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Gregory E. Gdowski

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HUMID AIR CORROSION OF YMP WASTE PACKAGE CANDIDATE MATERIAL

Gregory E. Gdowski
Lawrence Livermore National Laboratory
Livermore, CA 94550

ABSTRACT

Humid air corrosion of carbon steel under conditions of constant temperature and relative humidity was investigated. Carbon steel is a candidate material for the Yucca Mountain Site Characterization Project's Waste Packages (WP). The WPs are containers for storage of high level nuclear waste at a potential repository at Yucca Mountain, Nevada. A thermogravimetric analyzer was employed to investigate the short term corrosion of carbon steel under constant relative humidities, at elevated temperatures (60-90°C), and with various surface conditions. As expected, the initial corrosion rates are greatly enhanced by the presence of deposited sodium chloride under high relative humidity conditions. The corrosion product formed with deposited sodium chloride is porous and non-adherent. However, the corrosion rate decreases with time; this suggests that the components of the deposited salt are incorporated into the corrosion products. Characterization of the corrosion product formed gave an understanding of the long term corrosion processes.

Keywords: atmospheric corrosion, carbon steel, humid air corrosion, sodium chloride, NaCl, relative humidity

INTRODUCTION

The Yucca Mountain Site Characterization Project is evaluating candidate materials for high level nuclear waste containers (Waste Packages) for a potential deep geologic repository at Yucca Mountain, Nevada. The potential repository is located above the water table in the unsaturated zone. The rock contains nominally 10% by volume water and gas pressure in the emplacement drifts of the repository is expected to remain near the ambient atmospheric pressure. The heat generated by the radioactive decay of the waste will raise the temperature of the waste packages and the surrounding rock. This temperature rise will liberate water from the pores and micro-fractures of the rock. Waste Package temperatures above the ambient boiling point of water are anticipated for the waste emplacement scenarios. Because the repository emplacement drifts are expected to remain at the ambient atmospheric pressure, the maximum relative humidity obtainable decreases above the boiling point of water (see Figure 1). Temperatures of the Waste Packages and the surrounding rock are expected to reach maximum temperatures within 100's of years and then gradually decrease with time. Episodic liquid water contact with the WPs is also expected; this will result in the deposition of salts and mineral scale.

An understanding of the corrosion processes that occur under constant temperature and constant relative humidity are necessary for evaluation of candidate Waste Package materials. While there is much literature on the effect of humid air on the corrosion of materials under ambient atmospheric conditions, little information is available at higher temperatures [1]. This study investigated the humid air corrosion of carbon steel in the temperature range 60 to 90°C.

Hygroscopic salts are known to significantly enhance the corrosion of mild steel at relative humidities below 100% [1]. The aqueous salt solutions formed enable aqueous film electrochemical corrosion of the steel to occur. The severity of the corrosion is dependent on the particular salt and the relative humidity. It has been noted that, in general, the severity of attack of steel as a function of relative humidity increases significantly at RH values equal to or greater than the equilibrium relative humidity of the saturated salt solution. Bulk aqueous salt solutions will form at the equilibrium relative humidity. However, there is a noted increase in the corrosion of steel even at relative humidity values below the equilibrium value when compared to the corrosion in the absence of the deposited salt [1,2].

The equilibrium relative humidities versus temperature of several saturated salt solutions [3] and the boiling points of several saturated salt solutions [4] are plotted in Figure 1. In terms of the cations, salts of sodium (Na) and potassium (K) tend to have higher equilibrium RH's (less hygroscopic) than those of calcium (Ca) and magnesium (Mg). In terms of the anions, sulfates (SO_4) have higher equilibrium RH's (less hygroscopic) than those of chlorides (Cl) and nitrates (NO_3).

For some salts, such as, sodium chloride (NaCl), there is little change in the equilibrium RH as a function of temperature, this is probably because the solubility of NaCl

does not change much with temperature. For other salts, such as, sodium nitrate (NaNO_3) there is almost a 20% change in the equilibrium RH as a function of temperature, this is probably because the solubility of NaNO_3 doubles from 25 to 100°C.

At RH values less than the equilibrium value, bulk aqueous salt solutions will not form. At RH values greater than the equilibrium value, more dilute aqueous solutions will form. The amount of water that is taken up by hygroscopic salts, such as, NaCl, have been previously determined as a function of relative humidity [4]. At 100°C and 74% RH (the equilibrium RH), there are about 2.6 mg of water taken up per mg of NaCl. At 100°C and 85% RH, there are about 4.4 mg of water taken up by per mg of NaCl. At 100°C and 91% RH, there are about 7 mg of water taken up by per mg of NaCl.

The corrosive action of deposited salts, such as NaCl and Na_2SO_4 , on carbon steel is well documented [1]. Under normal atmospheric conditions, it is recognized that the effectiveness of sustaining the corrosion processes decreases with time for a given amount of initially deposited salt. It is documented that chloride ions are incorporated into the iron oxide akaganeite under marine conditions [5]. Sulfate has been identified within solid corrosion products [6]. The mineral jarosite, $\text{NaFe}_3(\text{OH})_6(\text{SO}_4)_2$ or $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$, has been suggested as an example of a potential iron and sulfate containing compound that could form during corrosion [5]. Graedel and Frankelthal [5] have discussed the topic of mineral formation during corrosion in some detail.

EXPERIMENTAL

Test specimens were made of 1020 carbon steel and ASTM A516 Gr 55. Test specimen dimension were nominally 1.5 in x 0.5 in x 0.062 in. Clean specimens and specimens with deposited NaCl were tested.

Experiments were performed using an extensively modified Cahn Model TG 131 thermogravimetric analyzer. The resolution of the analyzer was about 40 μg . The reaction chamber was a double walled glass cylinder. Temperature and relative humidity were measured in the reaction chamber by a combined temperature humidity sensor. Temperature was maintained by flowing a constant temperature fluid through the outer annulus of the glass reaction chamber. Temperature was maintained to less than $\pm 0.5^\circ\text{C}$.

Humid air was obtained by either bubbling cleaned laboratory air through a column of water or by use of a liquid injection system. In the liquid injection system, a micropump feed controlled amounts of water to a vaporizer, and then a carrier gas (air) transported the vaporized water to the reaction chamber. In both cases, the plumbing to the reaction chamber was heated to avoid condensation of water. Relative humidity was maintained to better than $\pm 4\%$.

Salts were deposited utilizing two techniques. Initially salts were deposited by immersing the specimen in NaCl saturated 50% water / 50% acetone solution, and then

drying the specimens in hot air. The process was repeated until the desired amount of salt was deposited. In the second technique, salts were deposited by placing the specimens in a salt aerosol stream, and then drying in hot air. The aerosol was formed by an atomizer apparatus. The amount of salt deposited was nominally 5 mg.

Specimens were tested under nominally constant temperature and constant relative humidity conditions. Test durations were typically 7 to 14 days. Specimens were initially brought to the test temperature in low humidity air. After the temperature was stabilized the humidified air was introduced. Relative humidity was controlled by varying the flow rate of the carrier gas in the vaporizer or by mixing dry air with the humidified air from the bubbler.

Temperature and relative humidity in the reaction chamber, and change in the specimen weight were all recorded as a function of time by a computer.

RESULTS AND DISCUSSION

Clean and polished specimens

Clean polished A516 specimens were exposed in the temperature range 60 to 90°C to relative humidities up to 90%. No oxidation of the specimens was detected for the RH < 75% for the test conditions. At nominally 90% there was typically a small increase in the specimen weight and some visible oxidation of the specimens. The small amount of oxide which formed was adherent. The weight gain of a specimen at a temperature of 75°C and 90%RH as a function of time is shown in Figure 2.

Numerous studies have investigated the adsorption of water as a function of relative humidity. On iron, water adsorption has been investigated up to 85°C and 95% RH [7]. At about 90-95%RH water adsorption is less than 5×10^{-7} g/cm². Averaged over the surface this corresponds to thickness of less than 5×10^{-3} μm (less than 20 monolayers of water). This estimate of water film thickness is obviously an over simplification of water adsorption characteristics, since water will form clusters and preferentially adsorb at high energy sites. However, it does indicate that water adsorption even at high relative humidity values is limited to relatively thin thicknesses. Oxygen resupply from the atmosphere and subsequent transport through water films of such thicknesses will be fast.

The electrochemical oxidation / corrosion of iron is limited by the conductivity of the oxide which is formed [8,9] because the oxygen reduction reaction occurs on the high conductivity oxide:

Magnetite (Fe₃O₄) has a much higher conductivity than the Fe(III) oxides, hematite (Fe₂O₃) and goethite (α-FeOOH). It is expected that under the oxidizing conditions of the thin

aqueous films that iron would be oxidized to Fe(III) and would then quickly precipitate because Fe(III) compounds have limited aqueous solubility except under acidic conditions. Scanning electron microscopy indicated a thin dense oxide formed under these conditions. There was an insufficient amount of oxide for identification by X-ray diffraction.

Specimens with deposited salt (NaCl)

A516 carbon steel specimens with deposited NaCl were exposed to relative humidities of up to 90% RH at nominally 80°C. The results are plotted in Figure 2. For comparison, the data for a clean specimen exposed to 90% RH (75°C) is also included in the figure. At all values of relative humidity tested there were weight gains recorded. Visual observation of the specimens during testing indicated that most of the weight gain was due to oxidation / corrosion of the specimen. Brownish oxide formation was observed simultaneously with the weight gain increases. The weight gain became significantly more rapid when the relative humidity was increased above 48%. Note that the equilibrium relative humidity of a saturated NaCl aqueous solution is about 75%.

For the 78% RH test, the weight gain data showed an initial rapid increase, followed by a more gradual increase, and finally a region of no increase or a slight decrease. Visually it was observed that the amount of corrosion / oxidation product was increasing with time under these conditions. The slight decrease of weight gain was in part due to some spalling of the corrosion product off the vertical specimens. It should be noted that with the deposited NaCl no visible water film was observed at any relative humidity. This was probably due to the rapid corrosion / oxidation of the specimen because of the extremely aggressive conditions on the surface. The sorbed water would form very concentrated sodium chloride brine, and in addition, ready availability of oxygen from surrounding air made the aqueous conditions oxidizing.

The corrosion / oxidation product that formed on the specimens with deposited NaCl was nonadherent. Scanning electron microscopy of the surfaces showed that the oxide had the characteristic whisker structure of the chlorine containing oxide akaganeite [10]. This oxide has been identified in corrosion products formed on carbon steels in marine environments [5].

An indication of the extent of the accelerating corrosion effect of relative humidity is illustrated by the rate of the initial weight gain of the specimens versus time. This data is listed in Table 1. It is expected that these rates would change as a function of the amount of salt deposited, but the trend does illustrate the accelerating effect of increasing relative humidity. There is a three order of magnitude increase in the initial weight gain rate upon increasing relative humidity from 48% to 88%RH. At a nominal value of 90% RH, there was almost a four order of magnitude increase in weight gain rate when salts were present than for the clean surface test. Part of the weight gain increase is due to water sorption, however, as noted above, the water sorption could contribute about 4.4 mg per mg NaCl to the weight gain at 85% RH. Water sorption into the porous structure of the corrosion product may also contribute somewhat to weight gain.

Table 1. Initial weight gains of carbon steel specimens covered with deposited sodium chloride at 80°C

Relative Humidity (%)	mg/hr
90 (75°C; no deposited salt)	0.004
48	0.02
63	2.3
78	6.2
88	38

CONCLUSIONS

In the absence of deposited salts the short term oxidation of carbon steel in high relative humidity (up to 90%RH) air is slow at temperatures of 60 to 90°C. With deposited sodium chloride, carbon steel at 80°C is susceptible to corrosion oxidation at even 48%RH. The initial degradation is accelerated at 63% RH and it significantly increases further at RH values above the equilibrium relative humidity of a saturated NaCl solution.

With time the corrosive effect of a small fixed amount of sodium chloride decreases. It is thought that this is due to the incorporation of the components of the salt into the corrosion product. The long term stability of this corrosion product is of interest because liberated salt would then be available for further corrosion.

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Equilibrium Relative Humidities and Boiling Points of Saturated Salt Solutions

Figure 2. Weight gain of salt covered A516 carbon steel versus time as a function of relative humidity. Specimens had nominally 5 mg of deposited NaCl. Also included for comparison is the plot for a clean specimen exposed to 90% RH.