Whats new in Corrosion Inhibitors?

Quite often, the structures we design and construct are exposed to increasingly corrosive conditions. Several options for mitigating the effects of corrosive environments are available. Corrosion-inhibiting admixtures for concrete provide one such option.

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One of the most serious and costly problems facing bridges and marine structures is the corrosion of steel in reinforced concrete. Corrosion is a major cause of repairs for concrete exposed to chlorides from marine environments, or deicing road salts. However, these effects can be mitigated by increasing the concrete cover, reducing the concrete's permeability, using reinforcement that is more resistant to corrosion, and using corrosion-inhibiting admixtures.

This article focuses on new corrosion-inhibiting admixtures for concrete. Several such products are now commercially available, and new modeling programs can be used to compare the benefits of different corrosion inhibitors and other concrete additives. Recent advances in reducing concrete cracking have made models more applicable. Most significantly, these models show that inhibitors with good, long-term track records lower lifecycle costs.

New Corrosion-Inhibiting Admixtures

Commercial corrosion inhibitors have been added to concrete since the mid-1970s. Calcium nitrite, for example, was first used in Japan to offset chlorides in sea sands which were part of the concrete mix. It was first introduced in the United States in 1978 *(ref. 1)*; however, because calcium nitrite acts as an accelerator in concrete, a more neutral-setting version of the product was introduced in 1988. More than 10 million cubic meters of concrete throughout the world contain calcium nitrite admixtures. Several admixture companies now sell it, as the original patent protection has expired.

In the early 1990s, new admixtures were introduced, including amino alcohols, morpheline derivatives, phosphates, benzoate, and a fatty ester of oleic acid amine *(ref. 2) (See Table 1)*. When added to the concrete mix, these admixtures can stop or slow corrosion. Moreover, many of these admixtures can be used in concrete repair, where they are applied to concrete surfaces and migrate to the embedded steel. At issue, however, is what effects these admixtures actually have on corrosion. Scant data is available. Although many independent studies have documented the effectiveness of calcium nitrite *(ref. 3)*, few have examined these new admixtures.

As a result, the ASTM has been hard at work developing a new test for corrosion inhibitors, which supplements the existing protocol, ASTM G109. A new test under development focuses on identifying the chloride threshold for the initiation of corrosion. It involves a combination of macrocell and polarization resistance measurements on a standard sample of mortar (cement paste and sand) and embedded steel bars which are subjected to alternate ponding of sodium chloride.

The macrocell measures the current between the top corroding steel bar and the bottom bar, simulating field conditions where steel bars exposed to chloride would corrode, much like the way a battery works. Polarization resistance is a sophisticated electrochemical test that measures corrosion.

At the initiation of corrosion, the chloride content is measured at the surface of the reinforcing bar. The measurements can be used in a deterministic or statistical based model to predict the length of time before corrosion will begin. At least 10 samples are used for each test.

The ASTM is also developing a corrosion inhibitor specification, which is based on ASTM G109. In effect, any product that meets this specification will be classified as a corrosion inhibitor.

Bridges in northern climates, such as the Jamestown Bridge (above) in Jamestown, RI, are exposed to damaging corrosive effects of road salts as well as marine environments.

Table 1. Commercial Corrosion Inhibiting Chemistries
Corrosion Inhibiting Admixtures for Steel Reinforced Concrete

Class	Chemistries
Volatile Inhibitors	amino acids, morpholine derivaties, benzoates, phosphates
Adsorption	benzoates, stearates, oleates, amines
Mixed	sodium nitrite, amines, morpholine derivatives
Anodic/Passivating	calcium nitrite

Note that all products except for oleates and stearates are used in products that migrate into the concrete for repair.

In Germany, a new passivating corrosion inhibitor specification, which relies on several tests, has been developed. It is worth noting that the neutral-set version of calcium nitrite has passed the requirements of this specification.

Are Inhibitors Effective in Cracked Concrete?

Because cracks in concrete provide conduits for chloride to reach the steel reinforcements, engineers have been concerned with the effectiveness of inhibitors when cracks are present.

Calcium nitrite, for example, is effective in good quality concrete provided that the concrete cover is 40 mm or more, and crack sizes are less than 0.3 mm. *Figure 1* shows the benefits of calcium nitrite in cracked concrete.

In addition, the admixture containing the ester of oleic acid amine has been shown to improve performance in cracked concrete, and other research on concrete without inhibitors has demonstrated that crack size, concrete quality, and concrete cover all play key roles in performance. Thus, if concrete meets the minimum requirements of ACI 318 of 40 mm of cover and water-cement ratio (w/cm) of less than 0.4 for chloride exposure, controlling crack sizes becomes critical to ensure good performance.

Recent advances in concrete technology have resulted in shrinkage reducing admixtures (SRAs) and non-corrosive, nonconductive structural synthetic fibers. These products can significantly reduce cracks that result from drying shrinkage and mechanical loading. *Table 2* shows reductions in drying shrinkage for some mixtures containing calcium nitrite and an SRA.

Effective Modeling of Corrosion Inhibitors

Fortunately, two excellent models are available to quantify the advantages of using corrosion inhibiting admixtures. To use these models, one needs to be able to predict three parameters: the chloride ingress over time, the critical threshold value for the initiation of corrosion, and the time to repairs after cracking starts.

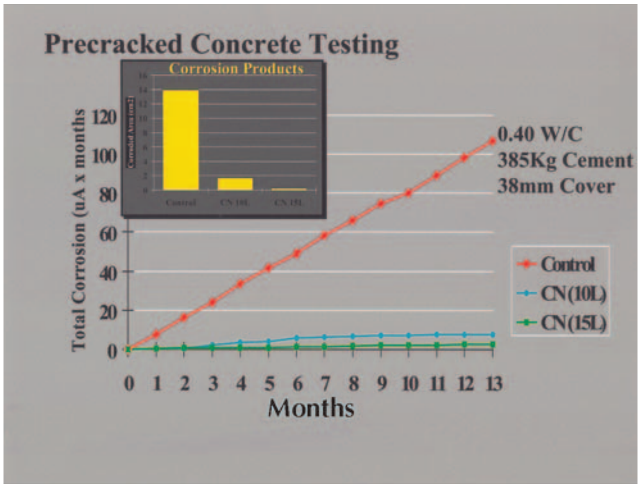
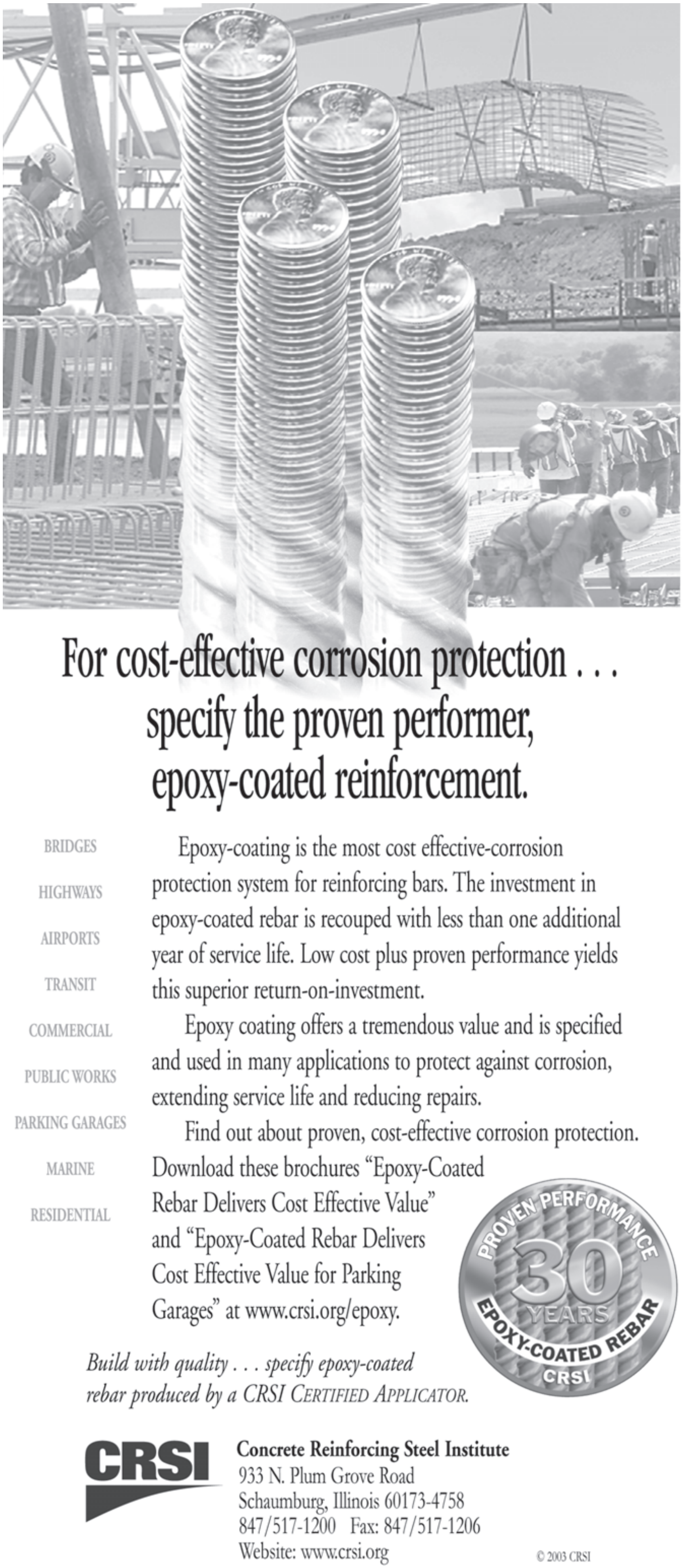


Figure 1 Performance of calcium nitrite in cracked concrete [15].



The Concrete Corrosion Inhibitor Association's model, known as Life 365, and the DuraModel™ *(ref. 4)* have been developed and refined in recent years. Both models have incorporated chloride threshold values for calcium nitrite and butyl oleate plus anime (OCI), and assume a 5-year window from the initiation of corrosion to first repair based on the government's Strategic Highway Research Program (SHRP). When modeling the use of OCI, the Life 365 model reduces chloride diffusivity by 10 percent.

Table 2. Advantages of using SRA in low permeability mixtures with or without inhibitor [23]

ASTM C 157 Free Shrinkage Length Change at 56 Days (%)	
Reference	0.049
7.5% SF	0.051
7.5% SF + 2% SRA	0.035
5% SF	0.058
5% SF + 1% CN + 2% SRA	0.043

A marine pile with a 75-year design life in a tropical environment was used to illustrate how low-permeability concrete with corrosion inhibitors can enhance durability. For this example, the DuraModel was used, but similar results have been obtained with the Life 365 model using the same parameters. The base concrete has a w/cm of 0.38, and diffusion coefficients are based on two-year ponding data adjusted to temperature. Because this example models a marine structure in a saltwater environment, a further reduction in the apparent diffusion coefficient over time is accounted for using an α value (m in the Life 365 model) of 0.2. Note that the Life 365 model starts with a 28-day apparent diffusion coefficient and uses a higher α value for pozzolans, but research in our laboratory indicates that after two years α becomes insignificant.

Three sets of costs are shown in *Table 3*: initial costs of the corrosion protection systems, repair costs, and total costs. Clearly, the reduction in permeability with silica fume or fly ash is beneficial, as is the addition of corrosion inhibitors. Based on these models, one can conclude that the best and most cost-effective solution combines low permeability concrete and corrosion inhibitors. This finding is highlighted by the cost rankings in *Figure 2*.

If structural synthetic fibers and an SRA are added, costs will increase by about $8 per linear meter of pile. Even when this additional cost is added to the cost of the corrosion inhibitor, the overall expense is more than offset by the savings in delayed or avoided repairs. Moreover, synthetic fibers and SRAs improve the concrete by reducing cracks and increasing toughness.

Conclusions

One of the best ways to protect bridges and other vulnerable structures from corrosion is to use the new corrosion-inhibiting admixtures in the original concrete mix. Moreover, treating existing structures with the same admixtures can be an effective way to address the ongoing problem of corroded bridges and marine structures. Recent advances in SRAs, which reduce cracking, and structural synthetic fibers further enhance structural performance and make the use of chloride prediction models more useful. These models have shown that corrosion-inhibiting admixtures can be a cost-effective solution to very expensive repairs. In either case, these new high-performing admixtures can help reinforced concrete structures reach their long-term design life.

Table 3. 75-yr design cost analysis for 600 mm marine pile in tropical environment with w/cm=0.38. Addition of 3 kg/m3 of structural synthetic fibr and 5 l/m3 of SRA increase cost by approximately $8.00/linear meter. Note that initiation of corrosion beyond 75 years is notes with 76 years in the DuraModel™.

	Case Description	Initiation Year	Propagation Time	T-T-R	First Cost per LM	NPV-R per LM	Total Cost per LM
1	Base Case	10	5	15	$0.00	$111.16	$111.16
2	FA20%	13	5	18	$0.00	$94.41	$94.41
3	SF7.5%	21	5	26	$4.53	$68.98	$73.51
4	CN15L	48	5	53	$7.85	$18.29	$26.14
5	OCIA	21	5	26	$4.95	$68.98	$73.93
6	CN15L + FA20%	64	5	69	$7.85	$6.28	$14.13
7	CN15L + SF7.5%	76	5	81	$12.38	$0.00	$12.38
8	FA20% + OCIA	28	5	33	$4.95	$48.01	$52.96
9	SF7.5% + OCIA	46	5	51	$9.48	$19.78	$29.26

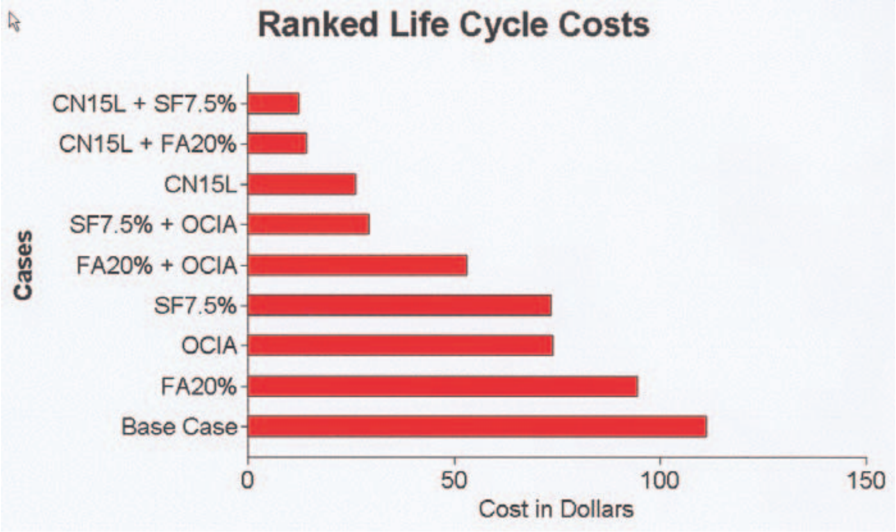


Figure 2: Ranked life cycle costs for various marine pile options. Note that the lowest cost options all contain corrosion inhibitors. The addition of structural synthetic fibers at 3 kg/m^3 and 5 1/m^3 of SRA would only add approximately $8/linear meter.

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