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Impact of Atmospherically Deposited Solid Contaminants on Materials of Interest for the Interim and Long Term Storage of High Level Nuclear Waste

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ABSTRACT

For both the interim and long term storage of high level nuclear waste, the storage casks/containers will be exposed to conditions under which considerable dust and/or atmospheric aerosols may be deposited on the surface. These dust layers may contain a sizeable portion of water soluble salts, particularly in marine environments where many interim storage systems are located. These soluble salts will deliquesce if sufficient moisture is present, resulting in the formation of potentially corrosive brine on the material surface. While this is not a concern for highly corrosion resistant materials such as Hastelloy C22 (which was pursued for long term geologic storage), it could be an issue for the less corrosion resistant stainless steels and carbon steels used for interim storage applications. Experimental results have illustrated that some stainless steels can and will undergo localized corrosion in elevated temperature conditions where a chloride rich brine has formed on the surface. In this presentation, the results of this test program, as well as efforts to address the potential for corrosion stifling under conditions where a limited quantity of reactant is present will be discussed.

Key words: Interim Storage, Spent Nuclear Fuel, Crevice Corrosion, Dust Deliquescence

INTRODUCTION

Any waste package which is exposed to the atmosphere will have particulates (i.e., dust) carried by the atmosphere deposited on its surface. A portion of most atmospheric dusts consists of various soluble salts. Given the correct combination of temperature and atmospheric moisture content, these salts may deliquesce. Deliquescence, illustrated schematically in Figure 1, is essentially the transformation of the solid salt to a saturated salt solution, or brine. It has been suggested by several researchers that the salts which are deposited on waste package or container surfaces may combine to form deliquescent brines on the surface of a waste package at temperatures well above the boiling point of water, and further, that these brines might be corrosive depending on the material used to construct the package.[1] Other researchers have suggested that for highly corrosion resistant/passive materials, several factors will prevent extensive localized corrosion due to deliquescence, including electrochemical limitations (e.g., insufficient cathode reaction area) and physical (e.g., limited concentration of brine coupled with consumption or sequestration of aggressive species in the corrosion product).[2]

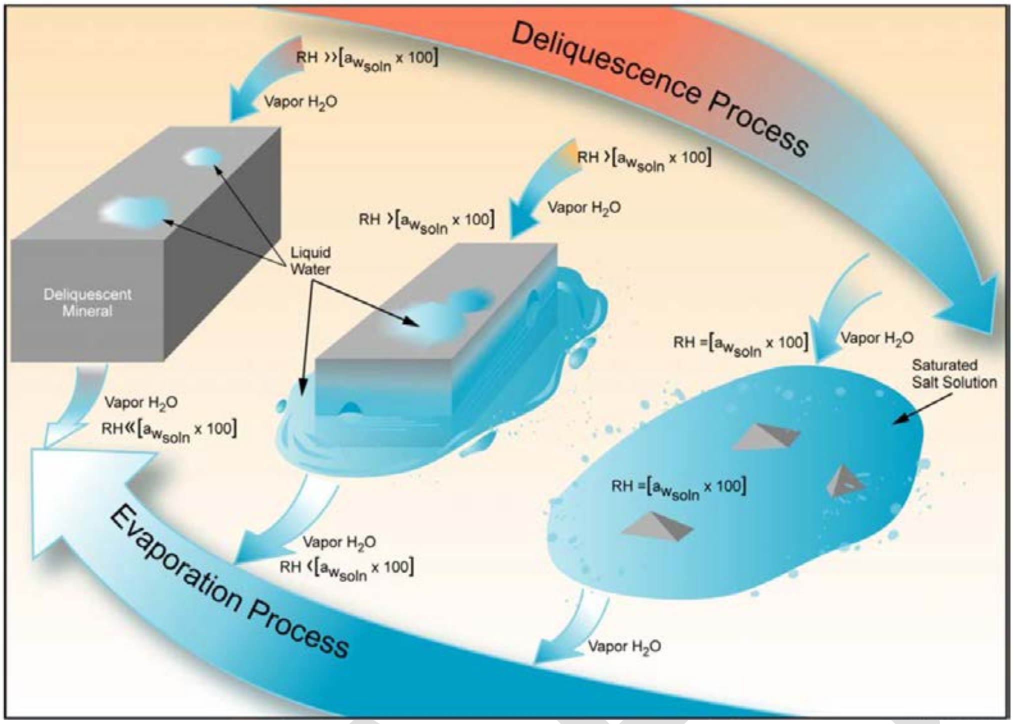

Figure 1: Schematic representation of the deliquescence process.[3]

In an effort to determine if there is indeed a potential for deliquescent brines to result in localized corrosion, a series of experiments have been performed. Materials of interest have been decorated with thin layers of salt in the presence of an occluded geometry in an effort to establish if localized corrosion (i.e., crevice corrosion) could initiate and propagate under such conditions. In these experiments, no inert species were added, and as such physical sequestration of the brine by the dust layer due to capillary forces have been eliminated, allowing all of the material deposited on the metal surface to participate in the corrosion reaction.

The chemical composition of the brines which can form is a function of temperature, as well as the available constituent materials. At very high temperatures, brines must be very nitrate rich, whereas at lower temperatures, the composition can be dominated by other species, such as chloride.[4] In terms of the corrosiveness of the brine, both the chemistry (e.g., concentration of aggressive species) and the exposure temperature have a strong impact on corrosion processes.

EXPERIMENTAL PROCEDURE

Materials

As discussed above, there were two goals of the work presented here. The first was to assess whether or not the material which had been selected as the outer corrosion barrier for the waste package design proposed for Yucca Mountain. The second was to assess the performance of less corrosion resistant materials, such as stainless steels, which are in use as the container material for dry fuel storage containers in marine (and other) environments. In the case of the former material, a wide range of brine chemistries and temperatures are of concern, whereas for the latter, the temperatures are lower and the brine chemistry is primarily chloride based.

To evaluate the performance of Alloy 22, specimens of Hastelloy 22 (UNS #N26022), along with Inconel 625 (UNS #N06625), Hastelloy C276 (UNS #N10276) and an 80:20 Ni:Cr (UNS #N06003) material were evaluated. These materials represented a series of alloys progressively less resistant to localized corrosion due to the reduced (or eliminated) quantities of W, Cr, and Mo present. For the dry storage applications, 303SS (UNS #S30300) (a highly susceptible, free machining stainless steel) and 304SS (UNS #S30400) were evaluated. All specimens were polished to a mirror finish and cleaned/passivated prior to exposure. Each sample was first cleaned ultrasonically in acetone, after which they were passivated in a 15 vol% HCl solution for 3 minutes at ambient temperature. Finally, the samples were rinsed in deionized water after which they were vapor degreased in trichloroethylene for 3 minutes and then rinsed for 1 minute in isopropyl alcohol.

Salt Deposition

Two different salt assemblages were evaluated in this study, the compositions of which are given in Table 1. The first contained a combination of nitrate and chloride, and was able to form liquid brines under atmospheric pressure at temperatures well above the boiling point of water. This salt assemblage was selected as it was representative of what might form from the dust deposited on a waste package surface within the proposed Yucca Mountain repository.[3] The third salt assemblage was entirely chloride based, and formed a liquid brine under atmospheric conditions at temperatures as high as 105°C. All materials were ACS reagent quality or better. The composition (as molar fraction) of the solids used to construct each brine is listed in the table below:

Table 1: Salt Assemblages Used to Simulate Dust Deposits

Constituent	**4 Salt Assemblage**	**2 Salt Assemblage**
NaCl	0.126	0.527
KCl	--	0.473
$NaNO_3$	0.228	--
KNO_3	0.268	--
$Ca(NO_3)_2$	0.378	--

Deposition of each salt assemblage was accomplished by first creating a dilute solution (approximately 0.1M) of the salt in a methanol carrier. The salt was then deposited via an air brush using a dry nitrogen carrier gas onto the metal surface. For the deposition, the air-brush was held rigidly in place while the sample was moved through the salt deposition cone at a fixed rate. A quartz crystal microbalance was mounted adjacent to each coupon and was used to monitor the total quantity of salt deposited on the sample surface (once the methanol carrier had evaporated.). The resulting deposit was extremely uniform, as illustrated in Figure 2 for the four salt assemblage (note that this assemblage forms a liquid brine at ambient temperature, hence the appearance of small droplets on the sample surface)

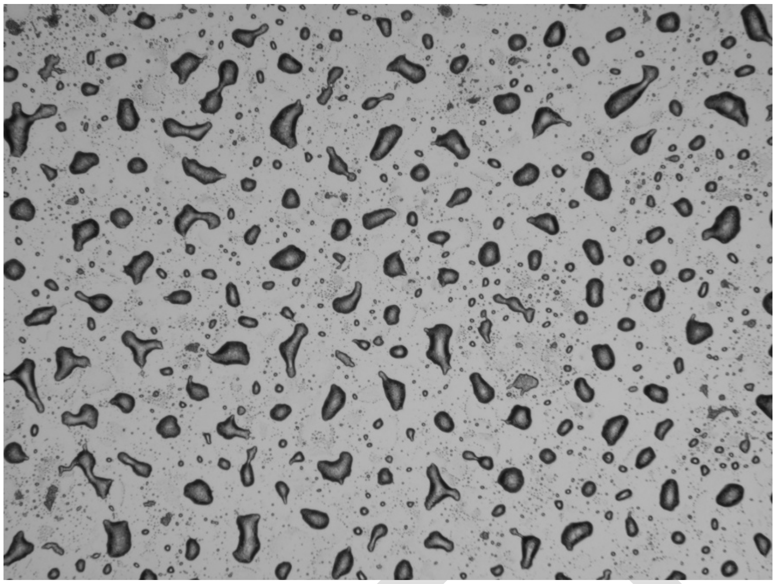

Figure 2: Small droplets typical of the airbrushed salt deposits. Note that the field of view presented in the image is approximately 1.15mm (typical droplet is approximately 25 microns in size or smaller.)

Salt was deposited only in the region where corrosion testing was to be performed (i.e., it was present in the area where the multiple crevice former assembly would be present, but only extended a few mm past that diameter) as illustrated in Figure 3 below.

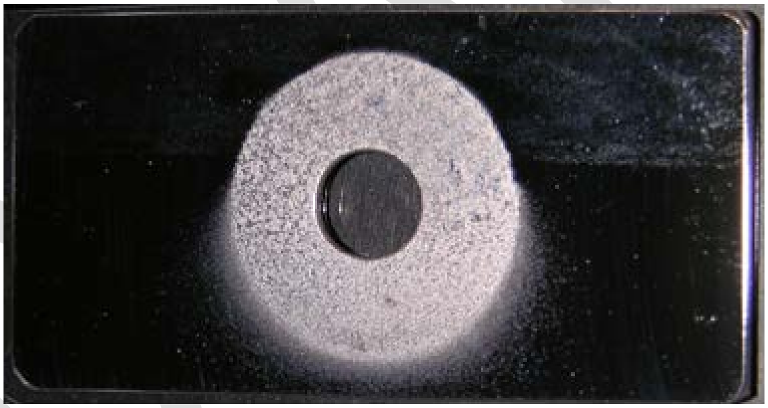

Figure 3: Typical salt deposition region. Note that the coupon is approximately 2 in. x 1 in.

Crevice Corrosion Testing

Once each coupon was cleaned and the appropriate quantity of salt deposited as discussed above, a multiple crevice former assembly (MCA) was attached to the surface. The ceramic MCA assembly was wrapped with PTFE tape prior to being torque down onto the metal surface. Titanium hardware, along with PTFE washers and the MCA were assembled as illustrated in Figure 4. The combination of coupon surface finish, PTFE wrapped MCA, and applied torque were based upon work performed by Shan and Payer (Shan, 2007) where they demonstrated that this was the most aggressive manner in which to evaluate the potential for crevice corrosion initiation.

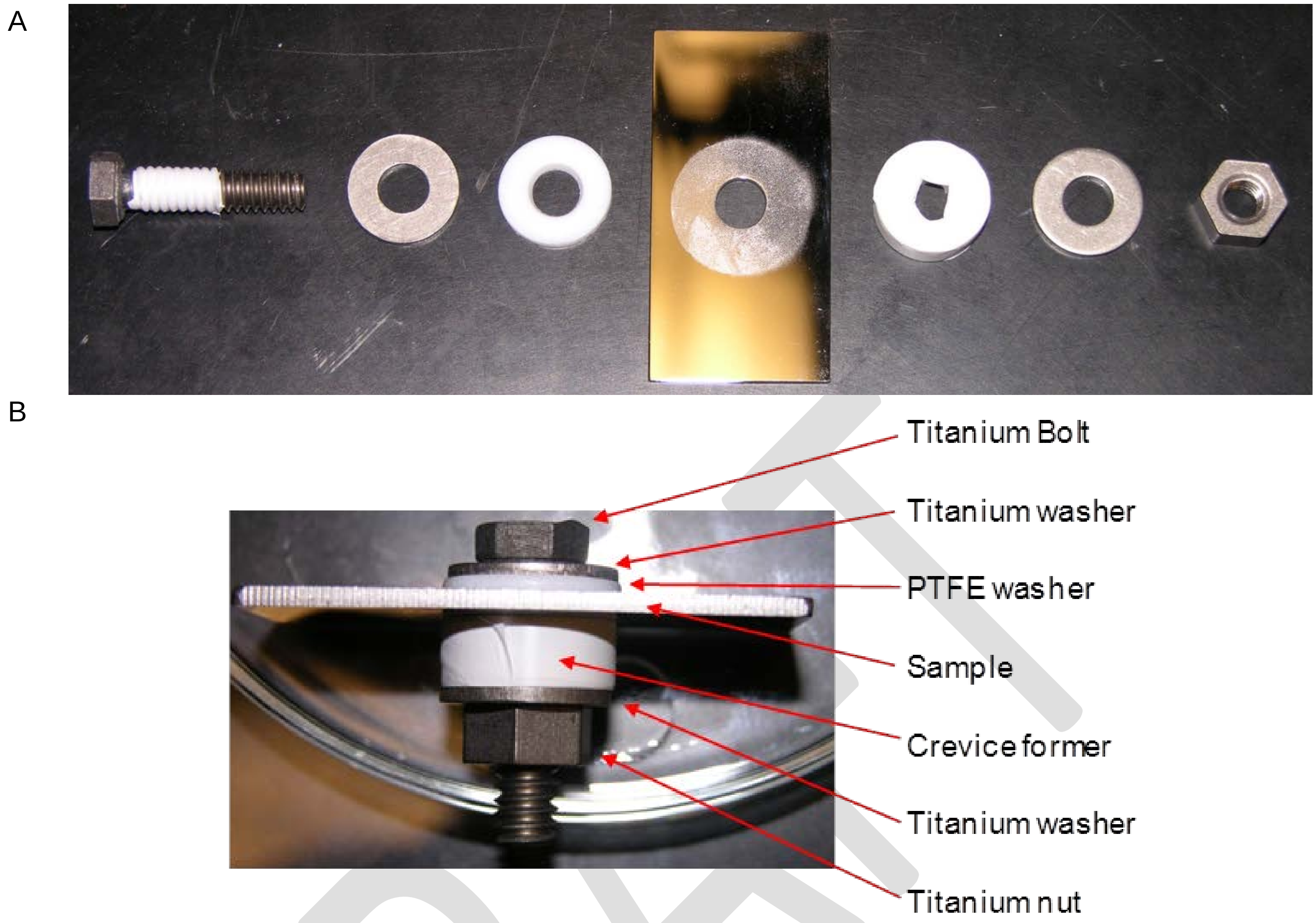

Figure 4: Crevice corrosion testing sample configuration. Titanium hardware was used to secure the MCA to the surface of the corrosion test coupon. Care was taken to electrically isolate the titanium hardware form the coupons itself. The MCA was made from zirconia and was wrapped in PTFE tape prior to being secured to the coupon surface at a torque of 70 in-lbs.

Once assembled, the coupons were placed within a high-temperature, controlled dewpoint test chamber at a prescribed temperature and moisture level. The system is illustrated schematically in Figure 5. The gas stream, which is predominantly water, is provided my utilizing a mass flow controller to feed liquid water to a steam generator. A second mass flow controller is then used to add however much air is required to meet the desired dewpoint. The reaction chamber itself is housed within an oven. Throughout each experiment, the conditions within the chamber are monitored via a series of thermocouples along with a chilled mirror.

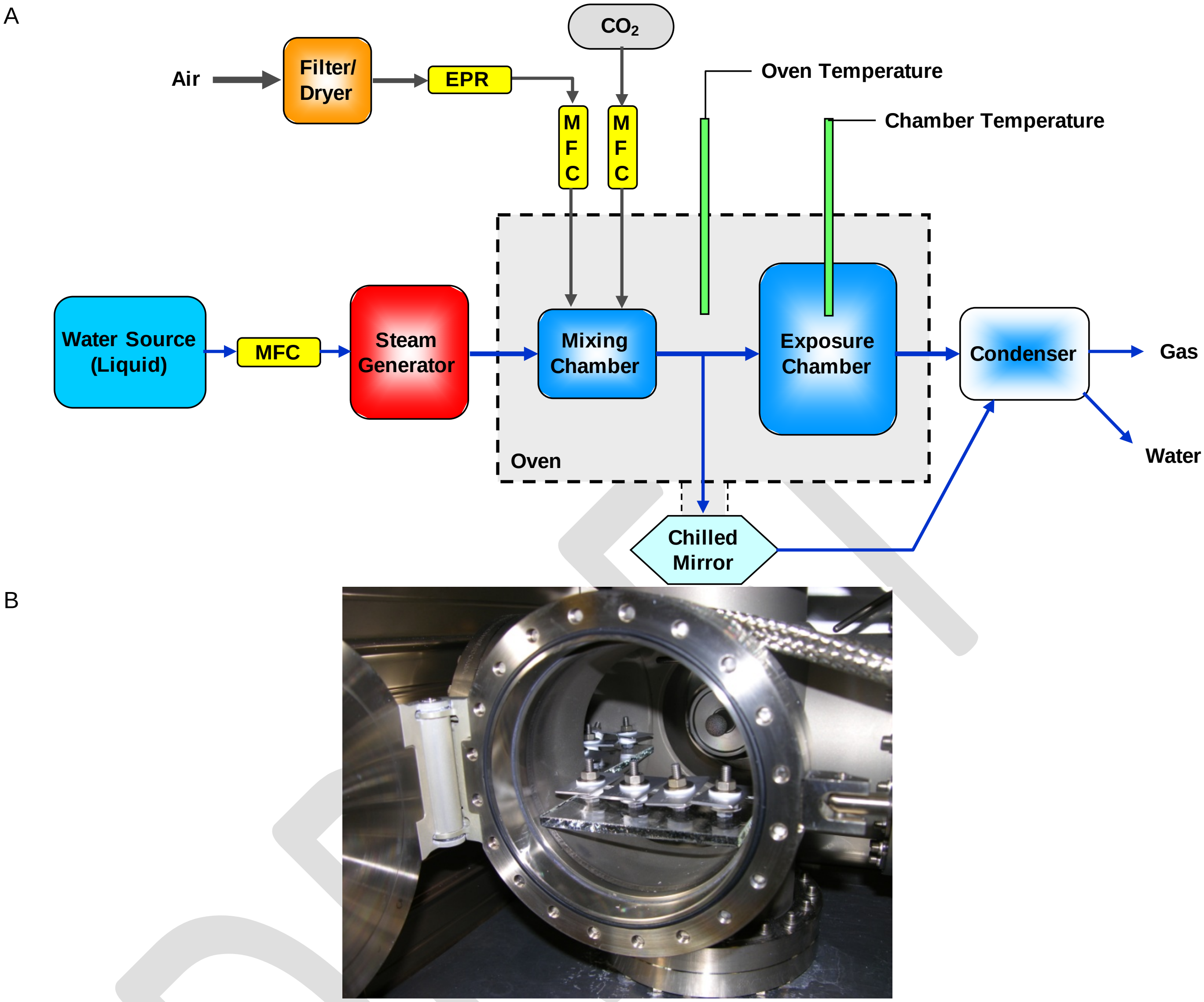

Figure 5: Schematic representation of the high temperature exposure system used for the elevated temperature experiments, along with a view of the loading port on the test chamber to illustrate the placement of coupons which was used)

Specimens were placed on a glass surface and were not in contact with either the chamber walls or with other specimens within the chamber, as illustrated in Figure 5. The gas flow rate through the chamber provided multiple environment exchanges per hour. Both the temperature and dewpoint were monitored continuously throughout the course of each experiment. In addition, a dish containing the salt assemblage under investigation was also placed within the chamber. Periodic observation of the bulk sample enabled verification that a liquid brine was stable and that little or no second phase precipitation was taking place (which would in turn alter the composition of the brine).

Upon completion of the each test, the MCA/coupon assembly was disassembled. As can be seen in Figure 6, most samples had a deposit remaining on the surface consisting of the initially deposited salt, as well as a film of PTFE tape from the crevice former. Each coupon was photodocumented in the as-removed condition, and then cleaned ultrasonically in deionized water, followed by immersion in a 15 vol% HCl solution to remove the surface contamination left behind by the test.

Figure 6: Hastelloy C-22 sample following long term exposure and removal of the MCA from the surface. Note the residual salt remaining on the surface, along with deposits from the PTFE tape which the MCA was wrapped with.

RESULTS

High Temperature Brines

The salt combinations capable of forming a brine at temperatures far above the boiling point of water are necessarily very nitrate rich. As such, experiments were performed using a multi-salt assemblage consisting of NaCl, $NaNO_3$, KNO_3, and $Ca(NO_3)_2$ with an overall nitrate to chloride ratio of 18. As discussed above, this particular combination was identified as one of relevance to the dust deposited at the proposed Yucca Mountain repository.

Samples of Hastelloy C22, Inconel 625, Hastelloy C276, and an 80:20 Ni:Cr alloy were evaluated. Each sample loaded with salt to over 350 $\mu g/cm^2$ using the procedure defined above, after which a multi-crevice assembly was fastened in place. Two sets of specimens were evaluated. The first was exposed to an environment at 180 to 185°C with a dewpoint of 94.5°C (tests were performed in Albuquerque, NM, and as such the boiling point of water is approximately 94.5°C and the environment was pure steam). The second set of specimens was identical to the first, save that the dewpoint was reduced to 92°C through the addition of air to the gas stream, thereby increasing the oxygen content of the environment. After 30 days exposure, the samples were removed, the crevice formers taken off, and the extent of any crevice corrosion measured.

For all specimens in both environments, no signs of localized corrosion initiation were observed, either optically or via scanning electron microscopy.

Lower Temperature Brines

In the nitrate containing brine experiments, while the temperature was very high (which would tend to increase corrosion rates), the nitrate to chloride ratio was very high. As nitrate is a potent inhibitor for localized corrosion initiation, a brine containing only chloride species was evaluated. Due to the removal of nitrate, the maximum temperature at which a liquid bring can be maintained is lower, approaching 100°C. Mixtures of KCl and NaCl are capable of forming a brine at temperatures as high as 105°C.

Experiments were performed in the same manner as those described above at a dewpoint of 94.5°C, chloride rich brine at a temperature of 101°C for 100 days. In addition to the materials used in the four component, nitrate-chloride brine, 303SS was added to the test matrix. 303SS is a free-machining stainless steel containing an elevated sulfur content and as such is extremely susceptible to localized corrosion. This material was selected to demonstrate that the test procedure could support localized corrosion for a sufficiently susceptible material. The test was run for a total of 100 days, and for the nickel based alloys, no discernable crevice corrosion was observed. The 303SS, however, did initiate localized corrosion for many of the MCA teeth, as illustrated in Figure 7.

Figure 7: Crevice attack observed on 303SS samples after 100 days of exposure at a dewpoint of 94.5C and an ambient temperature of 101°C.

SUMMARY/CONCLUSIONS

It has been asserted numerous times in the literature that highly corrosion resistant materials, such as Hastelloy C-22 and other Ni-Cr-X alloys, are not capable of supporting crevice corrosion in the presence of a highly concentrated brine due to a variety of chemical, electrochemical, and geometric factors.3 The experiments discussed here validated these assertions, illustrating that localized corrosion would not initiate on these materials, even when an extremely aggressive crevice former was combined with a chloride rich brine.

As the material becomes less corrosion resistant, and therefore capable of supporting a higher anodic and/or cathodic reaction rate on the metal surface, localized corrosion can initiate. This was demonstrated here for SS303 in the presence of a chloride rich brine. As the material becomes more electrochemically active, the cathodic reaction rate on the exterior surface becomes larger, reducing the cathode area required to support the active region beneath the crevice. In addition, the anodic reaction rate increases, facilitating maintenance of the critical crevice solution within the occluded geometry, an preventing stifling of the propagating crevice. Related to this effect, the critical crevice solution required by the less corrosion resistant material is less concentrated, further increasing the resistance of the advancing localized corrosion site to mass transport of metal ions out of the solution beneath the crevice.

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