

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 13, 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

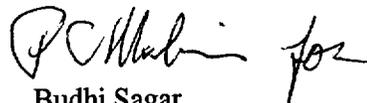
Subject: Programmatic review of an abstract

Dear Mrs. DeMarco:

Enclosed is an extended abstract entitled "Approaches to Confirm Waste Package Performance," to be presented at the IHLRWM Conference on April 29–May 2, 2001 in Las Vegas, NV. The abstract describes work in progress examining methods to confirm waste package performance that the DOE may use in its performance confirmation plan. This work will also enhance confidence in the models and assumptions used by the NRC/CNWRA in predicting waste package performance. 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. Contardi	J. Thomas	W. Patrick	O. Moghissi	



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

Approaches to Confirm Waste Package Performance

C.S. Brossia, D.S. Dunn, O.C. Moghissi
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute
San Antonio, Texas 78238

Introduction

The U.S. Department of Energy (DOE) is responsible for constructing, operating, and closing a geologic repository for disposal of high level nuclear waste (HLW). The current DOE plans call for the emplacement of this HLW in waste packages constructed of a Type 316 Nuclear Grade stainless steel (SS) inner container 5 cm thick, surrounded by a 2 cm thick outer container of Alloy 22 (57Ni-22Cr-13.5Mo-3W-3Fe), and placed in a horizontal drift (tunnel) at the proposed site in Yucca Mountain (YM), NV. The primary attributes in the selection of Alloy 22 as a container material are its low corrosion rate and high resistance to localized corrosion in many environments. However, the greatest uncertainty related to long-term material behavior is the nature of the environment to which the containers will be exposed. As a consequence, monitoring of the water chemistry on the outer container surface and assessing how this chemistry affects corrosion are important for detecting the onset of unanticipated conditions that may lead to rapid corrosion and container failure.¹

Based on previous work, as reported elsewhere,² several factors have been found to influence material performance, including chloride concentration, pH, redox potential, and through it, the corrosion potential of the metal in the environment. The chloride concentration is important as it has been shown to cause localized corrosion of Alloy 22 when sufficiently high.² In addition to the need for chloride to be present at a certain concentration to promote localized corrosion of Alloy 22, a critical potential

(represented by the repassivation potential as a lower bound) must also be attained to induce and sustain localized corrosion. Thus, if the repassivation potential and chloride concentration are known, the corrosion potential can be used as an indicator for the likelihood of localized corrosion (e.g., if the corrosion potential exceeds the repassivation potential, then localized corrosion is possible). The redox potential of the aqueous environment, which is a measure of its overall oxidizing or reducing nature, is known to influence the corrosion potential of the metal.

Work Description

Two primary approaches have been taken to develop methodologies for assessing the possibility or occurrence of corrosion: potentiometric methods, that rely on the measurement of a potential difference between a sensing electrode and a stable reference, and non-potentiometric methods. The potentiometric methods employed include monitoring pH and chloride concentration using an oxidized tungsten wire for pH and a chloridized silver wire for chloride. These wires, along with Alloy 22 and Type 316L stainless steel wires to measure corrosion potentials, have been incorporated into a sensor array cell designed to capture incoming water percolating through crushed tuff in a laboratory-scale drift heater test. A saturated calomel electrode connected to the array cell through a long salt bridge/Luggin probe has been used as a reference electrode.

The non-potentiometric methods employed include measurement of solution conductivity and the use of a galvanic couple to measure corrosivity. Solution conductivity has been determined through the use of two platinum wires incorporated into the sensor array cell. Conductivity measurements can provide some information regarding the overall corrosivity of the environment because increasing conductivity generally indicates a more corrosive environment.

A set of galvanic couple sensors has been developed based on the concept put forth by Shinohara et al.³ 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 stainless steel. Through the use of two substrates, a relative corrosivity scale can be developed. The carbon steel/Ag system is 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.

These systems have recently been incorporated into a laboratory-scale simulated drift heater test to examine the effects of thermal refluxing on material performance and environmental conditions. Results from this test are forthcoming. The results presented here are limited to the initial bench testing of the sensor systems described above.

Results and Discussion

Measurement of pH and chloride concentration using potentiometric methods was found to be accurate and predictable over a range of 2 to 10 for pH and from 10^{-3} to 1 M for chloride concentration. When water that was equilibrated with crushed tuff from YM for 5 months was dripped onto the sensor array cell, the chloride concentration was determined to be less than 10^{-3} M, even after repeated dryout and rewetting cycles. The solution pH was initially near 6 when the heater was turned on. After the heater was turned on and the solution began to evaporate, the pH was noted to increase to nearly 11, likely from exsolution of CO_2 as a result of the increased temperature.

The corrosion potential of a Type 316L stainless steel wire and an Alloy 22 wire exposed to

episodic wet and dry conditions at elevated temperature (using the tuff-equilibrated water) is shown in Figure 1. The decrease in corrosion potential observed during heating is thought to result from a combination of increased passive current densities of each material and the exsolution of oxygen. The increase in the corrosion potential up to the point of dryout is likely caused by an increase in oxygen diffusion kinetics. It is unclear why the corrosion potential of Alloy 22 is less than that of Type 316 SS, as the opposite is expected based on the lower passive current density for Alloy 22.² Though the sensor array cell was able to measure the corrosion potentials of Type 316L SS and Alloy 22, the implications of a particular value are difficult to discern without complementary knowledge (e.g., environmental conditions) and thus, such measurements cannot be used as a stand-alone method to predict the occurrence of localized corrosion.

The solution conductivity was also measured during the bench testing and can provide insight into the corrosivity of the environment. The conductivity was noted to increase markedly as the solution began to dryout, reaching a peak value at the point of dryout when electrical communication was lost between the two Pt wires. Conductivity, though useful for determining the presence of liquid water, cannot easily be converted to a corrosion rate. One of the primary reasons for this is that conductivity does not capture the effect of the redox potential that is known to strongly influence the corrosion rate by affecting the corrosion potential of the metal. Furthermore, conductivity cannot distinguish among anions and, consequently, cannot be used to determine the specific effect of the various anions on the corrosion mode.

The galvanic couple sensors were evaluated in a humidity chamber after deposition and dry out of a salt solution on the surface. Figures 2 and 3 show the resistance and current response of a carbon steel/Ag sensor measured as a function of relative humidity and concentration of a 2.5 mL salt solution added to 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 was monitored. Clearly, 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, current measurement made using a zero-resistance ammeter was highly sensitive to both chloride and %RH at higher chloride concentrations. Though not strictly providing information on corrosion mode or rate, this sensor design holds promise for detecting and determining the corrosivity of the environment.

Summary and Conclusions

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 using 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. Injection 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, metal 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 the corrosion on the metal coupons will be evaluated.

Acknowledgments

This work was supported by the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Material 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. 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).

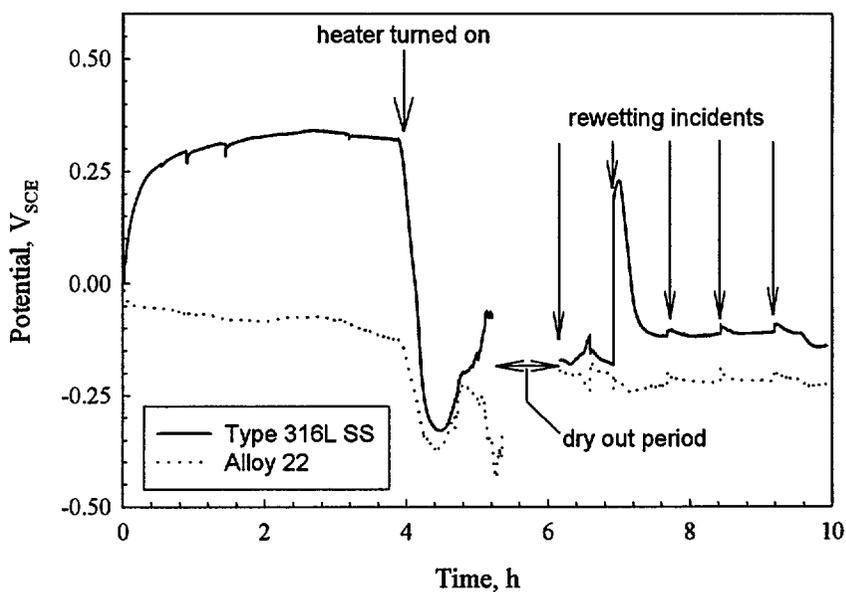


Figure 1: Open circuit potential of Type 316 stainless steel and Alloy 22 as a function of time under heated dripping conditions using deionized water that was equilibrated with crushed tuff for 5 months.

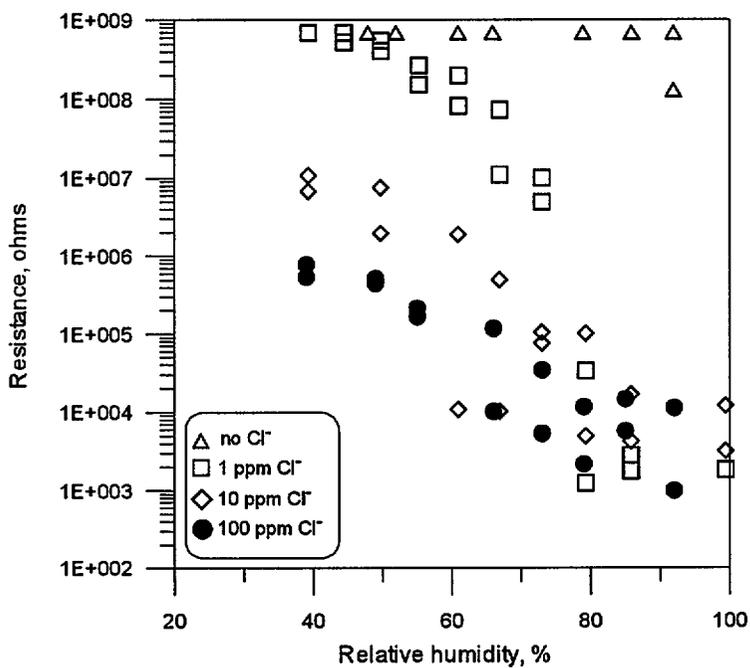


Figure 2: Measured resistance between carbon steel and interdigitated silver array as a function of %RH and chloride concentration.

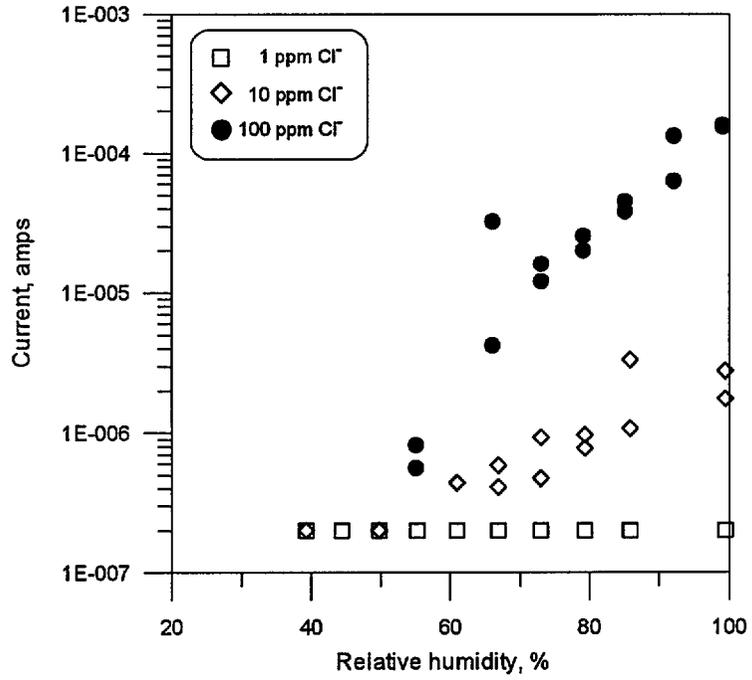


Figure 3: Measured current between carbon steel and interdigitated silver array as a function of %RH and chloride concentration.