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CORROSION INHIBITORS IN CONCRETE—PART I: THE PRINCIPLES

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ABSTRACT

Chemical corrosion inhibitors present an alternate method for preventing and/or delaying corrosion of reinforcement in concrete. However, not only is it necessary to evaluate their effectiveness as a corrosion inhibitors, it is also essential that the mechanism of inhibition be understood to ensure proper use. This review of the various possible mechanisms of inhibition and passive concerns regarding the suitability of inhibitors in a concrete environment is presented as Part I of a series of papers describing the results of an investigation of commercial corrosion inhibitors. © *1998 Elsevier Science Ltd*

Introduction

Corrosion inhibitors have been used successfully in steel pipelines, tanks, etc., for many decades. Their use as admixtures to concrete, however, is more recent and more limited. There is a natural reluctance to their use in concrete because they cannot be changed if found to be ineffective, replenished if found to be consumed, or removed if found to have deleterious effects.

Corrosion Inhibiting Admixtures

An ideal corrosion inhibitor has been defined as "a chemical compound, which, when added in adequate amounts to concrete, can prevent corrosion of embedded steel and has no adverse effect on the properties of concrete (1). For the purposes of this and the following articles in this series, only admixed corrosion inhibitors are considered, although migrating chemicals and concrete coatings could produce similar effects. If chloride-induced corrosion of steel reinforcement in concrete is considered, as illustrated schematically in Figure 1 (2), the factors that could be affected by the inhibitor are: (i) the rate of ingress of chlorides from the environment; (ii) the degree to which these chlorides are chemically bound or physically trapped in the concrete cover; (iii) the concentration of chlorides that the steel can tolerate without breakdown of the inherent passive film; (iv) the rate of ingress of dissolved oxygen

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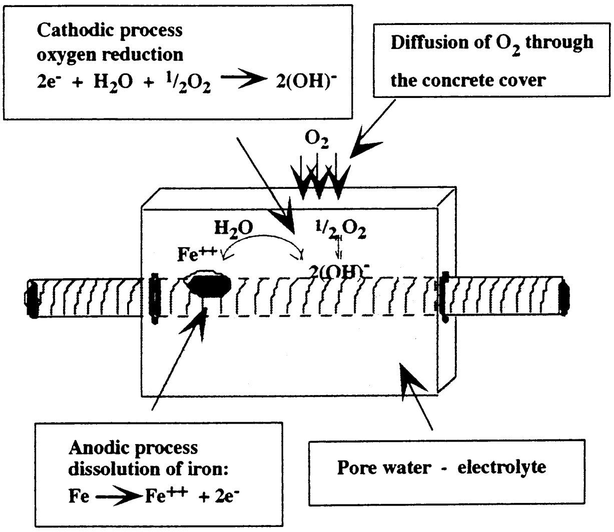

FIG. 1.
Schematic representation of chloride-induced corrosion of rebar in concrete (2).

to sustain the cathodic half-cell reaction; (v) the electrical resistance of the concrete; and (vi) the chemical composition of the electrolyte (i.e., the cement paste pore solution). Consequently, there can be several approaches to corrosion inhibition.

From the electrochemical viewpoint, these approaches can be summarised in the form of their effect on the polarization curves (3). Figure 2 shows the anodic and cathodic half-cell reaction rates (i.e., corrosion currents) as a function of the potential at the steel/concrete interface. The solid lines represent the anodic reaction ($Fe \rightarrow Fe2^+ + 2e^-$) and the cathodic reaction ($H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$) in the absence of any inhibitor and the corresponding equilibrium values of corrosion potential, E_1, and corrosion current density , i_1. An anodic inhibitor will raise the potential to a level, E_2, at which the anodic and cathodic curves intersect in the passive region of the anodic curve, as illustrated by the dashed line labelled ”anodic inhibitor“ and the corrosion current density is reduced to i_2 as shown. A cathodic inhibitor will simply reduce the rate of the cathodic reaction such that the corrosion potential and current density are both lowered as indicated by the dashed line labelled ”cathodic inhibitor,“ giving values E_3 and i_3. An inhibitor that blocks the pores will limit the ingress of oxygen and, consequently, reduce the cathodic current, as shown by the line ”pore blocker,“ giving values of potential and current of E_4 and i_4, respectively. The effects of these different inhibition mechanisms on the corrosion potential and corrosion current are summarised in Table 1.

There is some concern with anodic inhibitors that insufficient or excess inhibitor could actually exacerbate corrosion rather than reduce it. The influence of anodic inhibitor concentration on the cathodic polarization curves and the resulting corrosion rates is shown in Figure 3 (3). A review of the literature has not, however, revealed evidence of this being a problem for steel in concrete to date.

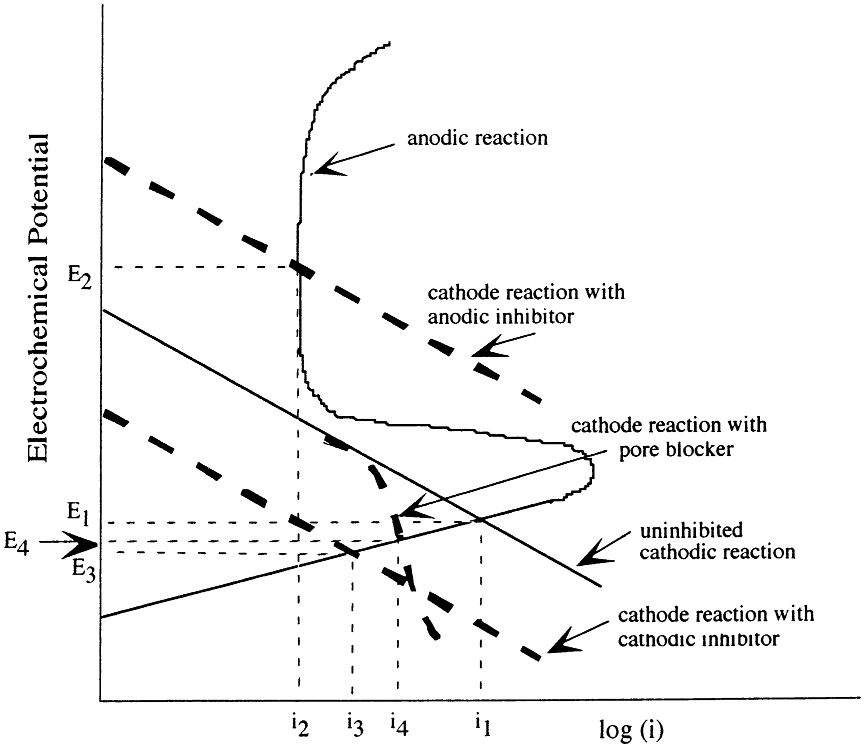

FIG. 2.
Effect of inhibitors on corrosion potential and corrosion current density.

The useful lifetime of a reinforced concrete structure has been described by Tuutii (4) as consisting of two phases, shown schematically in Figure 4. The first phase corresponds to the time, t_0, taken for chlorides (or other deleterious species) to penetrate the concrete cover in sufficient quantities to break down the passive film. This period will be dependent on the chloride diffusion rate, D_{Cl^-}, the degree of chloride binding (and, hence, the concentration

TABLE 1
Effect of inhibitors on the corrosion potential E_{corr} and corrosion current density i_{corr}.

Inhibitor type	E_{corr}	i_{corr}
Anodic	↑	↓
Cathodic	↓	↓
Pore blocker	↓	↓

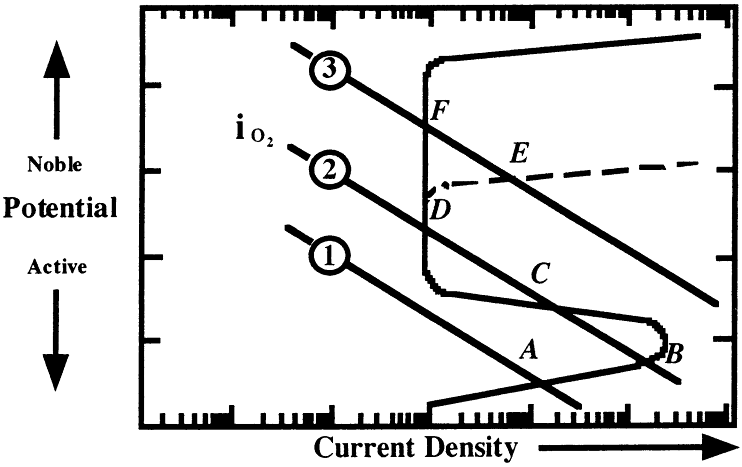

FIG. 3.
Effect of oxidizer concentration on the corrosion rate of an active-passive metal where: (*1*) no inhibitor; (*2*) inadequate inhibitor; and (*3*) adequate inhibitor. (Adapted from reference 3.)

of chlorides remaining in solution, $C_{Cl(sol)}$), and the chloride threshold value, Cl_{TV}, all of which could be influenced by an inhibitor.

The second phase covers the period of active corrosion from t_0 to the time at which the corrosion products cause spalling and/or delamination of the concrete cover and/or the rebar has lost its load-bearing capability. The length of this period, t_1, is determined by the rate of corrosion and the ability of the concrete cover to withstand the internal stresses imposed by the corrosion products. The corrosion rate is a function of the rate of oxygen ingress (D_{02}), the electrical resistivity of the concrete (ρ), and the environmental conditions, i.e., the relative humidity (RH) and temperature (T). The factors affecting the failure of the concrete cover

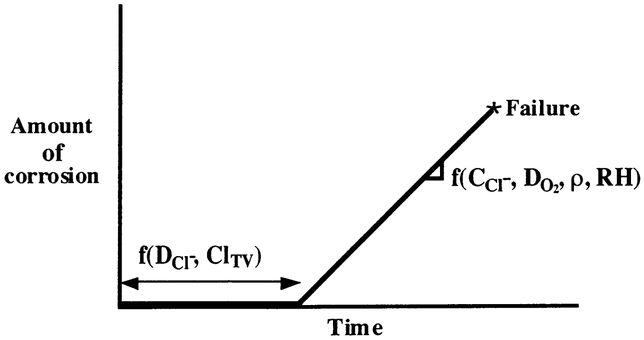

FIG. 4.
Corrosion rate of reinforcing steel as a function of the lifetime of the structure. (Adapted from reference 4.)

include its inherent strength and the degree of cracking due to plastic shrinkage, repeated freezing and thawing, etc., as well as its porosity, degree of saturation, and the pH of the pore solution, which determine the solubility and distribution of the corrosion products. However, the effect of the inhibitors on these properties has not been documented.

Furthermore, it is of relevance to consider the effect of chlorides on the concrete itself. Additions of chlorides to the concrete mix tend to increase the pore size distribution because of the set accelerating properties of chloride (5). On the other hand, it is possible that chlorides that have penetrated the concrete from the environment may decrease the porosity by precipitation of chloroaluminates in the coarser pores, although this has not yet been confirmed. Chlorides also can affect the pH of the pore solution: $CaCl_2$ decreases the pH whereas NaCl and KCl have the opposite effect (5). Chlorides tend to be hygroscopic and, in concrete, cause an increase in water absorption. However, the RH above highly concentrated salt solutions is usually lower than that above dilute solutions and, thus, the RH in the vapour phase in nonsaturated concrete containing chlorides may be lower than the corresponding RH in concretes with similar levels of water saturation but without chlorides. Finally, the increased ionic concentration of the pore solution due to the chlorides will increase its conductivity and, thereby, decrease the electrical resistivity of the concrete. Therefore, it is not sufficent only to consider the effect of inhibition on the concrete properties. The effect of chlorides on the properties of concrete containing inhibitors also must be considered (6). Moreover, the porosity and RH also will affect the value of ρ.

In summary, a corrosion inhibiting admixture to concrete could function by:

(a) Increasing the resistance of the passive film on the steel to breakdown by chlorides (increasing Cl_{TV}, thereby increasing t_0);
(b) Creating a barrier film on the steel (increasing Cl_{TV}, thereby increasing t_0);
(c) Blocking the ingress of chlorides (decreasing D_{C1^-}, thereby increasing t_0);
(d) Increasing the degree of chloride binding in the concrete (decreasing $C_{Cl(sol)}$, thereby increasing t_0);
(e) Scavenging the oxygen dissolved in the pore solution (increasing t_1); and
(f) Blocking the ingress of oxygen (decreasing D_{O2}, thereby increasing t_1).

Numerous compounds have been investigated in the laboratory as potential corrosion inhibiting admixtures to concrete and are summarised in Table 2. The sodium compounds have generally been found to reduce the compressive strength of the concrete (7,8), whereas calcium compounds do not. In fact, calcium nitrite has been found to increase the 28-day compressive strength of the concrete. The calcium salts are, therefore, more common as anodic inhibitors. Some of the organic compounds have been found to affect the air void content and the air entraining agent dosage must be modified accordingly. Similarly, the set accelerating properties of calcium nitrite and set retarding effects of some of the organics (6) must be taken into account in their use as a corrosion inhibitor.

Conclusions

Chemical corrosion admixtures present an easily implemented solution to the ever growing problem of corrosion of reinforcing steel in concrete. However, to be considered viable, these additives should not only prevent or delay the onset of corrosion, they must not have any

TABLE 2
Corrosion inhibitors in concrete.

Inhibitor	Corrosion resistance against chlorides	Comments	Reference
Sodium nitrite	Improved	Reduced compressive strength	Craig and Wood 1970 (7)
		Inexpensive	Bhaskara Rao et al. 1988 (8)
Sodium benzoate	Unchanged	Reduced compressive strength	Craig and Wood 1970 (7)
Potassium chromate	Unchanged	Reduced compressive strength	Craig and Wood 1970 (7)
Stannous chloride	Conflicting results	Insufficient solubility	Hope and Ip 1987 (1)
		Increased compressive strength	Berke 1991 (9)
		Relatively expensive	Arber and Vivian 1961 (10)
Na_2PO_3F	Improved	—	Andrade et al. 1992 (11)
OCIA*	Improved	<10% strength reduction	Nmai et al. 1992 (12)
GPH†	Improved	—	Monticelli et al. 1992 (13)
Calcium nitrite	Improved	Increased compressive strength	Tomosawa et al. 1990 (14)
		Can act as an accelerator	Berke and Rosenberg, 1989 (15)
		Slight increase in shrinkage	Hope and Ip 1987 (1)
			Andrade et al. 1986 (16)

* Organic corrosion inhibiting admixture: mixture of amines and esters in a water medium.
† Disodium β-glycerophosphate.

detrimental effects on the properties of the concrete itself, such as the strength, setting time, workability, air void content, or durability. They must also remain effective for the specified lifetime of the structure. It is, therefore, crucial to have a comprehensive and thorough understanding of the mechanism of corrosion inhibition and the effects of these admixtures on concrete to anticipate and predict internal and external factors that may affect their performance.

Acknowledgment

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