closes off the iron surface, stopping further reaction; as such, the amount of nitrite reacting is very small (12-17).

There was concern about the production of NO gas in concrete, nitrite ions changing the size of the anode, and dangerous cathodic reactions. If produced, NO gas changes to NO_3^- eventually in the presence of O_2 but only after corrosion would have taken place and the concrete had been destroyed. Nitrite does not enter the reactions involved in producing the anode but reacts with the resulting products of the anode. Thus, it cannot affect the size of the anode.

The dangerous cathodic (18) reaction is



which is a reaction that can take place only in an acid environment. Therefore, the preceding concerns were unwarranted.

More important than the theory is the actual performance of calcium nitrite in concrete. Calcium nitrite meets the requirements of ASTM C494, and Table 1 shows the effect on setting time and compressive strengths.

In the early 1970s the use of the Partial Immersion Corrosion Test to study corrosion in concrete was popular (12). Open circuit potentials of steel in mortars exposed to chloride using this method showed that calcium nitrite was a corrosion inhibitor (12).

TABLE 1 ACCELERATION WITH CALCIUM NITRITE

Cement Brand	Admixture % by Weight of Cement	3-Day Compressive Strength, psi (kPa)	Setting Time		
			Initial h:min.	Final h:min.	% change relative to control
A	none	1525 (10515)	8:45	12:21	-
A	1% calcium nitrite	1568 (10811)	6:00	10:20	31
A	1% calcium chloride	2151 (14831)	4:20	7:30	51
A	2% calcium nitrite	1924 (13266)	3:05	6:55	65
A	2% calcium chloride	2624 (18092)	2:10	4:55	75
B	none	1467 (10115)	8:38	---	---
B	1% calcium nitrite	1576 (10867)	5:24	9:05	37
B	1% calcium chloride	2220 (15307)	3:16	5:00	62
B	2% calcium nitrite	2075 (14307)	3:12	5:42	63
B	2% calcium chloride	2562 (17665)	2:15	3:40	74

Water/Cement ratio was 0.56 to 0.57; slump was 4.0 ± 0.5 in. (100 ± 12 mm); air content was 1.95 ± 0.25 percent.

In the late 1970s, the FHWA developed its own test for steel-reinforced concrete. Small bridge decks were constructed with steel closely spaced to accelerate the test. Salting was done daily, and potentials were measured over a long period. Several publications discussing the results from these tests can be found in the literature (13,17,19).

At the end of 2 years of accelerated testing, the most dramatic results with the corrosion inhibitor were found in the series where a water-reducing admixture was used. Here the control showed serious corrosion at the end of 6 months, whereas the protected deck was just beginning to show a slight amount of corrosion at the end of 2 years of continuous salting. Thus, with calcium nitrite and a water-reducing agent, the service life of a bridge deck under severe conditions will be extended. A finite amount of calcium nitrite, however, cannot protect against the unlimited addition of chloride. It was, therefore, important to determine the chloride:nitrite effectiveness ratio.

Concrete cylinders were cast with embedded rebar using 6-in. I.D. plastic pipe, 12 in. long, using ASTM C-185 mortar with admixed sodium chloride and admixed calcium nitrite. All the specimens with a $\text{Cl}^-/\text{NO}_2^-$ ratio less than 2.0 performed satisfactorily in the test without passing the -300 mV vs. SCE level, while more than half the specimens with $\text{Cl}^-/\text{NO}_2^-$ between 2.5 and 3.0 failed. It is apparent that if the chloride:nitrite ratio is below 2.0, or below 1.5 to be on the safe side, corrosion will be controlled.

If salt is continually put on bridge decks, however, the concentration of the salt will increase. Thus, it is important to know how salt concentrations build up with time.

It is generally believed that 1 to 2 lb. of chloride ion/yd³ of concrete will start the corrosion of steel in concrete. If it is assumed that 2 percent solids on cement by mass solids on solids (s/s) calcium nitrite will protect steel in concrete where 661 lb./yd³ of cement is used, corrosion will not begin until the chloride ion concentration reaches 12.8 lb./yd³.

Thus, in concrete unprotected with calcium nitrite, corrosion will begin when the level of chloride is 1 to 2 lb./yd³, although high-quality concrete will take longer to get to that level (20). In the concrete protected with calcium nitrite, on the other hand, the concentration must reach 12.8 lb./yd³.

The time it takes concrete to reach that level depends on the diffusion of chloride into the deck. Diffusion depends on several factors. For example, Ost and Monfore (21) found it to depend on the water:cement ratio, as shown in Table 2.

Stratfull et al. (22) examined chloride content in 16 bridges that had failed because of corrosion. They found the average chloride content of the steel to be 2.6 lb./yd³; the average age of the decks was 13 years. If calcium nitrite had been used at 2 percent s/s, then corrosion would not have started until the

chloride level reached 12.8 lb./yd³. Because the chloride levels at which corrosion occurs with calcium nitrite are substantially higher than those in unprotected concrete, there has been a recent switch to quantity of inhibitor added independent of cement content. One gallon of 30 percent $\text{Ca}(\text{NO}_2)_2$ solution provides approximately 2.27 lb. of nitrite. Chloride:nitrite ratios are now based upon the gallons per cubic yard of 30 percent calcium nitrite solution added.

RECENT CORROSION TESTING IN CONCRETE

In recent years improved electrical measuring techniques have been used to examine the effectiveness of calcium nitrite. New studies examining the effectiveness of calcium nitrite as an inhibitor in concrete are reported (23–30) in this section.

One of the most extensive studies of calcium nitrite involves more than 1,200 samples, 15 mix designs, and 0, 3, and 6 gallons/yd³ of 30 percent calcium nitrite solution; it is nearing completion after 4 years of accelerated testing (23,24). Samples were partially submerged in a 3 percent sodium chloride solution with 1.3 in. of concrete cover. This environment provided strong chloride wicking into the concrete with good access to oxygen—that is, an extremely severe exposure.

Corrosion rates were determined using the polarization resistance technique, electrochemical impedance, and periodic removal of specimens to permit the visual examination of the reinforcing steel appearance. Corrosion currents expressed as $1/R_p$, inverse polarization resistance ($\mu\text{mho}/\text{cm}^2$), were integrated over time to determine the total corrosion in $\mu\text{mho}/\text{cm}^2$ months. (Note that R_p is the polarization resistance, and the corrosion current is equal to B/R_p where B is a constant. Figure 2 shows the latest data, which are 1.5 years

TABLE 2 PERMEABILITY OF CHLORIDE ION IN CONCRETE (21)

W/C	% CaCl_2 at 2 in. Depth	
	After 12 Months Soaking	
0.61	5.3	
0.45	1.4	
0.37	0.1	

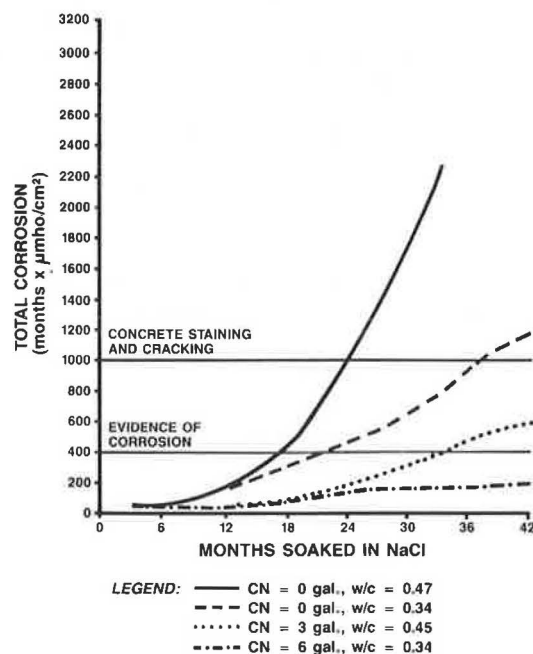


FIGURE 2 Total corrosion vs. time in 3 percent NaCl as a function of w/c ratio and calcium nitrite content.

TABLE 3 CORROSION INHIBITOR TEST RESULTS (26)

Time to Corrosion and Corrosion Current							
Water/Cement Ratio	Sample Type	Concrete Cover 1"			Concrete Cover 2"		
		Time to Corrosion (Weeks)	Corrosion Current, μa		Time to Corrosion (Weeks)	Corrosion Current, μa	
			48 Weeks	116 Weeks		48 Weeks	116 Weeks
0.50	Control	6	245	*	64	0	*
	4 gals CN	21	90	*	**	0	0
	6 gals CN	11	73	*	**	0	0
0.40	Control	5	128	*	***		
	4 gals CN	21	10	19	**	0	0
0.32	Control	2.5	110	*	***		
	4 gals CN	**	0	0	**	0	0

* Sample failed

** No corrosion activity after 116 weeks

*** Sample not made

CN - Calcium nitrite sample

Information Source:

1. Protection Systems for New Prestressed and Substructure Concrete
Report No. FHWA/RD-86/193, April 1987,
US Department of Transportation
2. Corrosion Protection Tests on Reinforced Concrete
September 1987
Wiss, Janney, Elstner Associates, Inc.

more current than those published earlier (24). A total corrosion measurement of $1,000 \mu\text{mho}/\text{cm}^2$ is roughly equivalent to 1 mil of average corrosion on the steel. This is considered enough to cause rust staining or cracking of the concrete. This was observed for several specimens that reached that degree of corrosion.

This study showed that calcium nitrite delayed the onset of corrosion, and in those cases where corrosion began, the rates remained lower than in unprotected cases. Furthermore, the benefits of calcium nitrite improved with lower water:cement ratios.

The FHWA examined the effectiveness of calcium nitrite in macrocell measurements made on minibridge decks, some of which had admixed chlorides (25). Even though they used a high (0.5) water:cement ratio and admixed chlorides in, they concluded that "calcium nitrite can provide more than an order of magnitude reduction in the corrosion rate."

Another major study in which calcium nitrite was tested was completed in 1987 (26). The macrocell corrosion rates of minislabs were investigated in this study. The minislabs were subjected to chloride ponding and severe drying for 48 weeks.

Additional slabs with calcium nitrite in concrete with different covers and water:cement ratios were added to the study, and tests were extended from 48 to 116 weeks. A synopsis of reported results and the additional results of the extended test program are presented in Table 3.

The preceding study showed that as concrete quality improved (w:c ratio decreased and cover increased), the benefits of adding calcium nitrite corrosion inhibitor became greater.

The South Dakota Department of Transportation conducted a study in which rebars were embedded in concrete cylinders with and without admixed chloride (27). Steel in cylinders with admixed chlorides without calcium nitrite went into corrosion almost immediately, whereas samples containing calcium nitrite remained passive for months. For samples without admixed chlorides, the benefits of calcium nitrite were significant.

Some of the preceding samples were further analyzed. Results of polarization resistance and electrochemical impedance tests using methods described elsewhere (23) are presented in Table 4. The corrosion rate is proportional to $1/R_p$ (R_p is the polarization resistance), and rates under $20 \mu\text{mho}/\text{cm}^2$ are consid-

TABLE 4 SOUTH DAKOTA LOLLIPOPS CORROSION RATES AT 3.5 YEARS (27)

Mix #	Concrete Mix (cf = 620 lb/yd ³)	E _{corr} , (mV, SCE)	Concrete Resistance (kohm-cm ²)	Measured Polarization Resistance (R _p), (kohm-cm ²)	Corrected (R _p), (kohm-cm ²)	1/R _p , (umho/cm ²)
4	4.1 gal/yd ³ Ca(NO ₂) ₂	-210	35	230	195	5
6	4.1 gal/yd ³ Ca(NO ₂) ₂ + 27 lbs/yd ³ NaCl	-491	13	27.4	14.4	69
19	27 lbs/yd ³ NaCl	-609	6.9	8.5	1.6	625

Concrete cylinder was cracked open by South Dakota DOT, which caused much higher corrosion rate. Note severe corrosion at 1/R_p s > 20 umho/cm².

ered passive (24). The corrosion rates were corrected for ohmic resistance (31) and clearly show that calcium nitrite significantly reduced corrosion.

After the corrosion rates were measured, the samples in Table 4 were broken open. The samples without calcium nitrite were severely corroded. Chloride and nitrite analyses were performed; chloride levels ranged from 18 to 40 lb./yd³ at the rebar level, and at Cl⁻/NO₂⁻ ratios of 1.6 to 2.2 calcium nitrite prevented corrosion.

This study showed that calcium nitrite significantly reduced corrosion of steel even when high chloride concentrations were present. Furthermore, it showed that until corrosion began there was no evidence of nitrite depletion at the reinforcement level.

Studies are now in progress examining the use of calcium nitrite with silica fume (28,29). Early results (one in 2 years) show that only the control samples without calcium nitrite or silica fume are corroding. Of interest is the observation that even though calcium nitrite increases the AASHTO T277 Rapid Chloride Permeability Coulombs value (see Table 5), it either lowers or has no effect on the effective diffusion coefficient for chloride. Thus, calcium nitrite is compatible with silica fume and should protect the reinforcement when chlorides reach it. This study also showed that calcium nitrite increased compressive strength.

Recent testing showed that calcium nitrite also protects galvanized steel and aluminum embedded in concrete (30). This study involved alternate ponding of minibeams with 3 percent NaCl. Corrosion rates were measured by both polarization resistance and macrocell corrosion. Visual observations were in good agreement with the electrochemical test results shown in Table 6.

Also, the benefits of calcium nitrite in cracked concrete have been demonstrated. Figure 3 shows the long-term total corrosion, to alternate ponding with 3 percent NaCl, for reinforced notched minibeams (16 in. × 4 in. × 3 in.) with third-

point loaded cracks that extend down to the reinforcing bar, halfway to the bar, and not at all. Cracked samples with calcium nitrite took longer to start corroding or are corroding at substantially reduced rates. The uncracked samples are not yet corroding because of the good-quality concrete employed, as can be seen in Table 7. Cracks were less than 0.01 in. wide. It was determined from this study that calcium nitrite is effective in the presence of cracks.

A recent study in Germany (32) showed that sodium nitrite was also effective in reducing corrosion in cracked specimens, even at much higher than recommended water:cement ratios and a low dosage rate for the exposure conditions. This is not surprising since two other studies showed that thin cracking was not a significant factor in corrosion (33,34).

A small study was conducted looking at the benefits of adding calcium nitrite to concrete containing fly ash. Figure 4 shows the long-term corrosion behavior of a control concrete compared to concrete with fly ash or fly ash and calcium nitrite. Calcium nitrite significantly improved corrosion resistance, and fly ash by itself offered only minimal improvement. Mix designs are given in Table 8.

IMPORTANCE OF MIX DESIGN

ACI 201 states that low water:cement ratios and good concrete cover should be employed when chloride exposures are moderate to severe (35). Several of the studies mentioned confirm the need for low water:cement ratio studies and adequate cover (23,24,26,28,29). Furthermore, research (23,24,26) clearly shows that calcium nitrite becomes more effective as concrete quality improves. This is significant because the higher-quality concretes outperform those of lesser quality; thus, the improvements with calcium nitrite in good-quality concrete are substantial.

ACI 201 also states the importance of air entrainment to

TABLE 5 EFFECTIVE CHLORIDE DIFFUSION COEFFICIENTS (D_{eff}) VS. AASHTO T277 COULOMBS (28)

Mix	Cement Factor		Microsilica		W/C	AASHTO T277 Coulombs	D_{eff} ⁻⁸ cm ² /s
	kg/m ³	(pcy)	%	L/m ³ (gpy)			
1	347	(587)	0	0	0.48	3663	11.0
2	343	(580)	0	20 (4)	0.48	4220	6.0
5	350	(591)	15	0	0.48	198	0.7
6	359	(607)	15	20 (4)	0.48	253	0.5
11	363	(614)	7.5	10 (2)	0.43	380	0.8
13	338	(571)	0	0	0.38	3485	2.0
14	352	(595)	0	20 (4)	0.38	1838	2.0
17	354	(599)	15	0	0.38	75	0.3
18	313	(580)	15	20 (4)	0.38	119	0.3

Note: D_{eff} at 22°C (72°F).

TABLE 6 CORROSION CURRENTS OF METALS IN MINIBEAMS AFTER 24 MONTHS OF CYCLIC PONDING IN 3 PERCENT NaCl

Type of Steel	Cover (in.)	Calcium Nitrite	Corrosion Current	
			Polarization Resistance ($\mu\text{A}/\text{cm}^2$)	Macrocell Testing ($\mu\text{A}/\text{cm}^2$)
Black Steel	0.75	0	1.575	0.831
		2	0.026	0.005
		4	***	0.001
Galvanized Steel	0.75	0	0.722	0.041
		2	0.006	0.007, -0.006*
		4	0.072	0
Chromate Treated Galvanized Steel	0.75	0	1.091	0.035, -0.25*
		2	0.325	0.005
		4	0.253	0.001
Aluminum Conduit (14 Months)	1 3/8"	0	2.200	0.370
		2	0.013	0.008
		4	0.011	0.011

* Negative values are for corroding bottom bars.

** Not Available.

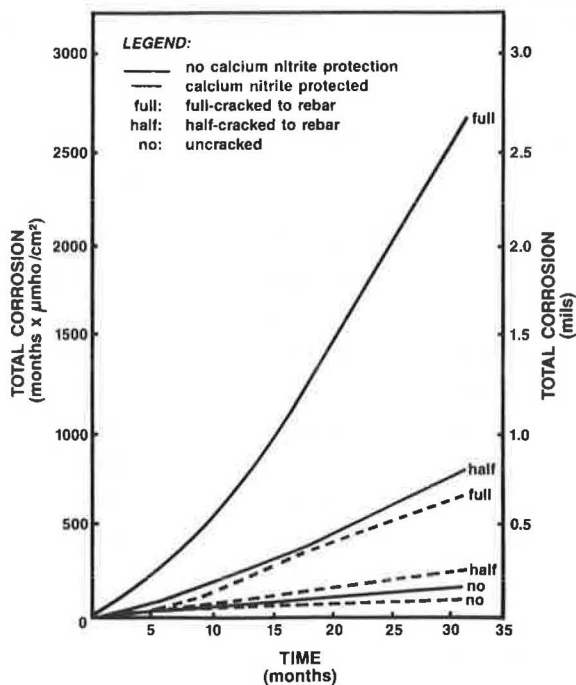


FIGURE 3 Total corrosion vs. time for precracked beams with and without calcium nitrite.

protect the concrete against freeze-thaw damage. Concretes that are properly air entrained with calcium nitrite and high-range water reducers are resistant to freeze-thaw cycles (28).

COMPATIBILITY WITH OTHER CORROSION PROTECTION SYSTEMS

As already shown, calcium nitrite is very compatible with concrete containing microsilica or fly ash to provide reduced chloride permeability. Sealers or membranes would be beneficial in reducing chloride ingress.

STUDIES TO CONFIRM ACTION OF CALCIUM NITRITE

A major study examining the effects of calcium nitrite in saturated calcium hydroxide solutions with and without sodium chloride was conducted (36). This study showed that calcium nitrite significantly increased the potential at which pitting begins and also increased the protection potential below which pitting and crevicing do not occur. This is indicative of the behavior of an anodic inhibitor and is beneficial in that it significantly broadens the range in which steel cannot severely corrode in concrete. Subsequent, unpublished work by one

TABLE 7 CONCRETE MIXTURE PROPORTIONS AND PROPERTIES OF SPECIMENS IN PRECRACK

Mix	CF (pcf)	W/C	Slump, (in.)	% Plastic Air	f'c (28 days), psi
Control	720	0.39	2.6	6.3	6771
Calcium Nitrite (2% solids by mass of cement)	689	0.40	3.6	7.4	6288

Note: Averages for 3 mixes each design.

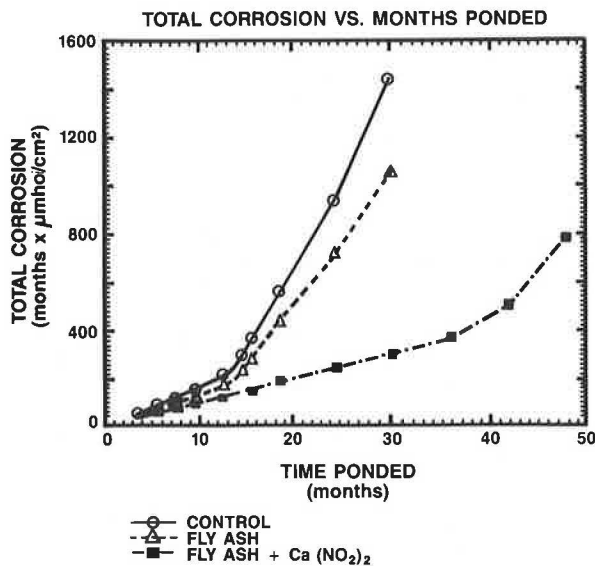


FIGURE 4 Effect of fly ash and fly ash + calcium nitrite on the total corrosion of concrete rebars ponded in 3 percent NaCl.

TABLE 8 BASIC MIXTURE PROPORTIONS FOR FLY ASH: CALCIUM NITRITE STUDY

Mix #	CF, lbs/cy	W/C	Admixture
1	499	0.62	Control
2	406	0.74	CF/Fly Ash = 406/122 pcy
5	406	0.73	Ca(NO ₂) ₂ = 1.9 gpy CF/Fly Ash = 406/122 pcy

of the authors in higher pH, sodium, and potassium hydroxide solutions showed no significant effect other than the trans-passive potential becoming more active, as would be expected for the decomposition of water (37).

Furthermore, the study showed that even extremely low concentrations of nitrite were beneficial. A recent study by Briesemann (32) also showed that low concentrations of nitrites are not detrimental in the high-pH environment of concrete.

Studies (36) were performed in solutions purged with oxygen-free nitrogen. In the absence of oxygen the nitrite did not participate in a detrimental cathodic reaction as found at lower pHs by Cohen (18).

In another unpublished laboratory study by one of the authors, there was no loss of nitrite in concrete samples exposed to fog room conditions for 5 years followed by 2 years of drying. In the absence of corrosion, nitrite is not consumed as shown by Cohen (18), by analysis of concrete in the South Dakota study (27), and by a 7-year-old Illinois bridge deck. Thus, nitrite is stable in concrete.

HOW TO USE CALCIUM NITRITE

Corrosion data from several studies (13,25,27,36) and chloride analyses performed on the concretes tested (or known from the solutions employed) were combined to develop a graph of chloride:nitrite ratios at which corrosion occurs versus admixed 30 percent calcium nitrite solution. The graph is provided in Figure 5. Based on Figure 5, Table 9 was developed as a guide on how much calcium nitrite is needed to protect steel from a given chloride ingress.

If one can estimate the amount of chloride that will reach the steel at the design life of a structure, an estimate of the calcium nitrite needed to protect the structure can be given. Chloride levels can be estimated from experience and con-

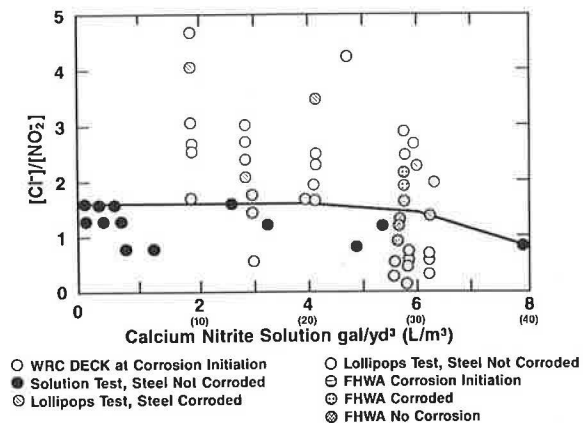


FIGURE 5 Chloride:nitrite ratios at which corrosion occurs based on testing in solutions and concrete.

TABLE 9 CALCIUM NITRITE DOSAGE RATES VS. CHLORIDE

Calcium Nitrite (gallons/c.y.)	Chlorides (pounds/c.y.)
2	6.0
3	9.9
4	13.0
5	15.0
6	16.0

crete properties, and several papers give methods and examples of predicting chloride levels (3,28–30,38).

CONCLUSIONS

Nitrites have been used in concrete for more than 30 years in Europe. Calcium nitrite has been available in the United States as a concrete admixture for more than 8 years. Extensive testing shows that it

- Protects steel against chloride-induced corrosion;
- Improves in efficiency as concrete quality improves;
- Improves compressive strength;
- Is beneficial to corrosion protection in higher quality concrete and lowers corrosion rates once corrosion begins; and
- Works in the presence of cracks.

REFERENCES

1. *Strategic Highway Research Program, Participant Workbook—National Workshop*. Strategic Highway Research Program, Washington, D.C., Sept. 1985, p. TRA 4-1.
2. *Focus*, Special Edition. Strategic Highway Research Program, Washington, D.C., Sept. 18–20, 1985.
3. R. D. Browne. Design Prediction of the Life for Reinforced Concrete in Marine and Other Chloride Environments. *Durability of Building Materials*, Vol. 1, 1982, pp. 113–125.
4. G. E. Monfore and G. J. Verbeck. Corrosion of Prestressed Wire in Concrete, *ACI*, Vol. 57, No. 5, 1960, p. 491.
5. R. H. Evans. Uses of Calcium Chloride in Prestressed Concrete. *Proc., World Conference on Prestressed Concrete*, San Francisco, 1957, p. A31-1.
6. K. W. J. Treadaway and A. D. Russel. The Inhibition of the Corrosion of Steel in Concrete. *Highways and Public Works*, Vol. 36, Nos. 19–20, 1968, p. 40.
7. R. J. Craig and L. E. Wood. Effectiveness of Corrosion Inhibitors and Their Influence on the Physical Properties of Portland Cement Mortars. *Highway Research Record* 328, 1970, p. 77.
8. V. H. Dodson, E. Farkas, and A. M. Rosenberg. U.S. Patent No. 3,210,207, 1965.
9. *A Report on a New Chemically Formulated Accelerator for Concrete*, Technical Bulletin ADM-1. W.R. Grace & Co., Cambridge, Mass., Oct. 15, 1964.
10. R. T. Foley. Complex Ions and Corrosion. *Journal of the Electrochemical Society*, Vol. 11, No. 122, 1975, p. 1493.
11. W. H. Hartt and A. M. Rosenberg. Influence of $\text{Ca}(\text{NO}_2)_2$ on Sea Water Corrosion of Reinforcing Steel in Concrete, ACI publication SP-65, 1980, p. 609.
12. J. M. Gaidis, T. G. Kossivas, R. W. Previte, and A. M. Rosenberg. A Corrosion Inhibitor Formulated with Calcium Nitrate for Use in Reinforced Concrete. ASTM Special Technical Publication No. 629, 1977, p. 89.
13. J. M. Gaidis and A. M. Rosenberg. Methods of Determining Corrosion Susceptibility of Steel in Concrete. *TRB Record* No. 692, 1978, p. 28.
14. J. M. Gaidis and A. M. Rosenberg. A Concrete Admixture to Control Corrosion in Concrete. CEFRACOR, Paris, France, Paper 154, 1979, p. 29.
15. J. M. Gaidis, J. T. Lundquist, and A. M. Rosenberg. Calcium Nitrite as an Inhibitor of Rebar Corrosion in Chloride. *Materials Performance*, Vol. 18, No. 3, 1979, p. 36.
16. J. M. Gaidis and A. M. Rosenberg. The Mechanism of Nitrite Inhibition of Chloride Attack on Reinforcing Steel in Alkaline Aqueous Environments. *Materials Performance*, Vol. 18, No. 11, 1979, p. 45.
17. J. M. Gaidis, A. M. Rosenberg, and J. Salek. *Improved Test Methods for Determining Corrosion Inhibition by Calcium Nitrite in Concrete*. ASTM, STP 713, 1980, p. 64.
18. R. Pyke and M. Cohen. Rate of Breakdown and Mechanism of Nitrite Inhibition of Steel Corrosion. *Journal of the Electrochemical Society*, Vol. 93, 1948, p. 63.
19. J. M. Gaidis and A. M. Rosenberg. The Inhibition of Chloride-Induced Corrosion in Reinforced Concrete. *ASTM, Cement, Concrete & Aggregates*, Vol. 9, No. 1, Summer 1987, p. 30.
20. *Corrosion of Metals in Concrete*, ACI, 222 R-85. Special Report by Committee 222, August 1985.
21. B. Ost and G. E. Monfore. Penetration of Chloride into Concrete. *Materials Performance*, Vol. 12, No. 6, 1974, p. 21.
22. R. F. Stratfull, W. J. Jurkovich, and D. L. Spellman. Research Report CA-DOT-TL-5116-12-75-03. California Transportation Laboratory, Sacramento, 1975.
23. N. S. Berke. The Effects of Calcium Nitrite and Mix Design on the Corrosion Resistance of Steel in Concrete (Part 1). *NACE Corrosion-85*, Paper No. 273. National Association of Corrosion Engineers, Houston, Tex., 1985.
24. N. S. Berke. The Effects of Calcium Nitrite and Mix Design on the Corrosion Resistance of Steel in Concrete (Part 2, Long-Term Results). *Proc., Corrosion-87 Symposium on Corrosion of Metals in Concrete*, NACE, Houston, 1987, pp. 134–144.
25. Y. P. Virmani, K. C. Clear, and T. J. Pasko. Time-to-Corrosion of Reinforcing Steel in Concrete Slabs, Vol. 5—Calcium Nitrite Admixture and Epoxy-coated Reinforcing Bars as Corrosion Protection Systems. Report FHWA-RD-83-012. FHWA, U.S. Department of Transportation, Sept. 1983, p. 71.
26. D. W. Pfeifer and J. R. Landgren. Protective Systems for New Prestressed and Substructure Concrete. Report FHWA-RP-86-193. FHWA, U.S. Department of Transportation, April 1987, p. 113.
27. *Laboratory Performance on Corrosion Control Methods*. Interim Report. Research Program Division of Planning, South Dakota Department of Transportation, Pierre, S. Dak., March 1984.
28. N. S. Berke and T. G. Weil. Corrosion Protection Through the Use of Concrete Admixtures. Presented at Second International Conference on Performance of Concrete in Marine Environment, St. Andrews by the Sea, New Brunswick, Canada, Aug. 21–26, 1988.
29. N. S. Berke. Resistance of Microsilica Concrete to Steel Corrosion, Erosion and Chemical Attack. Presented at the Third International Conference on the Use of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Trondheim, Norway, June 19–24, 1989.
30. N. S. Berke, D. F. Shen, and K. M. Sundberg. Comparison of the Polarization Resistance Technique to Macrocell Corrosion Technique. Presented at the ASTM Symposium on Corrosion Rates of Steel in Concrete, Baltimore, Md., June 29, 1988.
31. N. S. Berke, D. F. Shen, and K. M. Sundberg. Comparison of Current Interruption and Electrochemical Impedance Techniques in the Determination of the Corrosion Rates of Steel in Concrete. Presented at the ASTM Symposium on Ohmic Electrolyte Resistance Measurement and Compensation, Baltimore, Md., May 17, 1988.
32. D. Briesemann. *Corrosion Inhibitors for Steel in Concrete*. Civil Engineering Department, Munich Technical University, Munich, Federal Republic of Germany.

33. A. W. Beeby. Cracking, Cover, and Corrosion of Reinforcement. *Concrete International*, Vol. 5, No. 2, 1983, pp. 35-40.
34. P. S. Margat and K. Gurusamy. *Cement & Concrete Research*, Vol. 17, 1987, pp. 385-396.
35. *Guide to Durable Concrete*, ACI 201. American Concrete Institute, Detroit.
36. N. S. Berke. The Use of Anodic Polarization to Determine the Effectiveness of Calcium Nitrite as an Anodic Inhibitor. In *Corrosion Effect of Stray Currents and the Techniques for Evaluating Corrosion of Rebars in Concrete* (V. Chaker, ed.), ASTM STP 906. American Society for Testing and Materials, Philadelphia, Pa. 1986, pp. 78-91.
37. M. Pourbaix. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. National Association of Corrosion Engineers, Houston, Tex., 1974.
38. C. J. Pereira and L. L. Hegedus. Diffusion and Reaction of Chloride Ions in Porous Concrete. Presented at the 8th International Symposium on Chemical Reaction Engineering, Edinburgh, Scotland, Sept. 10-13, 1984.

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