Effect of Inhibitors and Admixed Chloride on Electrochemical Corrosion Behavior of Mild Steel Reinforcement in Concrete in Seawater☆

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ABSTRACT

Electrochemical potential monitoring experiments have been performed on the mild steel rebars embedded in concrete admixed with different inhibitors and sodium chloride salt and exposed to seawater environment. The electrode potential of the reinforcing steel was monitored during the experiments, and this paper reports the observed electrochemical response. The effects of admixed inhibitors on the compressive strengths of the used reinforced concrete are also reported. The inhibitors were added to the concrete to protect the steel from corrosion. Varied measures of protection were provided by the different inhibitors. Although the inhibitor must not be detrimental to concrete properties, loss of compressive strengths was recorded for the concrete admixed with formaldehyde. Sodium nitrite did not give any effect, and potassium dichromate gave an increase in compressive strength of the concrete exposed to seawater. The overall protective effect of the inhibitors was minimal.

KEY WORDS: corrosion potential E_{corr}, diffusion, electrochemical potential, open-circuit potential, steel-reinforced concrete

INTRODUCTION

Due to its versatility and acceptability, steel-reinforced concrete is one of the most widely used materials of construction. The embedded steel is protected from corrosion by alkaline environment of the concrete. However, the normally passive steel can begin to corrode when concrete is subjected to chloride and/or carbonation. The corrosion products have two to four times the volume of the original steel. The subsequent stresses produced cause the concrete to crack. This eventually results in delamination and spalling, and the integrity of the concrete structure is lost.[1]

The seawater environment used in this work was to simulate the marine corrosion effects. Seawater, with the high sodium chloride content plus the other constituent ions, is very corrosive to ferrous materials in particular. Concrete has had fluctuating fortunes as an offshore construction material. Marine conditions generally increase the chloride content of the concrete, leading to severe corrosion of the reinforcing steel. One of the most effective ways of controlling this is to decrease the permeability and porosity of the concrete by adding a selected pulverized fuel ash. Paints have been developed to protect reinforced concrete structures in the splash/tidal zones, and cathodic protection is used for the immersed zones, although the current density for protection is small and is determined by the availability of oxygen at the embedded reinforcing steel.

However, one means of protecting reinforced steel from corrosion in potentially corrosive environments is to add a corrosion inhibitor to the concrete. The use of inhibitors in concrete has been reviewed by Griffin,[2] Craig and Wood,[3] and Treadaway and Russel.[4] An update of new advances was presented by Slater.[5] These studies looked at numerous inhibitors with the most attention focussed on sodium nitrite, potassium dichromate, sodium benzoate, and stannous chloride. Very recently, a broad review on this subject was presented by Berke.[1]

Craig and Wood[3] examined the mechanical properties of mortars produced with sodium nitrite,

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potassium chromate, sodium benzoate, and calcium chloride. They found a marked decrease in compressive strength when the inhibitors were added to the mortars. In contrast, calcium chloride increases the compressive strength. Further work by Gaidis et al.[6,7] showed the effectiveness of calcium nitrite as an inhibitor in reinforced concrete. Treadaway and Russel[4] showed a decrease in compressive strength when sodium nitrite and sodium benzoate were added to concrete.

In this work, the sodium chloride content was deliberately increased by the addition of sodium chloride salt to all of the steel-reinforced concrete blocks used. This was done to enhance more corrosion of the embedded steel. Predetermined moderate quantities of inhibitors concentrations were used; variation of inhibitor concentration will form part of the subsequent work on this subject. This work takes a further look into the corrosion inhibition effect of formaldehyde, potassium dichromate, and sodium nitrite on the corrosion of reinforcing steel in concrete in seawater environment. The mechanical properties' compressive strength effect of the admixed chemical inhibitors on the concrete was also determined. This work aims at making a contribution to the existing knowledge in this research field. A good result emanating from this type of work could be subsequently beneficial technologically and economically.

EXPERIMENTAL PROCEDURE

Preparation of Steel Reinforced Concrete Test Samples

Concrete blocks made of Portland cement, gravel, sand, and water, each one with a reinforcing steel bar embedded in it, were used for the experiment. Each of the concrete blocks had a dimension of 160 mm long, 100 mm wide, and 100 mm thick. The formulation for the reinforced concrete specimens used, in kg/m^3, was: cement- 320; water-140; sand-700, and gravel-1150. The w/c ratio was 0.44.

Two sets of blocks were made. The first set, made of five specimens admixed with different inhibitors, is listed below. The second set was made up of two concrete blocks without any admixed inhibitor. They were made purposely for determining strength under different curing conditions. One of the concrete blocks in the second set was cured in air for two weeks, and the other was cured in water for the same period. All of the blocks were prepared with 1:2:4 cement: sand: gravel (C:S:G) ratio.

The first set of concrete block specimens was prepared with the different types and quantity of

— 100 g of sodium nitrite ($NaNO_2$) and 100 g of sodium chloride (NaCl) salt to accelerate corrosion.

— 100 g of formaldehyde plus 100 g of sodium chloride salt.

— 100 g of potassium dichromate plus 100 g of sodium chloride salt.

— 50 g of potassium dichromate, 100 g of formaldehyde, and 100 g of sodium chloride salt.

— 100 g of sodium chloride salt.

All of the predetermined quantities of each inhibitor presented above were added, in turns, to every 10 kg of the concrete from which the blocks were made.

All of the specimens were partially immersed in seawater. The block listed as specimen 5 served as the control test sample.

The steel rebars used for reinforcement was of DIN-ST 60 MM. It has the chemical composition of 0.3% C, 0.25% Si, 1.5% Mn, 0.04% P, 0.64% S, 0.25% Cu, 0. 1% Cr, 0.11% Ni, and the rest Fe. The rebars were cut into several pieces, each with a length of 160 mm and 16 mm diameter. An abrasive grinder was used to remove any mill scale and rust stains on the steel specimens before embedding in the concrete block.

Each steel rebar was symmetrically placed across the length of the block in which it was embedded and had a concrete cover of 42 mm. Only approximately 140 mm were embedded in each concrete block. The remaining 20 mm protruded at one end of the concrete block and were painted to prevent atmospheric corrosion. This part was also used for electrical connection.

Potential Measurement

Each concrete test block was partially immersed in the test medium. The potential readings were obtained by placing a copper sulfate electrode firmly on the concrete block. One of the two lead terminals of a digital voltmeter was connected to the copper sulfate electrode, and the other was connected to the exposed part of the embedded steel rebar to make a complete electrical circuit.[8,9] The readings were taken at three different points on each concrete block directly over the embedded steel rebar. The average of the three readings was computed as the potential reading for the embedded rebar in seven-day intervals. All of the experiments were performed under free corrosion potential and at ambient temperature.

Determination of Specimens' Compressive Strength

The effect of admixed inhibitors on the compressive strength of the concrete test samples was determined using the second set of concrete period, the original steel-reinforced concrete test specimens were removed from their respective test media and allowed to air-harden for seven days.

Then, each of the concrete blocks was carefully weighed, placed on a compressive fracture machine lengthwise, and carefully loaded until the concrete block gently disintegrated.

RESULTS AND DISCUSSION

Steel Reinforcement in Concrete with Different Premixed Inhibitors Partially Immersed in Seawater Environment

The potential vs time curves for the steel-reinforced concrete premixed with various inhibitors and immersed in seawater are presented in Figures 1 to 5. The curve in Figure 1 indicates a little fluctuating potential within the first three weeks of the experiment. The fluctuating potentials fall within the range of –310 to –340 mVcse. Very little corrosion would have occurred during this period. Although there was a repassivation on the fifth and sixth week, the very negative potential of –605 mVcse achieved on the fourth week indicates a drastic active corrosion during this period. Similar active corrosion ranging from –610 mV to –655 mVcse was obtained from the seventh week to the end of the experiment in the ninth week. The result obtained indicate that sodium nitrite provided a temporary protective/inhibiting film around the embedded steel rebar in the first four weeks of the experiment. The continued active but almost steady-state corrosion from the seventh week of the experiment to the end is due to the breakdown of the chemically formed protective film given by the sodium nitrite inhibitor. The film was not strong or stable enough to resist the chloride ions' (from the seawater) penetration. The chloride ions had diffused through the concrete matrix to depassivate the inhibiting film on the reinforced steel's surface.

Figure 2 represents the curve obtained for the steel-reinforced concrete admixed with formaldehyde. Figures 3, 4, and 5 show the curves obtained for the steel-reinforced concrete admixed with potassium dichromate, potassium dichromate and formaldehyde, and sodium chloride alone, respectively. In Figure 2, the potentials increased negatively from an initial value of –400 mVcse to approximately –650 mVcse within the first three weeks of the experiment. This active corrosion phenomenon indicates that formaldehyde, as an inhibitor for the embedded steel, was not effective at all when admixed with concrete and immersed in seawater environment. After the third week, the corrosion potential maintained an almost steady-state trend throughout the experimental period. However, at the ninth week, an insignificant, small negative potential deviation was observed.

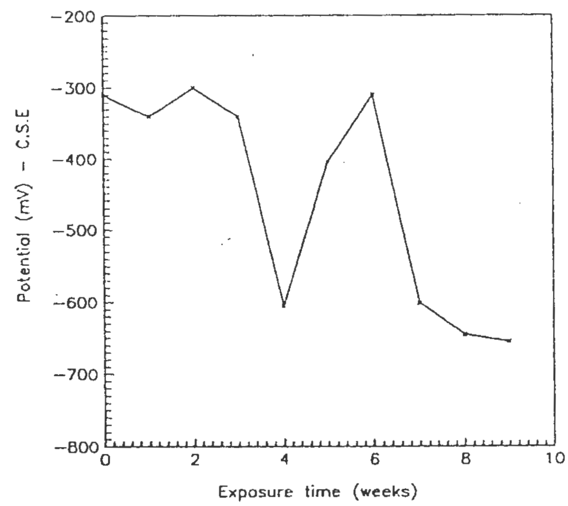

FIGURE 1. *Potential vs time curve for the reinforced concrete admixed with sodium nitrite in seawater.*

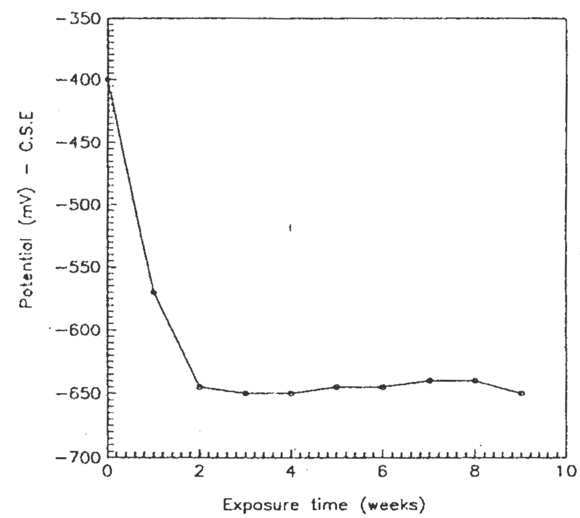

FIGURE 2. *Potential vs time curve for the reinforced concrete admixed with formaldehyde in seawater.*

The situation for the potassium dichromate admixed with the reinforced concrete and immersed in seawater (Figure 3) was not much different from that described in Figure 2. This was the case particularly in the first four weeks of the experiment. An initial, negative potential of –435 mVcse increased negatively to approximately –680 mVcse in the third and fourth week, respectively. The trend was that of active corrosion from the onset to the fourth week. The repassivation phenomenon observed from the fourth to the sixth week is difficult to explain. The last three weeks of the experiment showed a corrosion behavior that followed the same trend as observed during the first to the fourth week. This might not be a suitable inhibitor to use alone under this particular condition.

Figure 4, representing the potential vs time curve for the reinforced concrete admixed with potassium

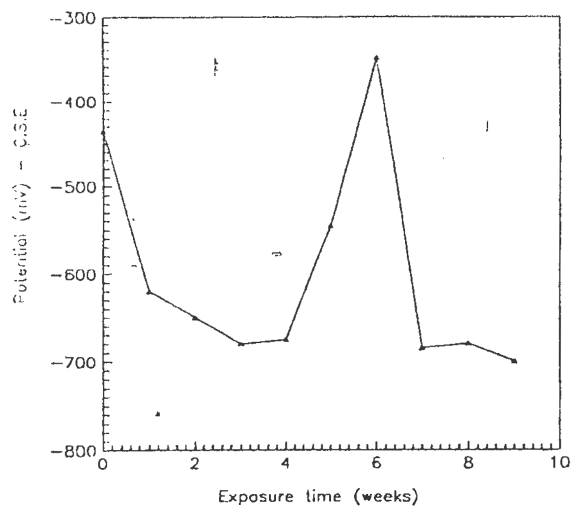

FIGURE 3. *Potential vs time curve for the reinforced concrete admixed with potassium dichromate in seawater.*

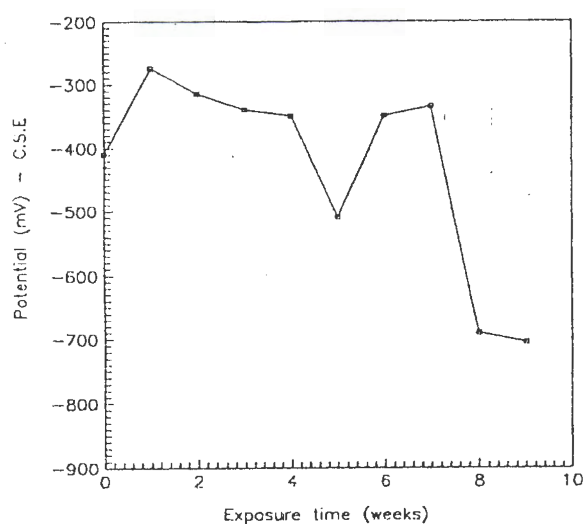

FIGURE 4. *Potential vs time curve for the admixed with potassium dichromate and formaldehyde in seawater.*

dichromate and formaldehyde together, gives a passivating effect up to the seventh week of the experiment. The only exception was the depassivation of the embedded steel's protective film in the fifth week. These combined inhibitors could not protect the embedded steel throughout the experimental period, as observed in the eighth and ninth week. Insufficient concentration of the inhibitors used could account for this corrosion behavior. However, the combined inhibitors were more effective than either of the two when used alone (Figures 2 and 3). The positive result obtained in Figure 4 is, therefore, clearly a case of synergism.

Admixing sodium chloride alone with the concrete (Figure 5) was not expected to protect the embedded

designed to serve as a reference for the comparison of the inhibitors used in this experiment. In general, chloride ions obtained from the NaCl content of the seawater and from the admixed sodium chloride salt are known to be particularly deleterious to the metals' surface passive films. The enormous penetrating ability of the ions had caused the depassivation of the chemical inhibitors' film, as observed in this work. It accounts for the active corrosion in most cases.

The overall picture of Figures 2 to 5 is presented in Figure 6 for the comparison of the effectiveness of each inhibitor used.

Concrete's Compressive Strengths

The analysis of compressive fracture load data for the steel-reinforced concrete test samples immersed in seawater are presented in Figure 7.

The compressive strengths of all reinforced concrete specimens used in the experiments and partially immersed in seawater were higher than those of the specimen cured in water for two weeks. This indicates that the admixed inhibitors had no adverse effect on the concrete samples used. The reason for the higher compressive strength in the former than in the latter is difficult to explain. It could probably be due to the relative chemical reaction's hardening effect of the inhibitors with concrete. In addition, the specimens used for the monitoring experiments were partially immersed in seawater. The other halves were exposed to the air throughout the experimental period. This dual hardening method might also account for the higher strength associated with the partially immersed specimens.

The values of the compressive strengths, obtained for the five specimens used for the monitoring experiments and partially immersed in seawater, did not follow a particular trend when compared with the compressive strength values of the concrete specimen cured in the air. The specimens admixed with formaldehyde and sodium chloride and the specimens admixed with potassium dichromate, formaldehyde, and sodium chloride together gave a loss of compressive strengths when compared with the specimens cured in air. However, the specimen admixed with sodium nitrite and sodium chloride did not show any difference in compressive strength. It had a value equal to that of the specimen cured in air for two weeks. Therefore, the inference here is that the addition of formaldehyde to concrete mix and the addition of a mixture of potassium dichromate and formaldehyde to concrete mix in cement block making will cause a loss of compressive strength of the blocks. The addition of potassium dichromate to concrete mix improves the compressive strength of the blocks immersed in seawater under laboratory

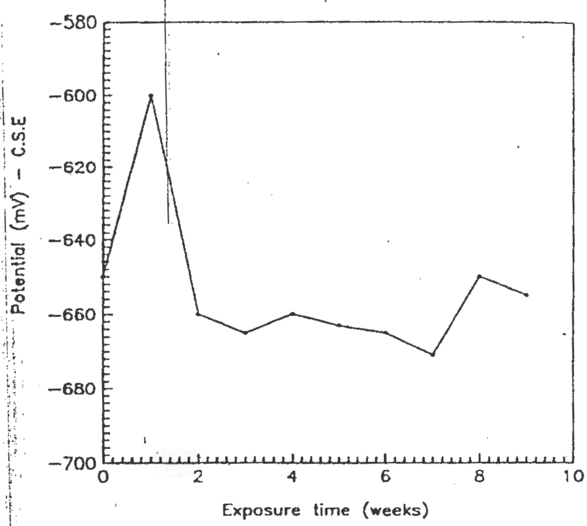

FIGURE 5. *Potential vs time curve for the reinforced concrete admixed with sodium chloride in seawater.*

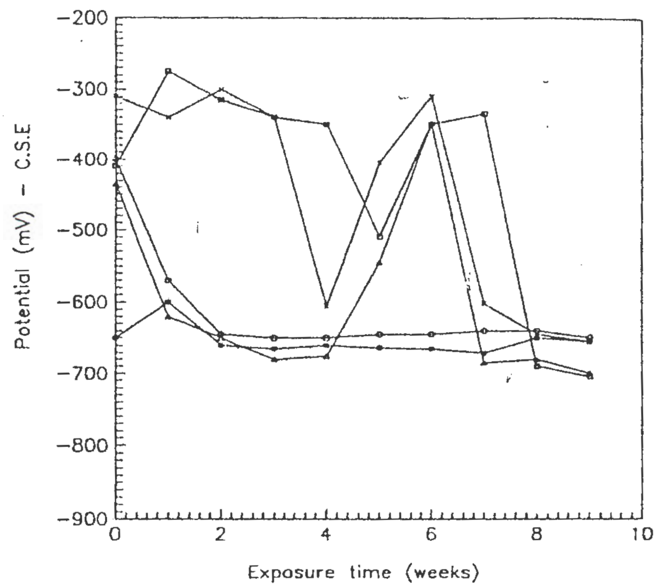

FIGURE 6. *Potential vs time curves for the reinforced concrete admixed with different inhibitors in seawater. x = $NaNO^2$; o = HCHO; Δ = $K^2Cr^2O^7$; □ = HCHO and $K^2Cr^2O^7$; and • = NaCl.*

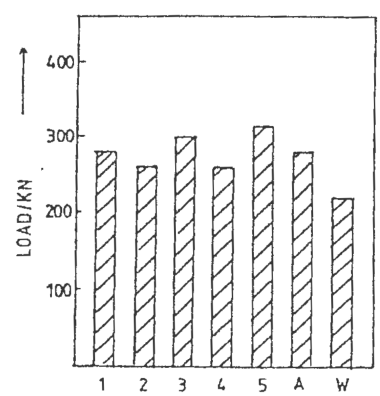

FIGURE 7. *Histogram of compressive fracture load for the reinforced concrete specimens immersed in seawater. W = concrete specimen cured in water; A = concrete specimen cured in air; 1 = reinforced concrete admixed with $NaNO_2$; 2 = reinforced concrete admixed with HCHO; 3 = reinforced concrete admixed with $K_2Cr_2O_7$; 4 = reinforced concrete admixed with HCHO + $K_2Cr_2O_7$; and 5 = reinforced concrete admixed with NaCl.*

the compressive strength of the block. The addition of sodium chloride only increases the concrete's compressive strength.

CONCLUSIONS

❖ The overall protective effect of the inhibitors was minimal except for the mixture of potassium dichromate and formaldehyde. Sodium nitrite also had a tendency toward effective protection.

❖ The mixture of potassium dichromate and formaldehyde caused a loss of compressive strength.

❖ Formaldehyde alone was detrimental to the compressive strength of the concrete.

❖ Potassium dichromate gave an increase in compressive strength, and sodium nitrite gave no apparent effect.

❖ The overall effectiveness of the inhibitors could not be fully determined. This is due to the non-variation of the inhibitors' concentration. Anodic inhibitors, for example, sodium nitrite, require high concentration of inhibitor for full, effective protection of metals against corrosion. In addition, the effects of administering large amounts of chloride could adversely affect the rating of inhibitor performance.

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