Corrosion Behavior of Carbon Steel and Stainless Steel Materials under Salt Deposits in Simulated Dry Repository Environments

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ABSTRACT

In-situ coupled multielectrode array sensors were used to measure the non-uniform corrosion of carbon steel and stainless steel materials under KCl salt deposit in simulated dry repository environments. It was found that the initiation of non-uniform corrosion occurs at a relative humidity that is 14% lower than the deliquescence relative humidity of the chloride salt. It was found also that once significant corrosion had occurred, the non-uniform corrosion process for the carbon steel material under the salt deposit continues at relative humidities as low as 27%.

INTRODUCTION

The deposition of aerosol and dust from ventilation air and the evaporation of water seeping into the drift of a proposed geologic repository at Yucca Mountain, Nevada, may lead to the accumulation of hygroscopic salts, such as KCl and NaCl, on the carbon steel ground support structures and on the surface of drip shields and waste packages [1–3]. At relative humidities at or above the deliquescence relative humidity (DRH) of the salt or salt mixture, these hygroscopic salts sorb moisture from the atmosphere and form a highly concentrated aqueous phase that could cause aqueous corrosion of metals. Initiation of aqueous corrosion of a metal is believed to occur at a critical relative humidity (CRH). In the Department of Energy’s modeling of the performance of waste package materials in the proposed repository, it was assumed that the CRH of the waste package materials is equal to the DRH of hygroscopic salts that could form on the waste package surface [4]. In our previous work [5], the conductivity of several salts and some of their mixtures that are likely to be present in the proposed repository system was measured as a function of relative humidity. It was found that the conductivity of a salt or salt mixture generally starts to increase at RHs that are about 15% to 20% lower than their DRH. Because ionic transport is a necessary condition for aqueous corrosion to occur, it was speculated that aqueous corrosion might initiate at RHs that are 15% to 20% lower than the DRH values.

In the present work, a coupled multielectrode array sensor was used to study the non-uniform corrosion behavior of carbon steel materials and determine their CRH under NaCl and KCl salt deposits in simulated dry repository environments. To verify whether the use of CRH is valid for other alloys, the non-uniform corrosion behavior of type 316 stainless steel material was also measured in the same environment.
EXPERIMENTAL

The schematic diagram of the multielectrode sensor used in the experiments is shown in Figure 1. The operating principle and the high-resolution current-measuring system for the coupled electrodes have been described elsewhere [6, 7]. In Figure 1, the sensing electrodes are coupled to simulate one piece of a metal, and the currents that flow from the anodes (or more anodic electrodes) to the cathodes (or less anodic electrodes) are measured as the corrosion signal. The sensing electrodes are made of type 1010 carbon steel (UNS G10100) and type 316 stainless steel (UNS S31600). Each sensor has 8 or 16 sensing electrodes cut from 1-mm (0.039 in) diameter wires. The chemical compositions of the carbon steel and the stainless steel wires are listed in Table 1. Prior to each test, the sensing surface of the sensors (the tip of the sensor) was polished with 600-grit paper and cleaned with acetone. Each sensor has a heat shrink plastic tube at the sensing end for placement of the salt powders (Figure 2).

The sensors were installed in a humidity chamber (Blue M Temperature/Humidity Cabinet by GS Blue M Electric) together with a hygrometer (Model 4085CC, Control Company, TX, USA), which has a ±1.5% accuracy, and two conductivity cells. The conductivity cell consisted of a filtration paper [dry dimension: 0.23 × 26 × 46 mm (0.00906×1.023×1.81 in)] that was soaked with saturated MgCl₂ and NaNO₃ salts. The DRHs of these two salts can be measured using the same equipment and method described previously [5]. By comparing the DRHs of MgCl₂ and NaNO₃ with published values [8] [(30.7% and 69.5%, respectively, at 49°C (120°F)], the measured conductivity of the two salts provides two reference RHs for the calibration and verification of hygrometer performance during the extended experiment. A glass beaker was placed upside down in the chamber so that it fully enclosed the sensors, the conductivity cells, and the hygrometer. This arrangement enabled the RH near the sensor surface and the conductivity cells to be controlled within ±1% (as indicated by the hygrometer), even though the humidity chamber has a lower precision (±5%). The glass beaker also acted as an extra drip shield (the humidity chamber has a built-in drip shield) to prevent water condensate at the top of the humidity chamber from dripping onto the salt powder above the sensor.

Table 1. Chemical compositions (wt %) of the metal wires used in the sensors

<table>
<thead>
<tr>
<th>Metals</th>
<th>UNS #</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>316 S.S.</td>
<td>S31600</td>
<td>11</td>
<td>17.7</td>
<td>Bal</td>
<td>&lt;2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.12</td>
</tr>
<tr>
<td>1010 CS</td>
<td>G10100</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
<td>0.31</td>
<td>0.04</td>
<td>0.042</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

Note: Bal: Balance
The experiments were conducted at 49°C (120°F) and used reagent grade chemicals and 18.2 Mohm-cm [7.1 Mohm-in] de-ionized water. Prior to the test, the salt powder was dried in an oven at 50°C (122°F), and the sensors were dried in the testing humidity chamber at an approximate RH of 35% and temperature of 49°C(120°F). After the drying step, the humidity chamber was opened and the salt placed on top of the sensors (Figure 2). Subsequently, the chamber was quickly re-closed, the RH in the chamber rapidly lowered to 35% (within approximately 5 minutes), and the sensor signal logged. After being held at about 35%, the RH in the chamber was slowly increased to the estimated CRH based on the results of previous conductivity measurements [5] and, subsequently, to the DRH of the salt on top of the sensors. The RH of the chamber was held at or above the DRH to allow corrosion to occur for a predetermined time period. Then, the RH was decreased slowly to determine the RH at which the corrosion process occurring on the sensor surface would stop.

RESULTS AND DISCUSSION

Figure 3 shows the response of the non-uniform corrosion currents from the carbon steel and stainless steel sensors under the KCl powder to changes in RH during a 64-day test. The non-uniform corrosion current from each sensor is represented by three times the standard deviation of the currents from the 16 electrodes [6]. Figure 4 shows the typical individual coupling currents from which the standard deviation signal was derived for the time period from the 25th to 27th day, as indicated in Figure 3. The coupled electrodes simulate one piece of metal, with some electrodes acting as anodic sites and others acting as cathodic sites. Each anodic coupling current represents the degree of charge transfer from a corroding (or more corroding) site to a non-corroding (or less corroding) site, which is part of the non-uniform corrosion process. Figure 4 also shows that a value of three times the standard deviation closely tracks the value of the most anodic current (from electrode #14 before and from electrode # 6 after day 27.3), thus its use as the corrosion current is justified. The16 mini-electrodes simulate a coupon that is divided into 16 areas, and the most anodic current from the 16 mini-electrodes simulates the corrosion rate of the most corroding area. However, a real coupon may develop hundreds of pits in a corrosive environment. The use of standard deviation signal is based on a statistical analysis and, thus, is considered a more reliable approach [6].

Figure 5 shows the relationship between the non-uniform corrosion currents from the carbon steel sensor and relative humidity at different times. According to Figures 3 and 4, the corrosion currents for both the carbon steel and type 316 stainless steel sensors remained at background level (10^{-11}A). On day 16, the RH was raised from 65.8% to 68.9%. The non-uniform corrosion current from the multielectrode sensors started to increase approximately one day after this RH change for the carbon steel sensor and after about three days for the stainless steel sensor.
Therefore, the CRH for the carbon steel and type 316 stainless steel materials under the KCl salt is approximately 67.4%, a value that is 14% lower than the DRH for KCl (81.3%) [8]. 67.4% is also the RH at which the conductivity of KCl salt starts to increase, as observed earlier [5].

For the carbon steel sensor, the non-uniform corrosion current increased with an increase in RH and reached a constant value at the DRH of KCl. Further raising the RH above the salt DRH seemed to have no significant effect on the non-uniform corrosion current. Decreasing the RH caused a decrease in the non-uniform corrosion currents from both the carbon steel and the stainless steel sensors. The non-uniform corrosion current density from the carbon steel sensor remained significant (slightly more than one order of magnitude higher than the background level) even after 12 days of holding the RH at approximately 27%. Because the RH could not be lowered

![Figure 3](image_url)  
**Figure 3.** Responses of the non-uniform corrosion currents from the multielectrode sensors under KCl salt to changes in relative humidity in the chamber.

![Figure 4](image_url)  
**Figure 4.** Typical currents and their standard deviation from the different electrodes of the carbon steel sensor during the measurements illustrated in Figure 3. The legend numbers represent the electrode number; 3xSTD represents three times the standard deviation.
further due to the limitation of the humidity chamber, no attempt was made to determine the new CRH at which non-uniform corrosion would stop or to test if this new CRH can be reproduced by subsequently raising the RH. The above observation suggests that once significant corrosion has taken place on the metal surface, the CRH could be changed to a value much lower than the original CRH. In the case of pure KCl, the new CRH is more than 40% lower than the original CRH. It is believed that the change in CRH is caused by the formation of corrosion products, such as FeCl₂ and FeCl₃, within the corroded pits or crevice [9,10]. The DRH of FeCl₂ and FeCl₃ salts is expected to be much lower than that of KCl.

Figure 3 also shows that the non-uniform corrosion behavior of the stainless steel is substantially different from that of the carbon steel. The non-uniform corrosion current from the carbon steel sensor increased gradually after reaching the initial CRH, whereas the non-uniform corrosion current from the stainless steel sensor stayed unchanged from the initial CRH to the DRH and increased abruptly at an RH slightly above the DRH. This behavior may be due to the fact that the corrosion rate was high for the carbon steel sensor and low for the stainless steel sensor after passing the initial CRH. The high corrosion rate at the carbon steel sensor caused continuous production of corrosion products that sorb water from the air and promote the corrosion process. In addition, the non-uniform corrosion current from the stainless steel sensor returned to background level when the RH was decreased from 49% to 38% on day 40; the new CRH for the type 316 stainless steel sensor after exposure to high RH is about 40%. The new CRH for the stainless steel sensor could be lower than 40% because the corrosion current for the type 316 stainless steel sensor had been low and only small amount of corrosion product was produced before the RH was reduced (4.1×10⁻⁷ A/cm² of average current density for the stainless steel sensor as compared with 5.1×10⁻⁵ A/cm² for the carbon steel sensor).

Unlike the case of uniform corrosion, where the corrosion rate can be calculated easily based on current density, the calculation of penetration rate based on current density from a multielectrode sensor is possible only if the surface non-uniform factor and current distribution factor are both known [6]. The non-uniform surface factor corrects the effect of non-uniform corrosion on the calculation. The current

![Figure 5. Relationship between non-uniform corrosion current from the carbon steel sensor and relative humidity at different times during the experiment](image5)

![Figure 6. Estimated non-uniform corrosion rate](image6)
distribution factor corrects the effect of internal current that flows from cathodic sites to anodic sites within a corroding electrode and, thus, cannot be measured by a multielectrode sensor. For the carbon steel sensor under a KCl salt where the corrosion current is relatively high, the most corroded electrode was probably completely corroded and may have few or no cathodic sites. Therefore, the current distribution factor is probably close to unity [6]. Figure 6 shows the estimated penetration rate for the carbon steel sensor based on the non-uniform corrosion currents shown in Figure 3 and the assumption that the most corroded electrode underwent uniform corrosion. This assumption is probably reasonable when the current density was relatively high because the electrodes are small (0.00785 cm² (1.217×10⁻⁵ in²)). Figure 6 shows that the non-uniform corrosion rate may be as high as 2 to 5 mm/y (0.0787 to 0.1969 in/y) under the KCl salt at RHs at or above the DRH of the salt. It should be noted that the estimation in Figure 6 may not be valid when the corrosion rate is low, in which case the corrosion may not be uniform and the internal current effect may not be neglected.

A similar experiment was conducted with an 8-electrode carbon steel sensor under NaCl salt. The results show that once significant corrosion on the sensor had taken place, lowering the RH to 29% does not stop the corrosion process.

CONCLUSIONS

The non-uniform corrosion behavior of carbon steel and type 316 stainless steel under NaCl and KCl salt deposits was studied using coupled multielectrode array sensors under simulated dry repository environments. It was found that the CRH at which aqueous corrosion initiates is 14% lower than the DRH of KCl. This CRH is close to the value reported previously at which the conductivity of KCl started to increase [5]. It was also found that, once significant corrosion had occurred on the metal surface under the salt deposit at a high relative humidity, the corrosion process is not stopped by lowering the RH to values much lower than the initial CRH or the DRH of the original salt. This phenomenon is believed to be due to the formation of corrosion products in the corrosion pits or crevices on the metal surface and that the corrosion products have DRHs significantly lower than those of the original salts.

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