
Abstract

A matrix of chamber tests has been carried out in order to det. corrosion rates under well-specified conditions and to develop a fundamental knowledge of the mechanisms involved in the process of corrosion. Zinc and 55% aluminum-zinc-coated steel were exposed to tests at a const. humidity of 100%, 90% and 80%, 60% or 40%. In the case of the 90% humidity test, controlled salt dosages of approx. 0, 15, 45 and 120 mg/m2 day were applied. Mass loss of exposed plates was detd., and FTIR and scanning electron microscope examns. were undertaken. The exptl. program had the dual aim of providing data to develop dose function models for predicting corrosion rates in service environments, and to defining the nature of the material response under well-defined conditions. The utility of the data for developing dose functions is discussed. In order to gain a better appreciation of the response of the various metals to the dose tests, an exploration of the pH and chloride stability of Al-Zn and Zn oxides, simple droplet expts. and a detn. of the free corrosion current was undertaken. The mechanisms of salt-induced corrosion for these systems are discussed.
RESPONSE OF 55% ALUMINIUM-ZINC COATED STEEL AND ZINC TO WELL-DEFINED SALT DOSES UNDER CONTROLLED ENVIRONMENTS*

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ABSTRACT

A matrix of chamber tests has been carried out in order to determine corrosion rates under well-specified conditions and to develop a fundamental knowledge of the mechanisms involved in the process of corrosion. Zinc and 55% aluminium–zinc-coated steel were exposed to tests at a constant humidity of 100%, 90% and 80%, 60% or 40%. In the case of the 90% humidity test, controlled salt dosages of approximately 0, 15, 45 and 120 mg/m²·day were applied. Mass loss of exposed plates was determined, and FTIR and scanning electron microscope examinations were undertaken. The experimental program had the dual aim of providing data to develop dose function models for predicting corrosion rates in service environments, and to defining the nature of the material response under well-defined conditions. The utility of the data for developing dose functions is discussed. In order to gain a better appreciation of the response of the various metals to the dose tests, an exploration of the pH and chloride stability of Al-Zn and Zn oxides, simple droplet experiments and a determination of the free corrosion current was undertaken. The mechanisms of salt-induced corrosion for these systems are discussed.

INTRODUCTION

In order to develop models of the life of corroding components, data on the dependence of the corrosion rate on environmental conditions is required. Numerous studies have provided information on the corrosion rate under varying climatic conditions, and define relations between the average corrosion rate and the average of the climatic factors (1–4). Other studies have defined the variation in electrochemical currents on bimetallic grids or uniform grids with changes with environmental conditions (5,6). Lastly, there have been significant studies of the effect of controlled doses of pollutants on corrosion rate (7,8). Recently, models have been proposed that are based on understanding the processes controlling atmospheric corrosion (9–12). These models require a clearer understanding of the relative role of electrochemical processes, moisture layer chemistry and oxide stability, and response of surfaces to microclimates in controlling the corrosion processes. This paper is a first attempt to combine dose function data, with experiments on oxide stability and moisture layer formation as a first step in developing process models for

atmospheric corrosion. As such, the paper will present results from controlled dose tests in climate chambers, pH measurements on droplets, oxide stability measurements and free corrosion potential and current (as a function of pH).

EXPERIMENTAL METHODS

Sample Preparation and Analysis

Materials studied included aluminium–zinc (Al-Zn)-coated mild steel grade AZ150 (55% aluminium, 45% zinc) and 100% zinc metal. All samples were cleaned with ethanol before testing to remove grease and any other surface impurities.

Dose Function Procedures

Nine dose tests in which the humidity and RH were altered were performed, with the conditions of each test being given in Table 1. The humidity in each test was constant at the given value, while the salt dosage was applied at regular intervals (normally once a week) to give the nominated average salt deposition. Thus, in tests 1–5, the chamber was equilibrated at 90% RH and 30°C for 72 hours, then a salt spray was applied followed by one week at 90% RH and 30°C prior to a second cycle. The application of one salt spray and one week at the above humidity will be referred to as one cycle. Six cycles were applied. This spray was either neutral 5% NaCl (pH of collected spray was measured as 6.7), natural seawater (approximately 4% salt solution of composition in mg/L is 12,000 Na, 1,880 Mg, 420 K, 460 Ca, 3,000 S and 21,000 Cl). In test 6 the same procedures were used except that a two-minute spray was given every three weeks. In tests 7–9 no sprays were applied and the chambers were simply kept at constant humidities for the designated periods. In all tests, four 100 × 150 mm plates of each material, mounted at an angle of 60° to the horizontal, were exposed. Mass loss was measured according to the following procedures: zinc plates were etched in a 20% solution of chromium, trioxide and Al-Zn plates were etched in a 10% chromium trioxide/5% phosphoric acid solution to remove corrosion products. Weight loss was calculated using a ‘blank’ as a reference. FTIR spectra and analysis was carried out using the procedures of Neufeld et al. (13).

Table 1. Test conditions for salt dosage testing

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Humidity/Temp.</th>
<th>Average salt deposition rate (mg/m²·day)</th>
<th>Salt spray per cycle (min)</th>
<th>Cycles</th>
<th>Length of test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90%, 30°C</td>
<td>120</td>
<td>10</td>
<td>6</td>
<td>6 weeks</td>
</tr>
<tr>
<td>2</td>
<td>90%, 30°C</td>
<td>45</td>
<td>2</td>
<td>6</td>
<td>6 weeks</td>
</tr>
<tr>
<td>3</td>
<td>60%, 30°C</td>
<td>120* sea salt</td>
<td>10</td>
<td>6</td>
<td>6 weeks</td>
</tr>
<tr>
<td>4</td>
<td>40%, 30°C</td>
<td>120* sea salt</td>
<td>10</td>
<td>6</td>
<td>6 weeks</td>
</tr>
<tr>
<td>5</td>
<td>40%, 30°C</td>
<td>0 distilled water</td>
<td>10</td>
<td>6</td>
<td>6 weeks</td>
</tr>
<tr>
<td>6</td>
<td>90%, 30°C</td>
<td>15</td>
<td>2</td>
<td>4</td>
<td>12 weeks</td>
</tr>
<tr>
<td>7</td>
<td>100%, 23°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6 weeks</td>
</tr>
<tr>
<td>8</td>
<td>90%, 25°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4 months</td>
</tr>
<tr>
<td>9</td>
<td>80%, 25°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>9 months</td>
</tr>
</tbody>
</table>
The salt dosage levels where chosen to reflect Australian marine environments; 120, 45 and 15 mg/m²·day are typical of conditions at a distance of approximately 100m from Australian surf beeches, protected surf beaches and bay beaches respectively.

**Procedures for Corrosion Current Measurement as a Function of pH**

The potentiodynamic polarisation resistance technique was used to measure the corrosion current \( \left( i_{\text{corr}} \right) \) values of zinc and Al-Zn in pH 2–10 NaCl solutions. The electrochemical cell had a sandwich-type configuration with a surface area of the working electrode of 0.283 cm². A saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrode, respectively. Electrolyte solutions (~25 mL) initially contained in a 100 mL beaker were thoroughly degassed with high-purity N₂ (BOC, Australia) for at least 5 minutes before being transferred to the electrochemical cell. The experiments were carried out using Solartron SI 1286 Electrochemical Interface equipment. The potential was scanned at a scan rate of 0.1667 mV/s from +20 mV to –20 mV relative to the open circuit potential. The electrolyte solution was 0.10 M NaCl with the pH adjusted using NaOH or HNO₃ solution.

**Procedures for Determining pH Stability of Oxides**

The pH stability of the oxides was measured by placing 0.05 g of the oxide in a test tube and adding 10 mL of distilled water that was adjusted to different pH values with nitric acid. The contents of the test tube were shaken and the pH adjusted (if required) to the desired pH. The test tubes were shaken again and then centrifuged for 15 minutes at 5,000 rpm. The supernatant was decanted and the remaining solids were oven-dried and weighed. The percentage of the oxide dissolved at different pH values was calculated from the difference in the weights.

**Procedures for Salt Drop Experiments**

In these experiments, 0.5 mL of 5% NaCl solution was pipetted onto either a zinc or Al-Zn plate and the pH was monitored in the centre and at the edge of the drop over a period of several days. The plates were within constant humidity chambers at 100% RH.

**RESULTS**

The mass loss data for Al-Zn and zinc are given in Tables 2 and 3 respectively. A number of overall trends are apparent. In dose function tests with high chloride levels the corrosion rate of zinc is more than 5 times that of Al-Zn, while in dose function with low or zero chloride levels it is only 2 or 3 times that of zinc. The high humidity but zero salt tests were much milder than the salt containing tests. The low RH high salt tests were as or nearly as aggressive as the high humidity, high salt test.
Table 2. Aluminium-zinc plates corrosion rate

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Salt deposition (mg/m²·day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>100 test 7</td>
<td></td>
</tr>
<tr>
<td>90 test 8,6,2*,1</td>
<td>0.004</td>
</tr>
<tr>
<td>80 test 9</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>60 test 3</td>
<td></td>
</tr>
<tr>
<td>40 test 4</td>
<td></td>
</tr>
<tr>
<td>40 test 5</td>
<td></td>
</tr>
</tbody>
</table>

*For test 2 (salt deposition rate of 45 mg/m²·day.) plates of Al-Zn were exposed for 12 weeks with a corrosion rate of 0.150 (g/m²·day).

Table 3. Zinc plates corrosion rate

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Salt deposition (mg/m²·day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>0.014</td>
</tr>
<tr>
<td>60</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.032</td>
</tr>
</tbody>
</table>

Surface Analysis of Dose Function Plates

Exposure of zinc to 100% RH resulted in the formation of zinc hydroxycarbonate. This compound is formed from layers of zinc hydroxide and zinc carbonate. Initially complex coordinations of zinc hydroxide exist and then carbonates are formed in a layered manner. The carbonate is formed from carbon dioxide dissolved in the water layers that exist in test conditions. Al-Zn coatings exposed to 100% RH leads to the formation of complex hydroxide-hydrates with both zinc and aluminium. A complex carbonate (distinct from zinc hydroxycarbonate) based on these hydroxide-hydrate complexes also forms. Both the products on zinc and Al-Zn are amorphous and voluminous.

Very few surface changes occurred at 90% or 80% RH without salt, however as the salt dosage increased so did the extent of surface changes. In the case of the zinc plate, zinc hydroxychlorides were formed in preference to zinc carbonates when the salt dosage was at least 45 mg/m²·day. The zinc hydroxychlorides have an analogous layer structure to the zinc hydroxycarbonates. When the humidity was decreased to 60% at a salt dosage of 120 mg/m²·day the corrosion product was primarily zinc hydroxychlorides with little evidence of hydroxycarbonates.

In the cases of high humidity and salt doses on Al-Zn coatings, zinc hydroxychlorides and aluminium aquo complexes were formed. When the humidity was reduced to 60% and natural seawater was used (test 3), instead of aluminium aquo complexes, metal-sulfates were formed. This change may be promoted by the presence of sulfates in the seawater and the decreased moisture coverage of the surface at 60% RH.
SEM Examination of Dose Function Plates

Scanning electron microscopy indicates that Al-Zn initial corrodes at the zinc-rich phase, leading to the development of numerous pores. A gel builds up over the aluminum-rich phase and later at the bottom of the developing pores. Initially at the top of the pores, zinc hydroxide and zinc hydroxychloride form. As the corrosion progresses, crystalline zinc hydroxychloride is evident above the Al-Zn gel across the whole surface. The corrosion progresses down the zinc-rich interdendritic areas. Although there is some widening of the pores indicating the aluminum-rich phase is attached, it is the zinc-rich phase which primarily dissolves. In contrast in the case of zinc, relatively few corrosion patches occur. These patches are relatively shallow and have fairly smooth forms. At the patch centre both zinc hydroxycarbonate and chloride are observed, with the carbonate being more prevalent at the bottom of the patch. Outside the patch, zinc hydroxycarbonate is observed.

Results From Supplementary Experiments

Figure 1 shows the relationship between corrosion current and electrolyte solution pH in the presence of zinc and Al-Zn-coated steel. Figure 2 presents the solubility of the zinc oxide, zinc hydroxychloride and the Al-Zn oxide. In the droplet experiment on zinc, the saline drop initially spread to a diameter of 25 mm, however after around 20 minutes a fine moisture film formed at the edge of this central droplet and then expanded to have an annulus of around 10 mm. The pH was monitored in both the central region and in two places on either side of the centre in this secondary spreading region. The pH of the central region rose from 6.3 to 7.4 over the first 9 minutes and then gradually fell, so that after 3,000 minutes the pH was around 5.9. The pH in the outer region was fairly stable with time and varied from 8.5 to 9.5 depending on position. At the end of the test the specimen was dried and examined by both SEM and FTIR. Optical examination of the surface indicated three discrete areas: an outer band consistent with the area of secondary spreading, a white ridge, and an inner area where the central droplet had resided. The outer band is covered with zinc hydroxycarbonate crystals or gel, whilst the ridge and inner area is covered with crystalline zinc hydroxychloride.
Figure 1 - $i_{\text{corr}}$ Results of Zinc and Aluminium-Zinc

Figure 2 - Stability of Zinc and Aluminum-Zinc Oxides
The solution on the Al-Zn formed a droplet with a radius of approximately 30 mm and remained that size for over two days when a fine secondary spreading region with an annulus of around 5 mm formed. The pH was monitored in the centre of the droplet where the pH gradually rose to a value of 7.5, and within this outer area where the pH rose to 10.5 before falling back to 7.5. SEM observations indicated two zones. On the outer zone the surface had been lightly attacked at the zinc-rich phase. Pores were evident at this phase along with crystalline corrosion product which EDS and FTIR indicated was predominately zinc hydroxychloride. Interestingly salt crystals are also apparent and are concentrated on the surface of the zinc-rich interdendritic region, although a few were on the aluminum-rich dendrites. The zinc-rich regions had the appearance of valleys between the dendritic ridges. Moving towards the centre, an Al-Zn hydroxide covers the complete surface. This compound takes both a gel and a crystalline form. In localised areas, zinc hydroxychloride crystal structure sits on top of the Al-Zn hydroxide.

DISCUSSION

Degradation Sequences and Mechanisms

The droplet, stability experiments, and SEM observations permit an interpretation of the stages in the corrosion process for dose experiments. When a salt droplet falls on the zinc, two regions develop: a central area where the pH is lower than 6, and an outer region where the pH is above 9. The study of Neufeld et al. (14) demonstrated that the central area was anodic relative to the outer cathodic area. The local pH close to the surface and within the pores of the oxide is likely to be more extreme than that measured in the general moisture layer. Thus, it is probably that zinc hydroxychloride and zinc hydroxide are soluble in this central area and anodic dissolution of zinc can continue without restriction by the build up of oxide films. At the edge of the patch, the pH rises and zinc hydroxychloride precipitate, whilst in the secondary spreading area the precipitation of zinc hydroxycarbonate is favoured. These conditions are such that oxide development does not significantly limit either the cathodic or anodic reactions (large cathodic area is provided by secondary spreading).

In the case of Al-Zn, the major mechanism controlling the corrosion processes is likely to be the electrochemical cells established with the formation of the pores in the zinc-rich region. Standard theory of pit growth would suggest that anodic activity occurs within the pit and cathodic activity occurs on the surface. This in turn should promote a lowering of the pH in the pore and a rising of the pH at the surface. A number of observations indicate that this is indeed the case. The pH of the salt droplet on the Al-Zn surface does indeed increase steadily as would be expected if contact between pore solution and the bulk droplet was restricted. SEM observation of pore growth indicates that zinc hydroxides and zinc hydroxychlorides form only at the top of the pore, whilst Al-Zn hydroxide forms within the pore. The capping of the pore by the zinc corrosion product would isolate the pore solution from the bulk, and the absence of the zinc products from within the pores would be expected if the pore solution pH was less than around 5.5. In contrast at this pH the Al-Zn hydroxide would have limited solubility. Al-Zn products also form above the surface of the aluminum-rich phase and the thickness of these layers remains relatively constant throughout the exposure period. Indeed these products should be quite stable at the moderately alkaline conditions occurring on the surface.
Comparison of Corrosion Rates

Both the data on the free corrosion current and the mass loss in the dose function experiment demonstrates a markedly slower corrosion rate for the Al-Zn coating than for the zinc. The lower corrosion current of the Al-Zn material could be expected on the basis of the lower anodic area of the zinc rich-phase in Al-Zn compared to the zinc surface. This is based on the assumption that the corrosion current density established by the zinc-rich phase is not substantially higher than that which develops on the anodic areas of the surface of the zinc specimen. The aluminum-rich phase is unlikely to support greater cathodic activity than the cathodic regions on the zinc plate as, given that zinc oxide is a semiconductor, the zinc surface will provide substantial cathodic current.

Accepting this explanation for the free corrosion current studies, it does indicate why at least initially the corrosion rate of Al-Zn specimens in the dose function tests should be lower than that of the zinc specimens. However, as the dissolution of the zinc-rich phase in the Al-Zn coating advances, classical theory of occluded pits would predict that acidification of the pit would promote enhanced corrosion. However, significant enhancement of the corrosion rate is not observed. The presence of Al-Zn oxides in the pores indicates that the pore pH must not be significantly below 3.5. The development of significant zinc corrosion products on the specimen surface indicates that there is significant migration from the pore. Thus, it is probable that the development of corrosion products on the pore surfaces limits rather than prohibits diffusion of species from the pore, and thus extreme pH differences cannot be established.

The pores do not appear to grow significantly into the aluminium-rich phase. This implies that the Al-Zn oxides that develop provide a reasonably stable barrier to chloride diffusion, which would otherwise promote dissolution of the aluminium phase. Once the zinc-rich phase across the interdendritic zone has dissolved, anodic activity will be restricted to the bottom of the pore where the zinc-rich phase is freshly exposed. Thus, the anodic area of the pore may remain relatively constant as the pore grows, and thus the corrosion current will not increase substantially. A model for the variation of pore growth with time is developed in Neufeld et al (15). This model predicts three stages, an initial fast corrosion as films are established, a slow rate during pore growth and a fast rate when the pores connect leading to isolation of the aluminum-rich phase. This pattern is supported by the available evidence in this paper, including the acceleration of the corrosion rate as the period of exposure is extended from six to twelve weeks for dose test 2.

When the variation of mass loss with salt dose (at 90% RH) of the zinc and the Al-Zn surfaces is compared a clear difference is apparent. The corrosion rate rises continuously with increasing chloride dosage for the zinc plates, whilst the maximum corrosion rate occurs for the Al-Zn specimens at an intermediate dosage. It will be recalled that the salt dose is applied once a week (or once every three weeks for the lowest salt dose) by a continuous application of salt spray from two to ten minutes. Flow calculations indicate that after a period of 15–30 minutes a uniform film of salt solution from 10 to 20 µm in depth will form on top of the whole plate. After 2 or even 10 minutes film coverage will not be complete. Thus, the increase in corrosion rate for the
zinc and steel samples is not hard to understand – higher dosages simply lead to a greater surface coverage and thus more corrosion cells being established. The dilemma then is why does the corrosion rate of the Al-Zn samples reach a maximum at a dosage when only a fraction of the total surface is covered by salt solution. It was noted previously that the zinc-rich interdendritic phase corrodes preferentially so that if these regions were covered with salt solution, the corrosion rate may reach a maximum even if substantial parts of the aluminum-rich phase remain effectively dry. The observation of salt crystals forming preferentially on the interdendritic phase in the salt droplet experiments indicates that surface texture or surface tension effects promote such an uneven distribution of salt solution. Further investigation is needed to determine if this is a general phenomena.

Relevance to Models of Atmospheric Corrosion

The paper has a number of implications (both from the data itself and the mechanisms proposed) for the development of processes or statistically based models of atmospheric corrosion. The data indicates that significant corrosion is produced from the deposition of seawater droplets even at humidities as low as 40%. As seawater contains MgCl which will wet at humidities down to 35% RH (at 20°C), significant corrosion rates above 35% are not surprising, however it does indicate the need for caution when developing statistical models using the ISO 9223 approximation of time of wetness (TOW). ISO 9223 assumes that TOW can be approximated by the time when the RH is >80% and temperature is >0°C, and thus models based on TOW concepts often assume that little corrosion occurs at RH <80%.

The analysis of the observations indicates that the observed corrosion is highly dependent on both the stability of corrosion products and the development of local pH in moisture films. If local pH is shifted the corrosion rate may change significantly. For example, in mixed marine/industrial locations additional acidification of moisture layers could destabilise the Al-Zn corrosion products, causing a dramatic increase of the sensitivity of Al-Zn to marine aerosol. More sophisticated models are required to take account of these interactions between oxide stability, electrochemical processes etc. Some models are being developed along these lines (12). It is probable that simpler process models or statistical models could be developed, but the climatic sequences being modelled would have to be partitioned into regimes where corrosion processes and the local pH stay within limited ranges.

CONCLUSIONS

A series of dose function tests have been carried out, supported by electrochemical measurements, salt droplet experiments and oxide stability determinations.

1. The dose function tests indicate that aluminium–zinc coatings corrode at significantly lower rates than zinc when subjected to human–saline environments. The free corrosion current derived in saline solutions across a range of pH values shows a similar trend.
2. A mechanism is put forward to explain these observations based on consideration of the stability of oxides under the pH ranges that are likely to form during the corrosion processes.

REFERENCES