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Using Corrosion Inhibitors to Avoid Damage to Reinforced Concrete

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Many bridges and other structures are being built near the seacoast, and roads are treated with salt regularly to keep them open in all weather conditions. Such conditions lead to corrosion of the reinforcing rods in concrete. The use of corrosion inhibitors in concrete has dramatically increased over the past several years to combat this problem. The predictive model Life 365, developed by the construction industry, demonstrates that corrosion inhibitors provide cost-effective protection of concrete from corrosion.

Steel reinforcing bars (rebar) routinely are used in concrete structures such as bridges and parking garages. Steel and concrete have similar coefficients of thermal expansion; hence the composite is stable over a wide temperature range. Reinforced concrete exhibits increased ductility, reducing the chances of brittle failure. In addition,

it is widely known that concrete provides a protective alkaline environment that protects embedded steel from corrosion.¹

Actual experience can be somewhat disappointing because reinforced concrete structures frequently require premature repair of damage caused by corroding reinforcement. Corrosion of reinforcing steel takes place only in an aqueous environment—consuming oxygen from the atmosphere—and only when effective catalysts such as chloride ions are present.² Reinforced concrete does not undergo corrosion in dry conditions, in the absence of oxygen (e.g., at great ocean depths), or when chloride ions are not present.³

The corrosion-failure mechanism in reinforced concrete is a volume increase of the oxidation products, which leads to spalling of the concrete cover and exposure of the steel. On bridges and in parking garages, spalling and delaminations cause traffic problems; the staining that accompanies them also is unsightly. Large safety factors or emergency measures keep most structures from corroding to the point of total collapse. Variables such as the number of freeze-thaw cycles, wetting and drying cycles, rainfall totals, salt exposure, and temperature contribute to a structure's total corrosion risk.

The structure already has its own complex combination of concrete properties (cement type and content, strength, permeability, mineral and chemical admixtures) and other structural features (percent steel, load-carrying needs, and construction details). Unexpected interactions also can lead to reduced performance. The authors know of an elevated highway system that was built with drain traps that froze in the winter, allowing deicing salts to remain on the roadway and producing unnecessary corrosion results. Minor details in workmanship, such as tilted rebar mats that have varying amounts of cover, can hasten corrosion by putting some of the steel closer to the chloride source.

Corrosion of steel in concrete was observed as long ago as 1912,⁴ and it was extensively studied in the 1960s. Premature corrosion-related failures occurred on the U.S. Interstate highway system after bridges were salted in winter to melt snow and prevent icing. This continues to be a major concern⁵ when corrosion inhibitors are not used. In Japan, concrete made for earthquake-resistant housing units from sea sand aggregate has been treated with corrosion inhibitors since the mid-1970s to prevent corrosion from residual salt. A corrosion inhibitor first was commercialized in 1980 to counteract such corrosion in U.S. structures.

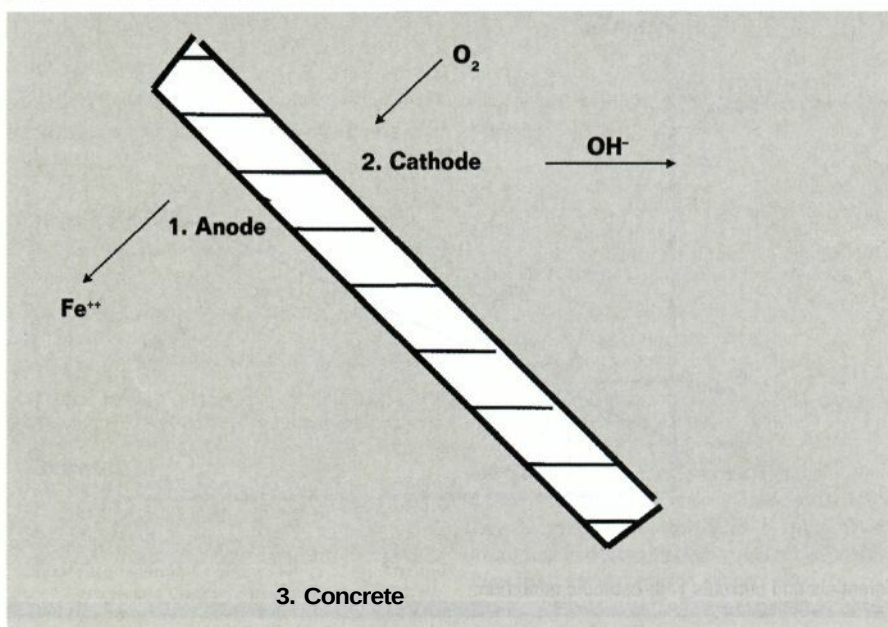
The Corrosion Mechanism in Reinforced Concrete

Corrosion in concrete may be described as the sum of chemical and electrochemical processes taking place at three different locations (Figure 1). In this case, the concrete is the solvent medium, which is water absorbed in the porous (hydrated) cement matrix. Ions diffuse away from the rebar through the liquid in small pores in the concrete. At the same time, oxygen diffuses in. Reactions taking place in this medium away from the rebar surface include oxidation of ferrous ions to ferric ions and precipitation of hydrated iron oxides, which then may block these pores.

Iron dissolution tends to make the rebar more negative at the cathode, thereby increasing the reaction rate of oxygen at the cathode. Speeding up one reaction favors speeding up the other. Conversely, slowing down one reaction forces the other to slow down as well. If one interferes with either reaction, one interferes with the entire corrosion process.

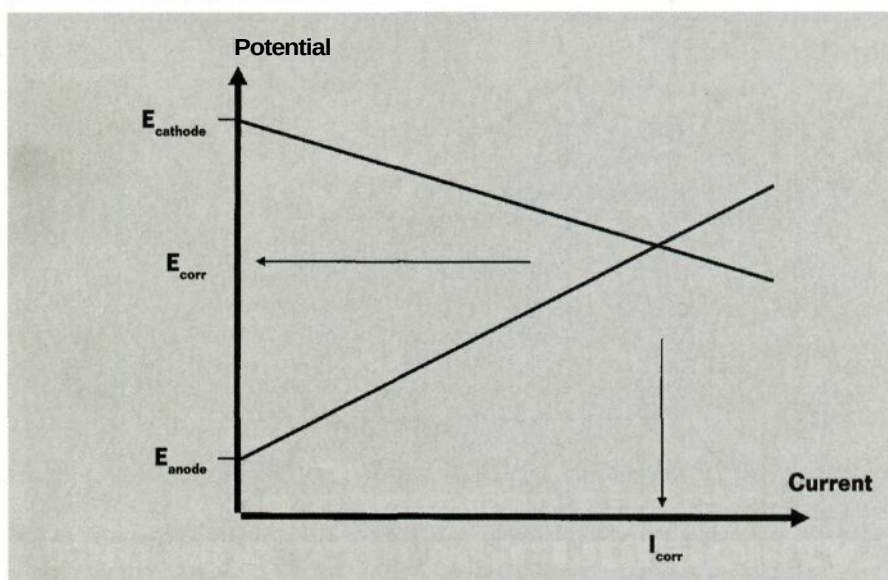
Chloride ions—the effective catalyst in the corrosion process—have two main sources: deicing salts (sodium, magnesium, or calcium chloride [CaCl₂]) for highways, bridges, and

FIGURE 1



Locations of chemical and electrochemical corrosion reactions in reinforced concrete.

FIGURE 2

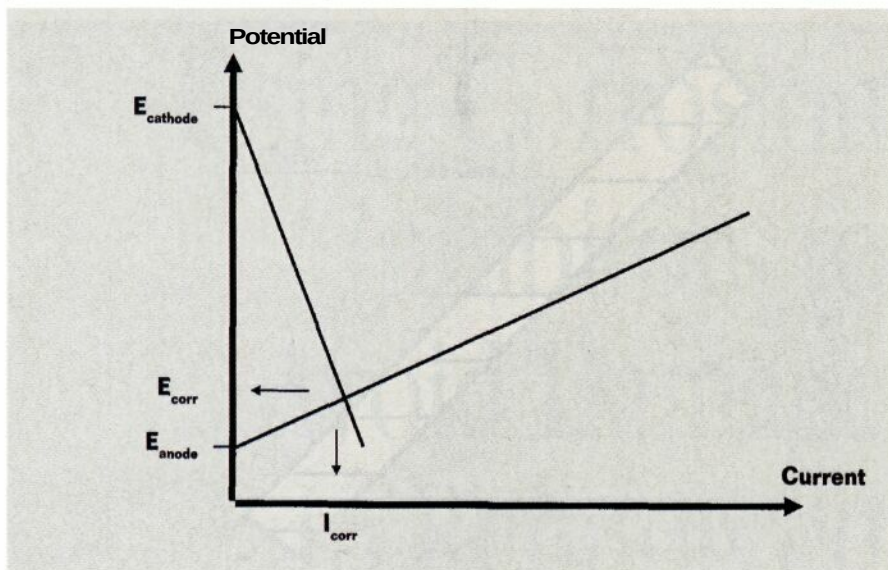


Schematic corrosion potentials and currents with no inhibition.

parking garages) and the ocean (for marine structures partially in the water or buildings close to the seacoast). Cement will react with a small amount of chloride and remove it from the aqueous medium, largely through reaction with the aluminate phases. As a result, a small level of chloride ion must

be exceeded before any is available to promote corrosion. Approximately 1 lb (0.5 kg) of chloride per cubic yard of concrete—depending on the cement composition and content in the concrete—usually is needed. Allowing the chloride level to exceed that threshold enables corrosion to develop.

FIGURE 3



Potentials and currents with cathodic inhibition.

zinc reacts with the alkaline cement. Epoxy-coated rebar has exhibited long-term difficulties in marine environments because of water permeability.⁸

How Inhibitors Work

Inhibitors function by increasing the threshold value of the chloride ion, preventing corrosion activity at the anode below that value. Some inhibitors also function by reducing the cathodic reaction. When the chloride ion level exceeds the threshold value, corrosion begins at that level.

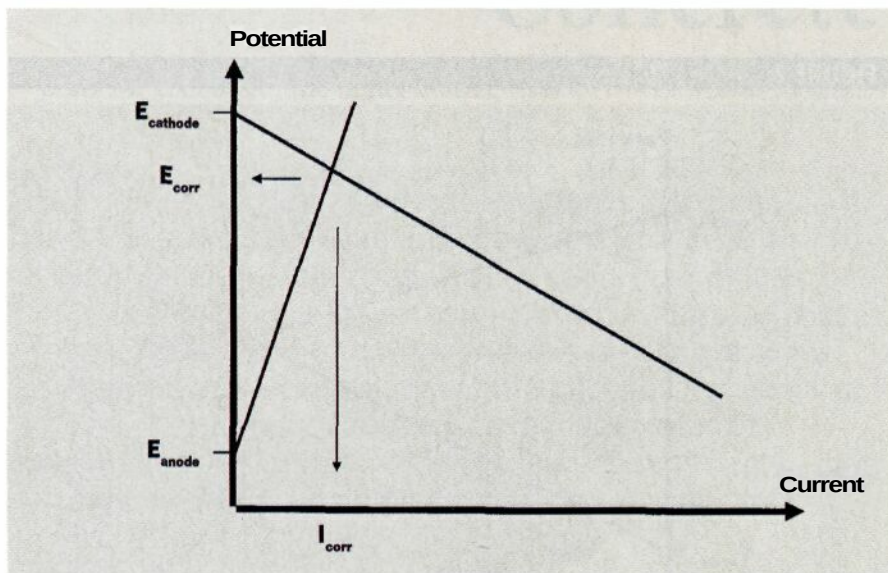
The potentials typically observed at an isolated rebar cathode in alkaline media (such as limewater or cement pore water) are ~ -200 mV; at an isolated rebar anode, they are -600 mV relative to a saturated calomel electrode. The anodic and cathodic currents are equal at a current called the corrosion current (i_{corr}) and at a potential called the corrosion potential (E_{corr}) (Figure 2). E_{corr} is not strictly an open-circuit potential, but it is the result of a balance of currents from anode and cathode activity.

Adding an inhibitor to a corroding system will, by definition, decrease the corrosion current. If the inhibitor acts primarily at the cathode by interfering with the chemical process involving electron transfer to oxygen (as in the case of steel rusting in concrete), the cathode polarization curve (Figure 3) dips more sharply than before. The slope of the anode polarization curve remains relatively unchanged.⁹

With the corrosion current reduced, the new corrosion potential E_{corr} will be closer to that of an ideal anode—that is, more negative than it was prior to the inhibitor addition.

If the inhibitor acts primarily at the anode, it raises the resistance of the anode (Figure 4) so that the intersection of the anodic and cathodic polarization curves occurs at a smaller current (i_{corr}) with a potential (E_{corr}) closer to that of an ideal cathode—that is, less negative. Anodic inhibitors generally function by oxidation processes. Cal-

FIGURE 4



Potentials and currents with anodic inhibition.

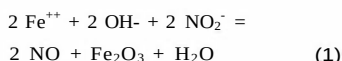
CONCRETE PERMEABILITY

An important parameter that protects concrete is its permeability, or its ability to transport chloride ions.⁶ Various methods have been employed to reduce permeability. They include increasing cement content, increasing concrete strength by adding admixtures to reduce water, or adding mineral admixtures such as fly ash, slag, or silica fume.⁷ Some corrosion inhibitors also reduce concrete permeability.

REINFORCING STEEL

The steel used to make reinforcing for concrete is not the most corrosion-resistant material available, but economics dictate against the use of more expensive materials such as stainless steel. Slightly rusted steel actually provides a better mechanical bond to the concrete than smooth, polished steel. Deformations on rebar also help to maintain a good mechanical bond. Galvanized steel has limited use because

cium nitrite [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], in particular, is known to function by oxidizing ferrous ions to ferric ions [Equation (1)]—precipitating them at the corrosion site and stifling formation of further corrosion.¹⁰



This precipitation process takes place so rapidly that migration of ferrous ions (as evidenced by staining) is blocked. In the process, the passive iron oxide film is strengthened.

Cathodic inhibitors based on hydroxyalkyl amines are used in some commercial corrosion inhibitors. They adsorb on the steel oxide surface approximately one monolayer thick. They are strongly and irreversibly adsorbed and cannot be completely rinsed off the iron oxide surface. A durable passivating film forms, and it hinders reaction of oxygen with electrons at the steel surface." A mixed inhibitor, affecting both the anodic and cathodic reactions of corrosion, has been commercialized. The inhibitor reduces the chloride-buildup rate and the chloride-diffusion coefficient but moderately increases the chloride threshold, slowing the rate of corrosion after initiation.¹²

Minimizing Corrosion with Inhibitors

In a given structure, the presence of water and oxygen may be considered essentially beyond our control. Controlling the penetration and corrosive effects of chloride ions is possible, however. Predictive models are available to help determine how much inhibitor is recommended for protection over a desired lifetime. A predictive model, such as Life 365,¹³ factors in the strength and permeability of the concrete and other parameters of the mix design, its cover over the steel (at least 2 in. [5 cm] of cover is recommended for highways and bridges), and other variables such as the temperature of

the environment. Because various inhibitors are available, a reputable manufacturer's recommendations are critical.

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