CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: Symposium on the Scientific Basis for Nuclear Waste Management XXVI
Project No. 20.06002.01.081; AI 06002.01.071

DATE/PLACE: December 2–6, 2002
Boston, Massachusetts

AUTHORS: C. Manepally, Y. Pan, O. Pensado, and L. Yang

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PERSON(S) PRESENT:

The symposium was attended by scientists from various U.S. and international organizations, from laboratories and universities. In addition to the Center for Nuclear Waste Regulatory Analyses (CNWRA) staff, T. Ahn, A. Csontos, D. Esh, and N. Rivera-Feliciano [U.S. Nuclear Regulatory Commission (NRC)] were also present. The complete roster of participants is available in the abstracts volume.

BACKGROUND AND PURPOSE OF TRIP:

The 26th Scientific Basis for Nuclear Waste Management Symposium continued the long historical tie with the Materials Research Society's Fall Meeting and comprised four days of technical sessions on a variety of topics relevant to nuclear waste management in the world. The purpose of staff attending this symposium was to present papers in various sessions and to keep up to date with recent developments in various high-level waste programs in the United States and other countries.

SUMMARY OF PERTINENT POINTS:

The symposium was organized into 11 sessions, including a total of 97 oral and 38 poster presentations. The session topics were (i) performance assessment and regulatory studies; (ii) archaeology and waste management; (iii) poster session; (iv) engineering barriers I—waste package materials; (v) glass waste forms; (vi) ceramic waste forms and radiation effects; (vii) chemistry I—speciation, colloidal and organics; (viii) engineering barriers II—backfill; (ix) spent fuel; (x) engineering barriers III—cement; and (xi) chemistry II—sorption, migration and processing. The summary provided in this report includes CNWRA staff presentations; the U.S. Department of Energy (DOE) and the State of Nevada work in the areas of solution chemistry, corrosion, and glass waste form; and other presentations on performance assessment.

CNWRA staff made four presentations, which are summarized below.

C. Manepally presented the paper Assessment of Near-Field Thermohydrologic Processes in an Independent Performance Assessment of the Proposed High-Level Waste Repository at Yucca Mountain, coauthored by the NRC and CNWRA staff. This paper provided a snapshot of the effort that is underway to determine if significant areas identified by the detailed process-level thermohydrological model have been captured in the abstracted model implemented in Total-system Performance Assessment by implementing a systematic performance assessment

framework. This ongoing analysis has identified several areas where modifications could improve both the detailed process model and the abstracted model. Implications of the differences between the detailed and abstracted models were discussed. The detailed model could be improved to incorporate drift details for a more accurate estimation of the temperature and relative humidity at the waste package. The abstracted model could be improved to better incorporate the edge effect temperatures in the system-level calculations, and improved estimates of effective bulk thermal conductivity that account for spatial and temporal variability using either conservative or time-dependent values. The iterative process in which system model development and detailed process-modeling activities are juxtaposed is an effective and necessary step toward risk-informing the independent assessment effort and building confidence in the NRC modeling approach.

O. Pensado presented the paper Long-Term Extrapolation of Passive Behavior of Alloy 22. In this paper, common assumptions used to predict the lifetime of proposed high-level waste disposal containers made of nickel-chromium-molybdenum alloys were evaluated. The assumptions were analyzed using a mechanistic model for the passive dissolution of nickel-chromium-molybdenum alloys. The decrease in the anodic current density, under potentiostatic condition, noted in two-week experiments was attributed to the accumulation of vacancies at the metal-oxide interface, produced by the passive dissolution of the alloy. Vacancy accumulation could potentially render the passive film unstable. However, model computations suggest enrichment of chromium with respect to molybdenum at the metal surface facilitating the reformation of a protective chromium oxide film, in case of film spalling. The model indicates that the alloy dissolution process is stoichiometric and regulated by vacancy-enhanced diffusion of the elements in the alloy. A possible film instability is not envisioned to be a significant contributor to the uncertainty in the lifetime of waste packages computed by performance assessments that include conservative assumptions. One conservative assumption of current performance assessments is ignoring the effect of the temperature on the corrosion rate. Experimental data were shown indicating an Arrhenius dependence of the potentiostatic passive current density in a temperature range from 25 to 95 °C.

Y. Pan presented the paper Corrosion and Stress Corrosion Cracking of Alloy 22 in Lead-Containing Solutions. In this paper, limited analysis was conducted to evaluate lead solution chemistry and its effect on the anodic polarization behavior and stress corrosion cracking of Alloy 22. Speciation calculations revealed the formation of Pb^{2+} cations and lead-chloride complexes in $PbCl_2$ solutions. The presence of lead species in a deaerated, super-saturated $PbCl_2$ solution (16,300 ppm lead) with a pH of 0.5 promotes the occurrence of a pronounced anodic peak, increases the passive current density, and simultaneously enhances the dissolution of Alloy 22. This enhanced dissolution in a crevice specimen was characterized by the presence of randomly distributed etch pits. No localized corrosion was observed in crevice specimens tested in solutions with lead concentrations ranging from 1,500 to 5,400 ppm. In addition, no stress corrosion cracking was observed at an applied potential of -100 mV_{SCE} when both single and double U-bend specimens were tested in super-saturated $PbCl_2$ solutions at 95 °C. The results indicate that Alloy 22 is not susceptible to localized corrosion and stress corrosion cracking in the presence of lead in the Yucca Mountain groundwater.

L. Yang presented the paper Corrosion Behavior of Carbon Steel and Stainless Steel Materials Under Salt Deposits in Simulated Dry Repository Environments. In this paper, *in-situ* coupled multielectrode array sensors were used to measure the non-uniform corrosion of carbon steel (Type 1010) and stainless steel (Type 316) materials under KCl salt deposit in simulated dry repository environments. The results show that the initiation of non-uniform corrosion of carbon steel and stainless steel occurs at a relative humidity that is 14 percent lower than the

deliquescence relative humidity of the chloride salt. This phenomenon was attributed to the adsorption of water by the hygroscopic salt below the deliquescence point. Measurements also show that once significant corrosion had occurred under KCl and NaCl salt deposits, the non-uniform corrosion process for the carbon steel material continued at relative humidities as low as 27 percent. This phenomenon was attributed to the formation of corrosion products during the corrosion processes because the deliquescence point of the mixture of the corrosion products and the original salts is much lower than those of the original salts. Based on experimental results, it was concluded that DOE should use a relative humidity value which is lower than the deliquescence point of the salts or salt mixtures that are likely to be formed on the surfaces of the drip shield or the waste package as the critical relative humidity in its modeling of aqueous corrosion, rather than the deliquescence point.

A number of presentations from DOE were focused on corrosion of waste package materials and dissolution of glass waste form. In the area of waste package degradation, R. Rebak (LLNL) presented the paper Review of Corrosion Modes for Alloy 22 Regarding Lifetime Expectancy of Nuclear Waste Containers. The paper was a summary of current DOE tests indicating that Alloy 22 is a highly corrosion resistant alloy. The main degradation modes for Alloy 22 and tests to quantify degradation rates were briefly outlined. The results presented are consistent with information currently available in the DOE Yucca Mountain literature arguing that Alloy 22 containers would be resistant to general corrosion, localized corrosion and environmentally assisted cracking.

R. Rebak also presented the work of D. Fix, et al. titled Characterization of the Corrosion Behavior of Alloy 22 after Five Years Immersion in Multi-Ionic Solutions. The paper briefly described corrosion rates measured after five-year exposure of Alloy 22 coupons to electrolyte solutions, simulating concentrated groundwater from pH 3 to 10 at 60 and 90 °C. The five-year data displays similar trends to two-year data published previously by the DOE. Data showed no evident correlation between the environment (electrolyte composition, pH, and temperature) and the corrosion rate. Crevice samples yield in general higher corrosion rates than non-crevice samples, although visual inspection does not reveal any localized corrosion. Rebak presented micrographs of the before and after washing state of a representative sample showing no evidence of localized corrosion. The measured corrosion rates are of the order of 10 nm/yr, which are more than one order of magnitude lower than those measured in short-term experiments at the CNWRA using electrochemical methods.

In his third talk, R. Rebak presented the work of T. Lian, et al. titled Changes in the Corrosion Behavior of Alloy 22 Influenced by Its Ennoblement in Aqueous Solutions. The paper stated possible changes to the oxide film resulting from positive shifts in the corrosion potential as time elapses. Changes to the film were indirectly studied using linear polarization resistance and impedance measurements. The paper concluded that ennoblement causes thicker and more protective oxide films. This conclusion was derived from polarization resistances, and equivalent circuit capacitances and resistivities from before and after potentiostatic experiments. It must be noted that no confidence intervals were reported for resistivities and capacitances (equivalent circuits are known not to have unique best fits). Also, constant phase elements were used in the equivalent circuits, as opposed to constant capacitances, obscuring the interpretation of changes in the capacitance due to changes in the oxide thickness. Although mentioned in the abstract, no analytical data of the composition of the oxide film were provided.

C. Orme (LLNL) presented the paper Characteristics of The Passive Films on Alloy 22. Orme showed limited analytical data for the passive film, that is consistent with previously reported

composition of the film in the DOE Yucca Mountain literature: the oxide film is a bilayer, with the internal layer Cr-rich and the external layer Ni- and Mo-rich. Orme also displayed surface microscope pictures of the oxide film which evolves from a surface of limited roughness when polarized in the passive regime, to a highly porous, spongy-like structure with intermingled filaments, when polarized in the transpassive regime. The porous film is not strongly adhered to the substrate and can be washed away easily. Most of the study by Orme was aimed at the porous oxide film. Limited information on the passive film was discussed.

P. Hailey (LLNL) presented the paper Thermogravimetric Thin Aqueous Film Corrosion Studies of Alloy 22. In this paper, the extent of reaction of Alloy 22 with limited amounts of aqueous calcium chloride was investigated. An aqueous film was formed by deliquescence of deposited $CaCl_2$ at 150 °C and 22.5 percent relative humidity. The reactant gas was a continuous flow of purified and humidified laboratory air. The reaction progress as a function of time was continuously measured *in-situ* by a micro-balance. An initial weight gain due to deliquescence of $CaCl_2$ was observed. A steady weight loss was observed over the next 72 hours, after which no further weight change was observed. During this weight loss, white precipitates formed and the specimens surface became visibly dry. The precipitate crystals were identified as $Ca(OH)_2$ by post-test Raman spectroscopy; however, energy dispersive X-ray spectroscopy indicated that there was a significant amount of chlorine contained in them. The authors proposed the following mechanism for this aqueous film corrosion. The $CaCl_2$ salt deposits initially deliquesces to form an aqueous solution. At the cathodic sites, calcium hydroxide precipitated with a significant amount of chlorine incorporated into the precipitated species. At the anodic site there was a loss of chloride in its acidic gas form, HCl. Water was lost from the surface as the aqueous calcium chloride was transformed into the insoluble chloride-containing calcium hydroxide.

P. Turchi (LLNL) presented the paper Stability and Ageing of Candidate Alloys for the Yucca Mountain Project: Calphad Results. Turchi applied the computational thermodynamics approach to study the phase stability and ageing of several candidate nickel-based alloys for use in waste disposal canisters. Validation of the thermodynamic database showed good agreement between the assessed and calculated results for binary nickel-chromium, nickel-molybdenum and chromium-molybdenum systems and a ternary nickel-chromium-molybdenum system. Calculation of phase fraction versus temperature for the nominal composition of Alloy 22 predicted formation of ordered phases, topologically close-packed phases, and carbide phases at different temperature ranges. Due to time limitation, ageing of Ni-based alloys as a result of phase stability was not discussed. In addition, the concern of different precipitation kinetics for carbides and topologically close-packed phases was not addressed.

In the area of waste form degradation, W. Ebert (ANL) presented the paper Accounting for Corrosion of High-Level Waste Glasses by Humid Air in TSPA. Vapor hydration tests were conducted to measure the degradation rates of several monolithic high-level waste glasses (SRL 131, 51S and 165) at various temperatures (70 to 200 °C) and relative humidities. The extent of corrosion was determined from the thickness of an altered layer that formed at the glass surface. These test results were used to verify that the Total System Performance Assessment model based on the results of tests in water is representative of glass degradation in a humid air environment. Ebert concluded that the vapor hydration test results provide a lower bound for the range of dissolution rates of high-level waste glass used in calculations supporting Total System Performance Assessment for License Application.

Ebert also presented the paper Accounting for Metallic Waste Form Degradation in TSPA. The metallic waste form will be used to immobilize cladding hulls recovered after electrometallurgical

treatment of spent sodium-bonded nuclear fuel. The objective of this study is to determine if the model used for the dissolution rate of high-level waste glasses for Total System Performance Assessment calculations can also be used to represent the dissolution rate of the metallic waste form. Static MCC-1 tests with monolithic samples were conducted at various temperatures (50, 70 and 90 °C) in buffered solutions at pH ranging from 4 to 12 for a test duration up to 70 days. The results indicate that the rate of radionuclide release from the metallic waste form can be adequately represented using the glass model.

In the third talk, Ebert presented the paper Effects of Iron and pH on Glass Dissolution Rate. The short-term MCC-1 test method was employed to evaluate the effects of pH and dissolved iron on the glass dissolution rate using monolithic high-level waste glass samples (SRL 202G). A series of tests was conducted at 90 °C in controlled pH solutions without iron and with added $FeCl_3$, Fe_2O_3, Fe_3O_4, and FeOOH. The results showed a V-shaped boron dissolution rate versus pH curve with minima at near-neutral pH. The pH dependence coefficients were determined to be 0.44 in basic solutions and -0.49 in acidic solutions, which are within the range of values used in the DOE glass degradation model. It is important to note that at a pH of about 1.0 the measured boron dissolution rate in $FeCl_3$ solution increased by a factor of approximately 2 in comparison with that without $FeCl_3$. The enhanced glass dissolution reported in this paper is consistent with the CNWRA results obtained in unbuffered $FeCl_3$ solutions.

Three presentations by Pulvirenti from Catholic University of America under the sponsorship of the State of Nevada were focused on groundwater chemistry and its effects on corrosion of Alloy 22 and Titanium Grade 7. Pulvirenti presented the first paper Effect of Differential Volatilization and Local Geometry on Groundwater Chemistry. The results from the experiments using simulated 62 times pore water have shown that the pH of the condensate at the late stages of evaporation/condensation was as low as -0.54. It was postulated that the preferential volatilization of HCl, followed by movement and condensation of vapors could result in local acidic environment some distance away from the initial volatilization site. Boiling experiments performed on simulated concentrated ground water compositions showed that both in the presence and absence of crushed tuff, significant concentrations (50 ppm) of fluoride were still present upon extensive thermal concentration (12,000 concentration factor). It was also reported that the experiment on the evaporation of simulated J-13 water to a final concentration factor of 12,000 resulted in a final fluoride concentration of 200 ppm. However, the questions raised by the audience concerning infiltration rate and mass balance under Yucca Mountain environmental conditions were not addressed.

In the second paper Effect of Fluoride and Other Anions on the Corrosion of Alloy 22, the corrosion rate of Alloy 22 was reported to be higher by a factor of 10 to 30 with the addition of 5000 ppm fluoride in a solution containing 0.1 M HCl or 0.1 M HNO_3. In the third paper entitled Synergistic Effects of Fluoride and Chloride on Corrosion of Titanium-7, Pulvirenti reported that the presence of chloride significantly enhanced the corrosive effect of fluoride on Titanium-7. The enhancement by the presence of chloride was more than an equal additional amount of fluoride. It was also reported that the local corrosion of Titanium-7 appeared to be slightly mitigated by the presence of large amounts of an inhibiting anion such as sulphate.

Vomvoris from Switzerland presented a talk on Grimsel Test Site—The Next Decades. This presentation provided an update of the Grimsel Test Site (GTS), operated by NAGRA. Grimsel is not considered for waste disposal, rather it is dedicated to applied research related to waste disposal issues. Experiments have focused both on the geosphere/rock characterization aspects, and on the engineered barriers. The controlled zone included in the GTS allows the unique ability

to perform *in-situ* experiments with a wide range of radionuclides, including isotopes of uranium, neptunium, americium and plutonium. International projects at GTS involve currently more than 18 partner organizations from 9 countries. The presentation highlighted the running projects and the current status of the development of Grimsel Phase VI. Further information can be obtained from their website—http://www.grimsel.com.

Esh from NRC discussed the paper Risks and Uncertainties Associated with High-Level Waste Tank Closure. In the process of tank closure, NRC is typically consulted to perform an independent review of DOE performance assessments. A generic performance assessment model applicable to high-level waste tank closure was developed. The generic simulation software GoldSim was utilized to develop the model because of its probabilistic capabilities and its adaptability to different problems. The performance assessment model is utilized to assess the risks of various source terms and also to evaluate the reasonableness of performance assessment models submitted by DOE. Performance assessment calculations are performed to evaluate the potential impact of key uncertainties. Pertinent examples of key uncertainties for DOE high-level waste tank closure at various sites were discussed in the presentation. GoldSim is also being used in the performance assessment analyses for the Yucca Mountain Project.

IMPRESSIONS/CONCLUSIONS

The multidisciplinary approach of the Scientific Basis for Nuclear Waste Management Symposium provided the opportunity to keep current with a variety of topics relevant to the NRC high-level waste program. The symposium was well attended by U.S. and international scientists. A growing trend is noted in the international participation. A significant number of papers were presented this year in the area of performance assessment and regulatory studies, suggesting an increasing trend in the use of risk insight concepts to guide decision making.

PROBLEMS ENCOUNTERED: None.

PENDING ACTIONS:

It is important to evaluate the groundwater chemistry results presented by Catholic University of America. CNWRA staff is conducting groundwater evaporation modeling to determine whether such low pH values are possible. Tests attempting to reproduce these experimental results are being planned.

RECOMMENDATIONS:

Attendance at future Scientific Basis for Nuclear Waste Management Symposia is recommended to keep up to date with worldwide trends in waste management. The meeting is an efficient forum to learn technical information in a collegial manner, besides allowing gathering of feedback among peers in the technical work performed at the NRC and CNWRA.

AUTHORS:

Chandrika Manepally, Engineer — **Date:** 12/18/02

Yi-Ming Pan, Sr. Research Engineer — **Date:** 12/17/2002

Osvaldo Pensado, Sr. Research Scientist — **Date:** 12/17/2002

Leitai Yang, Sr. Research Engineer — **Date:** 12/17/2002

CONCURRENCE:

Vijan Jain, Manager
Corrosion Science and Process Engineering Element — **Date:** 12/18/02

Budhi Sagar, Technical Director — **Date:** 12/18/2002