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***In-Situ* Monitoring of Chemistry and Corrosion
Processes Under Heat Transfer and Episodic Wetting
Conditions**

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The U.S. Department of Energy (DOE) is tasked with the permanent disposal of high level nuclear waste (HLW) generated during commercial power plant and research reactor operations. The current DOE plans call for the emplacement of this HLW in metallic containers constructed of an inner Type 316L stainless steel (SS) layer, 5 cm thick, surrounded by 2 cm of Alloy 22 (57Ni-22Cr-13.5Mo-3W-3Fe) with the containers to be placed in a horizontal drift (tunnel) at the proposed site in Yucca Mountain (YM), NV. The primary attribute in the selection of Alloy 22 as a container material was the low corrosion rate and high resistance to localized corrosion in many environments. The greatest uncertainty, however, affecting long-term material behavior is the nature of the environment to which the containers will be exposed. As consequence, monitoring of the water chemistry on the container surface and how this chemistry affects corrosion is important to detect the onset of unanticipated conditions that may lead to rapid corrosion and container failure.

Though the DOE has yet to clearly delineate the parameters it considers important to monitor to verify material performance [1], several key parameters have been identified through laboratory studies conducted by the authors and others and thorough reviews of the literature as presented elsewhere [2,3]. First, the mode and rate of corrosion is expected to depend on the presence of water on the container surfaces and how it is delivered. Dripping water will carry dissolved solids from interaction with the surrounding rock, condensed water (or water vapor at high relative humidity) will be relatively free of dissolved solids, and both will depend on the solids or scale on the container surface. Key characteristics of this water chemistry include pH and concentration of halides, particularly chloride for affecting localized corrosion and stress corrosion cracking of Alloy 22. The corrosion potential of a metal in an environment is also important as it, for example, can be compared to critical potentials for the onset of localized corrosion and stress corrosion cracking. Additionally, measuring the potential of a metal known to be inert in an environment (e.g., platinum) gives insight to the level of oxidants or reducing agents (redox potential).

The primary focus on chemistry monitoring has been aimed at measurement of the pH and chloride concentration using potentiometric methods (i.e., oxidized tungsten for pH and chloridized silver for chloride concentration). The main limitation that has been observed using these methods is the need for a stable reference electrode. Thus far, a SCE connected to the sensor array through the use of a long Luggin probe has performed reasonably well, but the long-term practicality of such an arrangement is questionable. Despite the reference electrode

limitation, W/WO₃ and Ag/AgCl electrodes have been incorporated into a sensor array cell designed to capture water percolating through crushed tuff and into a simulated drift that is actively heated. It is anticipated that these sensor electrodes will provide information as to the evolution of pH and chloride concentration on initial solution capture and wetting followed by dryout during heating.

Using the same sensor array cell the corrosion potentials of Alloy 22 and Type 316L SS are also being monitored in an attempt to detect the onset of localized corrosion. The primary limitation of using the corrosion potential to predict localized corrosion is that the critical potentials for localized corrosion (e.g., E_{pr} , E_p) are dependent on environmental factors, primarily chloride and temperature. As a result, the measurement of the corrosion potential is a complimentary measurement that needs to be placed in context with the material and the environmental conditions and cannot be used as a stand-alone localized corrosion determinator.

In addition to the potentiometric based approaches, the conductivity of the environment has been used to detect the presence of an aqueous phase and to serve as a rough indication of corrosivity since the conductivity increases with increasing ionic strength in the sensor array cell. It is recognized, however, that the relationship between increased conductivity and increased ionic strength is primarily applicable only in dilute solutions and that at higher ionic strengths, especially when approaching solubility or in the presence of precipitated salts or minerals (which may occur in the proposed repository), significant increases in conductivity are generally not observed. Furthermore, measurement of conductivity cannot easily be correlated with corrosion rate as conductivity cannot capture the effects of redox potential nor can it distinguish various anions (e.g., chloride) that are known to influence corrosion rates or corrosion modes.

Beyond the sensor array cell, a set of galvanic couple sensors has been developed in line with the concept put forth by Shinohara et al. [4]. These sensors consist of an interdigitated array of silver that is electrically isolated from the substrate. The substrates investigated thus far are carbon steel and Type 304L SS. Through the use of two substrates a relative corrosivity scale can be developed with the carbon steel/Ag system being more sensitive to a low overall corrosivity whereas, given the increased resistance of Type 304L SS to corrosion, the Type 304L SS/Ag system would respond only in more aggressive environments. The possibility that the Type 304L SS/Ag system may be used to detect the onset of localized corrosion is also being investigated. Figures 1 and 2 show the resistance and current response of a carbon steel/Ag sensor measured as a function of relative humidity and concentration of salt solution added as 2.5 mL on an area of approximately 14 cm². After deposition of the 2.5 mL of solution, the solution was allowed to dry out at a RH of 39%. Then the RH was increased to 99% and the sensor response monitored. Clearly, monitoring of the sensor resistance was sensitive to both changes in chloride concentration and %RH, especially at low %RH. At higher %RH, the resistance measured was independent of the chloride concentration. In contrast, the current measurement using a ZRA was highly sensitive to

both chloride and %RH at higher chloride concentrations. Though not strictly providing corrosion rate or mode information at this point, this sensor design clearly holds promise for detecting and determining the corrosivity of the environment.

To date, the sensor array cell and the galvanic couple sensors have performed adequately during bench testing. These systems, along with metal coupons and solution catch cups, have been incorporated into a laboratory scale test constructed of crushed tuff from YM to simulate a drift. The drift is being heated to an air temperature of ~ 105 °C to simulate the thermal load that would result from radioactive decay within the waste containers. Percolation of deionized water that has been equilibrated with the tuff for over 6 mo has been initiated and will eventually begin dripping onto the sensor arrays, galvanic couple sensors, coupons and solution catch cups. The results from the sensor systems will then be compared with the results obtained through traditional solution analysis of water aliquots (e.g., capillary electrophoresis, ion chromatography, inductively coupled plasma spectroscopy) and metal coupons.

Acknowledgments

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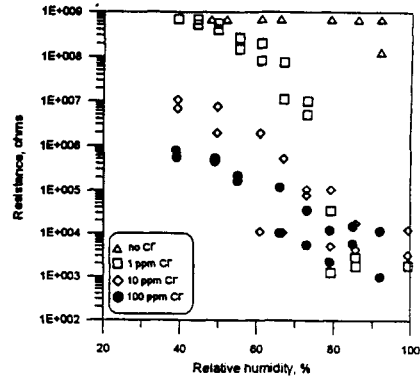


Figure 1: Measured resistance between carbon steel and interdigitated silver array as a function of %RH and chloride concentration.

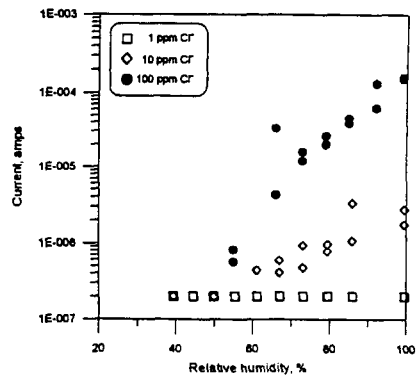


Figure 2: Measured current between carbon steel and interdigitated silver array as a function of %RH and chloride concentration.