Studies on Galvanized Carbon Steel in Ca(OH)₂ Solutions
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The behavior of galvanized carbon steel samples was studied in Ca(OH)₂ solutions, simulating the alkaline environment in reinforced concrete. Under shorter periods, it was seen that a passive layer was formed on the surface of the zinc coating. The film, however, was not stable for long periods of time. This was revealed by the long duration tests where the passive layer was disrupted and the carbon substrate was protected sacrificially by zinc dissolution. The presence of chlorides accelerated the passive layer breakdown. The role of calcium nitrite in inhibiting the corrosion process of zinc was also studied. It was found that zinc was not protected by nitrite in the presence of chloride ions. The inhibitor, however, significantly reduced the corrosion rate of the underlying steel.

Keywords: concrete; corrosion; reinforcement.

INTRODUCTION

Due to its versatility and acceptability, steel-reinforced concrete is one of the most widely used construction materials. While the cover provided by concrete is normally sufficient to protect steel reinforcement from corrosion, exposure to chloride environments necessitates additional protection. The presence of chlorides is one of the major causes of concrete reinforcing bar corrosion, because chlorides can destroy the passive film that protects the steel substrate in alkaline solutions. Zinc is known to resist chloride attack better than iron. One of the common forms of steel protection in concrete is zinc coatings. Zinc dissolves in alkaline media and protects iron sacrificially.

Extensive studies exist on the passivation of zinc under anodic polarization in alkaline NaOH and KOH solutions. The passive layer is believed to be made of a mixture of zinc oxide, peroxide, and/or hydroxide. While interest in the behavior of zinc in NaOH and KOH remains steady, the dissolution and passivation of zinc in Ca(OH)₂ has not been studied in detail.

Macias and Andrade studied the corrosion rate of galvanized steel in a wide range of alkaline pH values. They found that for alkaline solutions saturated with Ca(OH)₂ with various additions of KOH/NaOH/CaSO₄/N₂H₄SO₄/K₂SO₄, the zinc substrate was passivated below pH 13.3. Beyond this value, no passivation occurs and an exponential increase in the corrosion rate is seen. According to Unz, at excessive chloride concentrations, pitting occurs on the zinc substrate regardless of any existing passivation films. This attack occurs in poor quality concrete reinforced with galvanizing reinforcing bars. For sound concrete, however, the zinc acts as a sacrificial anode and protects the steel below. Corderoy and Herzog studied sodium chromate and chromic oxide as inhibitors for the zinc coatings with and without chloride. In the absence of chlorides, the addition of these inhibitors passivates the zinc, but the addition of chlorides destroys the passive film formation. Calcium nitrite is a well-known inhibitor commercially used to protect reinforcing bar corrosion in concrete. The effect of nitrite ions on the passivation of zinc in Ca(OH)₂, however, is not well known.

Therefore, the objective of this study is to understand the mechanism of active dissolution and passivation of zinc in alkaline Ca(OH)₂ solution. In addition, the behavior of zinc in the presence of C⁻ ions is investigated. Finally, the effect of nitrite ions on the passivation of zinc in Ca(OH)₂ is also studied.

RESEARCH SIGNIFICANCE

Few studies have investigated the passivation processes of zinc in Ca(OH)₂ solutions. Understanding this process, however, is critical to understanding the role of galvanized coatings in protecting steel in reinforced concrete. Both short- and long-term studies were performed to understand the alkaline behavior of zinc. The short-duration studies focused on the formation of a passive film in the absence of chlorides. The presence of C⁻ ions on the film formation was also studied. Long-term studies were performed on galvanized steel in Ca(OH)₂ solutions simulating the pore water in concrete. Similar studies were also performed using a nitrite inhibitor. The objective was to determine if the corrosion of the sacrificial zinc was slowed down either by a natural passive film or by use of nitrite inhibitor.

EXPERIMENTAL PROGRAM

Alkaline solutions of different pH values were prepared by dissolving a known amount of Ca(OH)₂ in deionized water. pH measurements were carried out by means of a 0 to 14 range combined pH electrode and a pH meter. Separately, two different solutions with 3.5% chloride for pH values 9.5 and 12.5 were prepared. The solution compositions, pH values, and Ca(OH)₂ concentrations used are given in Table 1.

Pure zinc samples were polished and degreased with acetone. They were then immersed in a cell containing the previously mentioned solutions. A saturated calomel electrode was used as the reference electrode and platinum gauze was used as the counter electrode. A potentiostat interfaced to a personal computer was used for data acquisition. The variation of the corrosion potential of these pure zinc samples was tracked over time. Linear polarization and potentiodynamic scan measurements were performed at the end of the test period. On a separate zinc sample, linear polarization and Tafel studies were performed for all the solutions at the start of the experiments. The scan rate for the linear polarization studies was 1 mV/s. The Tafel studies were performed at a scan rate of 5 mV/s.

Apart from the previously mentioned studies, long-duration experiments were performed on galvanized and half-galvanized samples. Thin sheets of carbon steel were initially
Table 1—Solution composition, pH, and Ca(OH)\textsubscript{2} concentration for different test solutions

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Ca(OH)\textsubscript{2} g/L × 10\textsuperscript{3}</th>
<th>NaCl g/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4167</td>
<td>—</td>
<td>7.1</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>—</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>—</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>10.6</td>
<td>—</td>
<td>10.2</td>
</tr>
<tr>
<td>5</td>
<td>65.6</td>
<td>—</td>
<td>11.7</td>
</tr>
<tr>
<td>6</td>
<td>224.4</td>
<td>—</td>
<td>12.5</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>3.5</td>
<td>9.5</td>
</tr>
<tr>
<td>8</td>
<td>224.4</td>
<td>3.5</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Fig. 1—Potential time studies for zinc samples in pH 9.5.

ous equilibrium reactions between the dissolved substances are as follows

\[
\begin{align*}
\text{Zn}^{2+} + \text{H}_2\text{O} & = \text{ZnOH}^+ + \text{H}^+; \quad \log \left( \frac{\text{ZnOH}^+}{\text{Zn}^{2+}} \right) = -9.67 + \text{pH} \quad (1) \\
\text{ZnOH}^+ + \text{H}_2\text{O} & = \text{HZN}O_2 + 2\text{H}^+; \quad \log \left( \frac{\text{HZNO}_2}{\text{ZnOH}^+} \right) = -17.97 + 2\text{pH} \quad (2) \\
\text{Zn}^{2+} + \text{H}_2\text{O} & = \text{HZNO}_2 + 3\text{H}^+; \quad \log \left( \frac{\text{HZNO}_2}{\text{Zn}^{2+}} \right) = -27.63 + 3\text{pH} \quad (3) \\
\text{HZNO}_2 & = \text{ZnO}_2 + \text{H}^+; \quad \log \left( \frac{\text{ZNO}_2}{\text{HZNO}_2} \right) = -13.11 + \text{pH} \quad (4)
\end{align*}

With the increase in pH, the equilibrium is shifted to the right in all of these reactions. For Eq. (2) and (3), the effect is greater because of the increased dependence on the H\textsuperscript{+} concentration. Between pH 8.98 and 13.11, HZNO\textsubscript{2} dominates. Beyond this, ZNO\textsubscript{2} is present. Macias and Andrade's\textsuperscript{5,6} results indicate that beyond pH 13.3, the passive film is no

ACI Materials Journal July-August 2000

RESULTS AND DISCUSSION

Figure 1 and 2 show the results of the potential time study for the period of 15 h. All potentials were measured with respect to a saturated calomel electrode (SCE). Figure 1 shows the potential variation over time for a pH 9.5 solution. The potential profile without Cl\textsuperscript{-} shows passivation by the change in potential to more positive values. The same behavior can be seen for pH 12.5 as well. The potential for the cell without chloride, however, is more negative than the one for pH 9.5. In alkaline solutions, the corrosion rate of zinc increases exponentially with an increase in pH.\textsuperscript{14} Therefore, as the pH increases, the corrosion rate increases, and the potential becomes more negative.

According to Pourbaix,\textsuperscript{14} zinc exists in the various forms in solution, some of which are given in Table 2. The vari-
Fig. 2—Potential time studies for zinc samples in pH 12.5.

Fig. 3—Potential time studies for zinc samples in alkaline calcium hydroxide solutions of different pH.

longer formed. The conversion of bizzinate ion to zincate at this pH value could be the reason for this result. Bizzinate ions could have a higher tendency to adsorb on the surface of the zinc and form a passive film compared to zincate ions. In both Fig. 1 and 2, it can be seen that with the addition of chloride, the passive film is not formed and the potential remains close to the open circuit potential of zinc. This result is in agreement with Corderoy and Herzog in that the chloride ions adsorb on the zinc surface and prevent passive film formation. As chloride ions are added, the corrosion rate increases and the potential becomes more negative.

The effect of Ca(OH)₂ concentration is seen clearly in Fig. 3. With an increase in hydroxide concentration (increase in pH), the potential changes to more positive values. When zinc dissolves in aqueous solutions, varieties of the hydroxide can be formed. The zinc hydroxides are amphoteric and dissolve in alkaline solutions to give bizzinate or zincate ions. Of these, the amorphous Zn(OH)₂ is the most soluble. The oxides and hydroxides of zinc have a minimum solubility at pH 9.3. The product of the complete precipitation of a zinc salt by a base is the unstable amorphous hydroxide. The amorphous hydroxide becomes converted into β-Zn(OH)₂, or oxide in slightly alkaline to neutral solutions. In very alkaline solutions, amorphous Zn(OH)₂ is rapidly converted into γ-Zn(OH)₂. Formation of a stable oxide film is a prerequisite for zinc to passivate. The passivation and subsequent depassivation of zinc could be due to the preferential adsorption of one or a mixture of the previously mentioned compounds on the zinc substrate. With an increase in hydroxide concentration, more of this species is formed, leading to a more stable passive film. This is also reflected in the more positive equilibrium potentials seen in Fig. 3.

The film is much more stable with an increase in the concentration of Ca(OH)₂. In this case, an increase in pH directly corresponds to an increase in Ca(OH)₂ concentration. An increase in OH⁻ concentration would result in increasing the dissolution of zinc. The dissolved zinc precipitates as hydroxides or oxides, which constitutes the passive protective film on the zinc surface. This is reflected in more positive potentials for the pH 12.7 sample. If the solution is exposed to carbon dioxide, the region of passivity increases. That increase, however, is toward a lower pH. This suggests that galvanized steel would be stable in a carbonated environment (provided the coating could survive in concrete that is not carbonated).

To study the nature of the passive film, scanning electron micrograph (SEM) and electron diffraction analysis (EDAX) of the samples immersed in concentrated Ca(OH)₂ for a week were performed. Figure 4 presents the SEM of the passivated zinc sample. The surface reveals the presence of corrosion products contributing to the passive film formed. The film is porous in nature; however, and this could lead to passive layer disruption and corrosion under long-duration exposure. Furthermore, the porous nature also makes the passive film more vulnerable to chloride attack. EDAX analysis of the surface before and after exposure to chloride ions is presented in Fig. 5. Because EDAX is an elemental analysis, it only reveals the components of the passive film, namely, Ca and Zn. Previous investigators have suggested that the passive film is composed of calcium hydroxide zincate. Figure 5 reveals the presence of Cl⁻ on the surface after the samples are exposed to chloride ions. This shows that chloride ions break down the passive film and contribute to increasing the corrosion of zinc. The initial porous nature of the film hastens this process.

Table 3 presents the results of the corrosion potential measurements of the fully galvanized samples as a function of time. The corrosion potential for pure zinc in aqueous solutions at unit concentrations of all reacting species was -1.005 V versus SCE. In Table 3, this value was observed initially for the fully galvanized substrate (no inhibitor) at pH 9.5 with 3.5% NaCl, indicating that the sample was corroding.
As time progressed, however, the potential became more positive. Similarly, in the absence of chloride, the potentials were much more positive than that of zinc at both pH values. This indicates either the formation of a passive film on the zinc surface, or shifting of the potential to the corrosion potential of the substrate iron due to the dissolution of zinc.

In-place corrosion measurements of the samples were performed with the linear polarization technique. Varying the potential 10 mV in either direction of the equilibrium potential yielded the polarization resistance $R_p$. The corrosion rates from these samples were calculated according to the Stearn Geary equation (Eq. (5))

$$i_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \frac{1}{R_p} = \frac{B}{2.3(\beta_a + \beta_c)}$$

where $i_{corr}$ is the corrosion rate of the sample, and $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes, respectively. The polarization resistance $R_p$ is calculated from the slope of the current-potential curve obtained from the linear polarization measurements. Values of $B$ of 52 mV when the galvanized coating remains and 6 mV under active corrosion have been used. For iron values of $B$ of 52 and 26 mV were used under passive and active corrosion conditions, respectively.

Figures 6 and 7 present the corrosion rates of galvanized samples in pH 9.5 and 12.5, respectively. The corrosion rate increases with time at both pH values. This clearly proves that the mixed potential seen in Table 3 is due to the Zn/Fe couple arising due to the dissolution of zinc. It can be seen that, initially, the corrosion rate is low, indicating the existence of a passive film. As time progresses, however, the corrosion rate increases rapidly for samples in the presence of chloride. In the absence of chlorides, the corrosion rates remain low. Furthermore, the corrosion rate is low at pH 9.5 as compared to pH 12.5, which agrees with the potential data in Table 3. It is evident that a passive film is initially formed on zinc, which is destroyed due to the aggressive Cl⁻ anion ingress inside the film after which the zinc dissolves, sacrificially protecting iron. The protection offered to iron will depend on the thickness of the zinc coating.

Once the zinc dissolves, the corrosion rate decreases. In the presence of chloride ions, however, iron starts corroding, which leads to an increase in the corrosion rate. At pH 12.5, the corrosion rate is an order of magnitude higher than when compared to pH 9.5 in the absence of chloride (Fig. 7). The addition of chloride catalyzes the dissolution of zinc. This is consistent with the high solubility of ZnCl₂.

The effect of nitrite ions in protecting zinc in Ca(OH)₂ solutions is investigated next. Calcium nitrite is a commonly used inhibitor for protection of iron in concrete and in alkaline solutions. The same inhibitor, however, is also used for the protection of galvanized steel. In this case, the substrate to be protected is zinc and no detailed study has been done to evaluate the effectiveness of nitrite ions in protecting zinc.

Table 4 presents the potential-time study for pH 9.5 with different concentrations of nitrite inhibitor. The potential data for the samples without any inhibitor is also presented for comparison. The potential becomes more positive with time for the samples with inhibitor, indicating the corrosion or passivation of zinc. For the sample with no inhibitor, the potential initially becomes positive and then subsequently becomes more negative. Figure 8(a) presents the corrosion rate of galvanized zinc samples in pH 9.5 without chloride. The corrosion rates are significantly higher when compared to the sample without any inhibitor. Similar results are also observed in the samples with chloride (Fig. 8(b)).

An interesting phenomenon occurring in this case is that the corrosion rate is initially high and then decreases with...
time, both in the presence and absence of chloride. This arises due to the dissolution of zinc from the samples. Because corroding, galvanized samples have both zinc and steel exposed to the electrolyte, a galvanic cell is established between the two metal substrates. Iron acts as the cathode, is protected, and zinc dissolves rapidly. Thus, the corrosion rate initially is very high. Once all the zinc has dissolved, the corrosion rate decreases and the iron starts corroding. Therefore, the potentials for the sample without inhibitor in Table 4 become initially positive with time, indicating zinc dissolution. Subsequently, iron starts corroding and the potential becomes negative again. For samples with nitrite, the inhibitor is incapable of protecting zinc, and hence the corrosion rates are very high initially. The potential becomes positive with time. Once iron is exposed, however, the corrosion rate decreases due to the inhibition by the nitrite ions. Hence, the potential remains close to the open circuit value of iron.

Similar results are also seen at pH 12.5. Figure 9 presents the corrosion rates of galvanized samples with different concentrations of inhibitors in pH 12.5. Similar to pH 9.5, corrosion is high initially and then decreases. The corrosion rate in the absence of and in low concentrations of nitrite ions, however, remains high, even after zinc dissolution. At higher concentrations of nitrite ions, iron does not corrode. In addition, the zinc dissolution rate decreases at high nitrite contents in pH 12.5.

In previous studies, chloride ions were added to the samples initially, not allowing any time for the samples to passivate in the model pH solutions. To see if this had any effect on the corrosion behavior of galvanized steel, a new set of samples was prepared. The sample preparation was similar to the previous preparations. The studies were performed in three different pH solutions, namely, 9.5, 10.5, and 12.5. The pH was obtained by adding appropriate amounts of Ca(OH)$_2$ to the deionized water. No chlorides were added to any of the samples initially. After allowing 30 days for the sample to passivate in the respective inhibitor solutions, chloride ions (3.5% NaCl) were introduced into the solution.

The potential of zinc immersed in various pH solutions is shown in Fig. 3. As seen from Table 5, after 30 days, the samples with chloride show more negative potentials, indi-
cating that zinc was corroding at a faster rate, thus protecting the underlying steel sacrificially. These results are the same at all pH values. Figure 10 presents the corrosion rates of these samples in different concentrations of nitrite ions in pH 12.5. The corrosion rates were initially low, indicating the presence of a passive film. After the addition of chloride ions, however, the corrosion rate increased drastically and reached a maximum. The other factor potentially giving rise to the increased zinc current or corrosion rate in the presence of nitrite was the passivation of exposed iron. As more and more iron was exposed, the nitrite promoted the passivation of iron, giving rise to an increasing anodic current. At this point, the zinc corro-

Fig. 8(a)—Corrosion rate of galvanized samples in pH 9.5 with different nitrite concentrations without chloride.

Fig. 9—Corrosion rate of galvanized sample in pH 12.5 with different nitrite concentrations in presence of chloride ions.

Fig. 8(b)—Corrosion rate of galvanized samples in pH 9.5 with different nitrite concentrations with chloride.

Fig. 10—Corrosion rates of galvanized steel samples in pH 12.5 for different inhibitor concentrations. (Note: Chloride ions added to samples after 30 days exposure to nitrate + Ca(OH)₂ solution.)

CONCLUSIONS

Preliminary studies on active dissolution and passivation of galvanized samples indicate that initially, the zinc coatings are passivated due to adsorption of dissolved zinc ions. The initial positive change in potential and the lowering of
ACKNOWLEDGMENTS

The authors acknowledge the financial support of the South Carolina Department of Transportation (SCDOT) under Contract No. 804-4-27-95.

REFERENCES


