

# **CNWRA** A center of excellence in earth sciences and engineering

A Division of Southwest Research Institute™  
6220 Culebra Road • San Antonio, Texas, U.S.A. 78228-5166  
(210) 522-5160 • Fax (210) 522-5155

October 2, 2000  
Contract No. NRC-02-97-009  
Account No. 20.01402.571

U.S. Nuclear Regulatory Commission  
ATTN: Mrs. Deborah A. DeMarco  
Two White Flint North  
11545 Rockville Pike  
Mail Stop T8 A23  
Washington, DC 20555

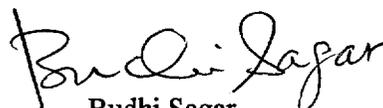
Subject: Programmatic review of an abstract

Dear Mrs. DeMarco:

Enclosed is an extended abstract entitled "*In-Situ* Monitoring of Chemistry and Corrosion Processes Under Heat Transfer and Episodic Wetting Conditions," to be presented at the Electrochemical Society symposium on Corrosion Sensors in March 25-30, 2001 in Washington, DC. The investigations conducted by the CNWRA have been focused on examining possible corrosion and chemistry monitoring methods that the DOE may utilize to confirm waste package performance and examining their performance in a simulated drift experiment (third lab-scale heater test). Furthermore, these tests may provide valuable information in terms of possible water chemistry changes from rock-water interactions at elevated temperatures and how these changes may alter the corrosion behavior of waste package materials. This abstract is being submitted for your programmatic review. Please advise me of the results of your programmatic review, so that we can submit the paper for publication in a timely manner.

If you have any questions regarding this paper, please feel free to contact Gustavo Cragnolino at (210) 522-5539 or Sean Brossia at (210) 522-5797.

Sincerely yours,



Budhi Sagar  
Technical Director

BS:NS:jg

Enclosure

cc:	J. Linehan	T. Bloomer	J. Holonich	CNWRA EMs	G. Cragnolino
	D. DeMarco	T. Ahn	B. Leslie	CNWRA Dirs.	P. Maldonado
	B. Meehan	K. Stablein	C. Greene	S. Brossia	T. Nagy (contracts)
	E. Whitt	J. Greeves	J. Andersen	D. Dunn	
	J. Centardi	J. Thomas	W. Patrick	O. Moghissi	



Washington Office • Twinbrook Metro Plaza #210  
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

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

C.S. Brossia, D.S. Dunn, and O.C. Moghissi  
Center for Nuclear Waste Regulatory Analyses  
Southwest Research Institute  
6220 Culebra Road  
San Antonio, TX 78228

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/WO<sub>3</sub> 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.,  $E_{pit}$ ,  $E_p$ ) 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 cm<sup>2</sup>. 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  $\sim 105^\circ\text{C}$  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

This work was supported by the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Materials Safety and Safeguards, Division of Waste Management (Contract No. NRC-02-97-009). The work is an independent product of the Center for Nuclear Waste Regulatory Analyses and does not necessarily reflect the views or the regulatory position of the NRC.

#### References

1. Civilian Radioactive Waste Management System, Management & Operating Contractor, *Performance Confirmation Plan*, TDR-PCS-SE-000001, rev 1, TRW Environmental Safety Systems, Inc, Las Vegas, NV (2000).
2. G. Cragolino, D. Dunn, C.S. Brossia, V. Jain, K. Chan, *Assessment of Performance Issues Related to Alternate Engineered Barrier System Materials and Design Options*, CNWRA 99-003, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX (1999).
3. C.S. Brossia, D.S. Dunn, O.C. Moghissi, and N. Sridhar, *Assessment of Methodologies to Confirm Container Performance Model Predictions*, CNWRA 2000-06, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX (2000).
4. T. Shinohara, S. Tsujikawa, S. Motoda, Y. Suzuki, W. Oshikawa, S. Itomura, T. Fukushima, and S. Izumo. Evaluation of corrosivity of marine atmosphere by ACM (Atmospheric Corrosion Monitor) type corrosion sensor, *International Symposium on Plant Aging and Life Predictions of Corrodible Structures*, Japan Society of Corrosion Engineering: Sapporo, Japan (1995).

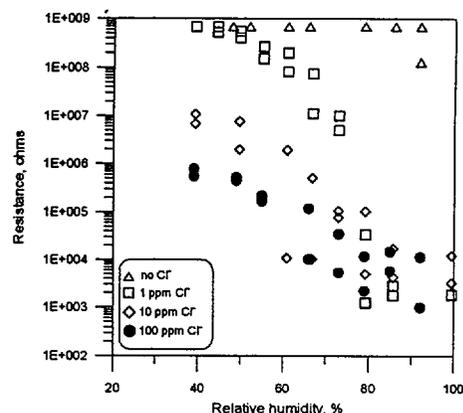


Figure 1: Measured resistance between carbon steel and interdigitated silver array as a function of %RH and chloride concentration.

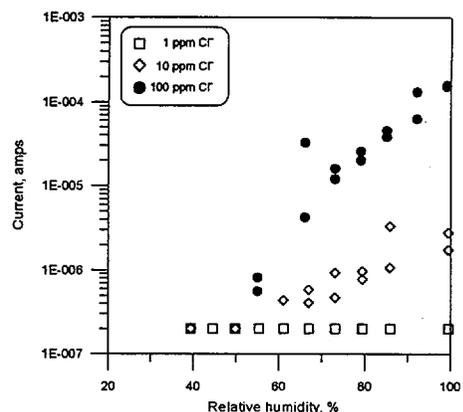


Figure 2: Measured current between carbon steel and interdigitated silver array as a function of %RH and chloride concentration.