CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: Materials Research Society Symposium
Scientific Basis for Nuclear Waste Management XXVIII
Project Number 20.06002.01.081; AI Number 06002.01.081.323

DATE/PLACE: April 13–16, 2004
San Francisco, California

AUTHORS: D. Pickett, L. Browning, G.A. Cragnolino, D.S. Dunn, Y.M. Pan, and L. Yang

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PERSONS PRESENT: L. Browning, G.A. Cragnolino, D.S. Dunn, Y.M. Pan, D. Pickett, and L. Yang (CNWRA), T.M. Ahn (NRC)

BACKGROUND AND PURPOSE OF TRIP:

The Scientific Basis For Nuclear Waste Management XXVIII Symposium, held as part of the Materials Research Society (MRS) Spring Meeting, was an international symposium that included presentations, posters and panel discussions on the storage and disposal of nuclear waste. The main goals of attending the symposium were to:

- Present papers authored by the CNWRA staff
- Review the presentations from the DOE HLW program and work.

MEETING SUMMARY

Approximately 120 oral and poster presentations were made at the symposium. Travel restrictions at the NRC and DOE reduced the level of participation of both organizations relative to previous years. Despite this, the Scientific Basis for Nuclear Waste Management Symposium received the largest number of papers submitted of any MRS symposium from the 2004 Spring Meeting. The greatest attendance levels occurred during the Tuesday morning session on Container Studies, and Wednesday morning session on Performance Assessment Approaches. In addition to technical presentations made by several CNWRA and NRC staff, CNWRA staff also served as session chairs (D. Dunn and L. Browning), invited speaker (G. Cragnolino), Performance Assessment panel discussion participant (D. Pickett) and moderator (L. Browning), and Symposium co-Chair (L. Browning). Browning and Cragnolino participated in the meeting of the Steering Committee, composed of the previous Symposia chairs, to plan future Symposia. The next meeting will take place on September 14–16, 2005 in Ghent, Belgium and the following one during the 2006 MRS Fall Meeting in Boston, Massachusetts. D. Dunn was selected as a co-chair for the 2006 Symposium.

Papers co-authored by the NRC and CNWRA staff and presented at the symposium are listed below:

"Developments in High-Level Radioactive Waste Disposal Container Materials Through 25 Years of MRS Symposia" (Invited Paper), G.A. Cragnolino.

"Long-Term Effects in the Initiation of Non-Passive Corrosion of Corrosion-Resistant Passive Waste Packages under the Geological Repository Conditions", T.M. Ahn, T. Shinohara and S. Fujimoto.

"The Conductivity Behavior of Potential Salt Deposits on the Surface of Engineered Barrier Materials for the Potential High-Level Nuclear Waste Repository at Yucca Mountain", L. Yang, M. Juckett, R.T. Pabalan.

"The Effect of Fabrication Processes on the Governing Mechanical Failure Criteria for Alloy 22 and Ti-Grade 7 and 24 Alloys", A.A. Csontos, D.S. Dunn, Y.M. Pan, and G.A. Cragnolino.

"Effect of Inhibiting Oxyanions on the Localized Corrosion Susceptibility of Waste Package Container Materials", D.S. Dunn, L. Yang, C. Wu, and G.A. Cragnolino.

"The Effect of Environmental Chemistry on the Pb Assisted Stress Corrosion Cracking (PbSCC) Susceptibility of MA and GTAW Welded Alloy 22", A.A. Csontos, Y.M. Pan, L. Yang, D. S. Dunn, and G.A. Cragnolino.

"Dissolution Kinetics of Spent Nuclear Fuels (SNF) in the Proposed Yucca Mountain (YM) Repository Environment", T.M. Ahn and S. Mohanty.

"Preferential Radionuclide Release Due to Alpha Decay: Effects on Repository Performance," D.A. Pickett and W.M. Murphy.

"Electrochemical Evaluation and Surface Characterization of Josephinite as a Natural Analog for Container Materials"' Y.M. Pan and G.A. Cragnolino.

"Estimated Effects of Temperature-Relative Humidity Variations on the Composition of In-Drift Water in the Proposed Nuclear Waste Repository at Yucca Mountain, NV," L. Browning, L. Yang, R. Pabalan, C. Manepally and R. Fedors.

"The Dissolution of Uranophane in $CaCl_2$-SiO_2(aq) Test Solutions," J.D. Prikryl and W.M. Murphy.

Summaries of other notable presentations of particular interest for the NRC program follow.

<u>Container Studies</u>

D. Shoesmith (University of Western Ontario) presented a paper titled "A Probabilistic Model for Degradation of the Engineered Barriers System in the Yucca Mountain Repository (NV, USA)." In his presentation, a probabilistic model was developed for the key processes that would affect corrosion degradation of the Ti-7 drip shield and Alloy 22 waste package materials under potential Yucca Mountain repository conditions. For Ti-7, the key processes included in the model were general passive corrosion and hydrogen-induced cracking caused by hydrogen adsorption during passive corrosion. For Alloy 22, the key processes included in the model were general passive corrosion, crevice corrosion under salt deposits, and stress corrosion cracking in lid closure welds. The Monte Carlo method was employed to predict the lifetimes of the drip shield and the waste package. Sensitivity analyses showed the influence of key parameters and model components such as critical hydrogen adsorption by Ti-7, the form of the

crevice growth law for Alloy 22, the deliquescence of salts formed by evaporation of ground waters, and variations in the susceptibility of Alloy 22 to crevice corrosion.

Shoesmith also presented a paper titled "The Influence of Passive Film Properties on the microbial inducted corrosion (MIC) of Engineered Barriers in the Yucca Mountain Repository." In this presentation, the evolution of environmental conditions was divided into three phases: high-temperature dry phase, medium- temperature wet phase, and low-temperature wet phase. In the high-temperature dry phase, the relative humidity in the drift will be low and no aqueous electrolyte will be present to cause corrosion. In the medium-temperature wet phase, the relative humidity will be above the deliquescence relative humidity of certain salts that may be present on the surfaces of drip shields and waste packages, leading to formation of an aqueous electrolyte, and the temperature will be above the critical temperature (T_c) for localized corrosion of Alloy 22. In the low-temperature wet phase, the temperature will be below T_c and localized corrosion will be unlikely despite the presence of aqueous electrolyte. It was suggested that T_c is about 85 °C [185 °F] and microbial activity is only possible at T< 60 °C [140 °F]. Based on the results obtained using electrochemical and surface techniques (x-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectroscopy, scanning electron microscopy), it was concluded that the passive film on Ti-7 and Alloy 22 materials at T< 60 °C [140 °F] would be resistant to MIC at T< 60 °C [140 °F].

J. Smith (University of Western Ontario) presented a paper, titled "Corrosion of Copper Nuclear Waste Containers in Aqueous Sulphide Solutions," that discussed corrosion mechanisms for copper under the reducing conditions of the proposed Canadian repository.

H. Andersson (Swedish Institute for Metals Research) presented a paper titled "Creep Testing of Thick-wall Copper Electron Beam Welds and Friction Stir Welds," and T. Kallgren (Royal Institute of Technology-Sweden) presented a paper titled "Finite Element Modelling of the FSW Process for Safe Storage of Nuclear Fuel Waste." These two presentations were on the characteristics of the copper containers to be used by the Swedish nuclear waste disposal program.

Three papers scheduled for presentation in this session by authors from Lawrence Livermore National Laboratory were canceled.

<u>Spent Fuel and UO_2 Studies</u>

L. Werme (SKB-Sweden) gave a review presentation on "Spent Fuel Studies, Past and Current Emphasis," discussing experiments on the stability of spent fuel in water, both in the U.S. and the Europe, over the past two decades. Almost all experiments were performed under oxidizing conditions, primarily due to experimental and analytical difficulties, even though most spent fuel disposal programs assumed reducing repository conditions. With better tools, it is now possible to study (i) fuel behavior in oxygen-free environments, (ii) the specific effects of α-radiolysis on fuel stability, and (iii) the actual fuel matrix conversion rate at the UO_2 solubility level. Werme concluded with a discussion of current issues including spent fuel matrix dissolution under reducing conditions, radiolysis effects, hydrogen build-up, and helium diffusion. He emphasized the need for experiments conducted at lower water-to-fuel ratios.

C. Poinssot (CEA-France) presented a paper titled "Radionuclide Release Model for Spent Nuclear Fuel in Geological Disposal for Performance Assessment." The spent fuel source term

was described as a combination of instantaneous release and matrix dissolution. The "instantaneous" release fraction, which includes radionuclides from gaps, grain boundaries, and the rim zone, also includes a time-dependent model of preferential release of fission products due to alpha-related displacement. Fuel matrix alteration is governed by dissolution by radiolytic oxidants.

B. Hanson (Pacific Northwest National Laboratory) presented a paper, coauthored by R. Stout (Lawrence Livermore National Laboratory) and titled "Reexamining the Dissolution of Spent Fuel: A Comparison of Different Methods for Calculating Rates," that focused on effective surface area. Spent fuel dissolution rates have typically been reported in terms of a fractional rate normalized to the surface area of the specimen. Experiments typically show decreasing release rates with time, despite apparently increasing surface area. Recent evidence has shown that neither the geometric surface area nor that measured with BET methods accurately predicts the effective surface area of spent fuel. It appears that while the BET method overestimates surface area measurements, changes in fuel chemistry may result in a reduction in active sites for dissolution. Both surface-area-normalized and cumulative release plots should be considered when evaluating parametric dependence.

Two later talks—"On the Effective Surface Area of Corroding Spent Fuel" by J. Fortner (Argonne National Laboratory) and "The Effective Surface Area of Bare Spent Fuel for Dissolution: The Effect of Less-Soluble Fission Products and Actinides" by B. Hanson—furthered explored the notion that effective surface area does not increase during spent fuel corrosion. Hanson also presented flow-through spent fuel corrosion test results that (i) suggest that plutonium in solid-solution with uranium may slow uranium dissolution and (ii) confirm that release rates for plutonium and epsilon-phase metals are lower than congruent.

Fortner also presented "Technetium and Molybdenum in Oxide Spent Nuclear Fuel: Impact on Release Estimates," in which he stressed the importance of characterizing the distribution of technetium in commercial spent nuclear fuel in order to under its release behavior. Technetium is present in multiple oxidation states in both metallic and fuel oxide phases, and in diverse grain locations.

Performance Assessment Approaches

P. Swift (Sandia National Laboratories) opened this session with a summary of the DOE performance assessment model titled "The Role of Uncertainty in Performance Assessment for Radioactive Waste Repositories." The talk focused on how uncertainty is treated and analyzed in the DOE model.

R. Ewing (University of Michigan) followed with "Performance Assessments of Geologic Repositories for High-Level Nuclear Waste: Are They Necessary or Sufficient?," a critique of the use of performance assessments for demonstrating repository safety. Ewing likened a performance assessment repository simulation to a mechanical duck—which never becomes a real duck, no matter the complexity with which it is designed. He also feels that performance assessment is incapable of capturing uncertainty and is "inherently contestable." Alternative regulatory strategies mentioned were: more explicit reliance on passive barriers (especially in the near field), separate barrier performance standards, and natural analogs. He feels that the 10 CFR 63 multiple barriers requirement is too vague.

In "The Impact of Uncertainties in Geochemical Modeling on Performance Assessments," C. Palenik (University of Michigan) used the Oklo natural analog to demonstrate how geochemical uncertainties may dramatically affect predictions of spent fuel behavior.

W. Murphy (California State University, Chico; CNWRA consultant) gave a talk titled "Measures of Geologic Isolation" that focused on how natural systems data may be used to characterize the ability of a geologic system to isolate nuclear waste. The talk touched on natural analogs, but also addressed how repository site data may be used, not only to support performance assessment, but also to provide quantitative measures (e.g., isotope systematics) of likely system performance.

J. Kessler (Electric Power Research Institute) completed the session with a description of his organization's performance assessment model for Yucca Mountain, titled "Risk-Based Evaluation of Long-term Safety for a Yucca Mountain Repository Using the IMARC TSPA Code."

Presenters in the Performance Assessment Approaches session also participated in a panel discussion moderated by L. Browning. The discussion focused on topics related to the role of model uncertainty and model validation in performance assessment models. Performance assessment approaches applied to Yucca Mountain were used as examples, but the discussion included other examples. Specific discussion points included the feasibility, importance, and criteria of successful model validation and the potential role of uncertainty analyses in performance assessment during the performance confirmation period. The audience actively participated in the discussion. Positive comments about the discussion topics were received from audience members and panel participants with notably different points of view.

Ceramic Waste Form Studies

J. Hanchar (George Washington University, Washington, DC), in a talk titled "Investigation of ^{239}Pu Incorporation in Single Zircon Crystal," showed that synthetic zircon is capable of incorporating over 10 weight percent plutonium as a waste form. Other talks in this session discussed the ability of ceramic waste forms such as monazites, pyrochlores, and perovskite to contain actinides, cesium, and strontium. B. Metcalfe (Atomic Weapons Establishment, Reading, UK) described a particularly promising calcium phosphate-based ceramic that performed well in self-irradiation ageing studies. K. Helean (University of California, Davis) used thermodynamic principles to predict radiation damage susceptibility of pyrochlore.

Glass Waste Form Studies

This session was opened by an invited presentation from P. van Iseghem (SCK CEN Mol, Belgium) titled "GLAMOR: A Critical Evaluation of the Dissolution Mechanisms of High-Level Waste Glasses in Conditions of Relevance for Geological Disposal." The European GLAMOR project was conceived to achieve a common interpretation of the decrease in long-term dissolution rate of nuclear waste glasses observed in most experimental programs. A group of experts was brought together to select long-term dissolution experiments carried out by various laboratories. Selected analytical models will be applied to this data set by the participating laboratories. Through this effort the relative importance of the processes that control the long-term dissolution rate, such as saturation effects and the diffusion limitation due to surface

layer alteration, and the consequences of the modeling options on source term evaluation, may be elucidated.

W. Ebert (Argonne National Laboratory) presented the paper "Applicability of the TSPA Glass Degradation Model to Nonstandard Waste Forms." The source term for the release of radionuclides from high-level waste glasses in DOE's TSPA is based on a degradation model developed for borosilicate waste glasses. A methodology for determining if the TSPA glass degradation model can be used to represent the release of radionuclides from non-conformed waste forms was presented. Evaluation of two alternative waste forms—ceramic and metallic—was discussed. Since the dissolution rates measured with the alternative waste forms are lower than those calculated with the model, the glass dissolution model is assumed to bound the performance of the waste forms in TSPA calculations.

S. Gin (CEA-France) discussed the long-term behavior of R7T7-type nuclear waste glass during a dry, thermal phase (0-300 years) and a geological disposal phase in contact with water (up to 10,000 years). The two main factors likely to modify glass performance during the dry period (i.e., devitrification and self-irradiation) showed no effect on the long-term behavior of R7T7 glass. For aqueous alteration of R7T7 glass after disposal, four alteration mechanisms documented include interdiffusion, hydrolysis of network formers, condensation of hydrolyzed silica at the reaction interface, and precipitation of secondary phases. Gel formation on the glass surface was found to be responsible for the rate drop from a high, initial rate to a low, residual rate and radionuclide retention in the alteration layers. An activation energy of 53 kJ/mole [13 kcal/mol] was determined for the residual rate of R7T7 glass over the temperatures ranging from 50 to 180°C [122 to 356 °F]. Corrosion products in contact with glass, however, maintain the initial rate by consuming Si and delaying the formation of alteration layers. CEA has developed an operational model to obtain robust and reasonably conservative predictions of the quantity of altered glass after disposal.

Waste/Tank/Site Cleanup and Decommissioning

G. Koroll (AECL, Canada) began this session with a programmatic look at the complex and lengthy process of decommissioning a nuclear site (Whiteshell, Manitoba).

I. Baikie (UK Atomic Energy Authority) gave two presentations on marine contamination associated with the Dounreay, Scotland, facility. Spent fuel particles dispersed during the past 40 years in the foreshore and offshore environment are being collected and characterized. Analyses to date suggest that surface alteration of these metallic uranium alloys in seawater is preventing further disintegration and radionuclide release.

In the talk "Evolution of Technetium Speciation in Reducing Grouts Investigated by X-ray Absorption Fine Structure," W. Lukens (Lawrence Berkeley National Laboratory) discussed the long-term ability of grouts (used to encase residual tank wastes) to effectively reduce technetium to less mobile species. The study showed that formation of cracks in the grout lead to rapid technetium oxidation. This work is relevant to the effectiveness of *in situ* encasement of residual material in high-level waste tanks.

Radionuclide Solubility, Speciation, Sorption, Diffusion and Migration

T. Heath (Serco Assurance) discussed "Application of a Monte Carlo Approach to Surface Complexation Modeling" for low- and intermediate-level nuclear waste repository evaluation, and A. Emren (Chalmers University of Technology, Sweden) described alternative surface complexation and surface phase approaches for non-electrostatic sorption modeling.

P. Vilks (AECL, Canada) gave a talk titled "*In-situ* Diffusion Experiment in Sparsely Fractured Granite" based on results from AECL's Underground Research Laboratory. Diffusivities and permeabilities measured on core samples in the laboratory were consistently higher than those measured *in situ*. The results point to the importance of fracture alteration in limiting mobility, particularly in higher-stress settings.

In another talk on residual tank wastes, "Diffusion of Iodine-129 and Technetium-99 through Waste Encasement Concrete and Unsaturated Soil Fill Material," S. Mattigod (Pacific Northwest National Laboratory) presented data on diffusion of technetium and iodine in concrete and soil relevant to the Hanford site. Diffusivity measurements reflected the importance of moisture content and will be used in quantitative assessments of waste isolation.

Q. Hu (Lawrence Livermore National Laboratory) presented "Field-Scale Migration of ^{99}Tc and ^{129}I at the Nevada Test Site," in which he discussed groundwater data at the Test Site in the light of recently declassified bomb test source term data. Most notably, the data suggest substantial retardation of technetium, due to reducing conditions in the bomb cavity near field or, more generally, in Nevada Test Site groundwaters. (It should be noted that the talk included errors in the calculation of retardation factors.) Iodine also does not behave conservatively, but it is not retarded to the same extent as technetium. These data should be more extensively utilized in assessments of groundwater transport at the potential Yucca Mountain repository site.

In two presentations, H. Xu (University of New Mexico) discussed novel thermodynamic approaches to calculating (i) stability constants of aqueous metal-organic complexes and (ii) "intrinsic sorption constants" for metal cations.

Poster Session

In the poster "Initial Results From Dissolution Testing of Spent Fuel Under Acidic Conditions," B. Hanson and others presented results from flow-through tests in the pH range 2 to 7—which may possibly be relevant for the potential Yucca Mountain repository. Reaction rates were highest at low pH and technetium was observed to be released less than congruently.

W. Murphy, in the poster "Distributions of Concentration Limits for the Source Term in Performance Assessment," pointed to potential problems in using water concentration data in constructing solubility limits for performance assessment. Statistical analyses of concentration data were used to explore whether or not solubility control was relevant.

There were three colloid posters of note. The poster "Experimental study of colloid interactions with rock surfaces," by U. Blanca Alonso (CIEMAT, Spain) and others, demonstrated that colloid interaction with a granite surface was controlled by iron minerals. The surface area available for colloid sorption by the rock was therefore lower than expected. In "Experimental and Numerical

Studies on Colloid-enhanced Radionuclide Transport: The Effects of Kinetic Radionuclide Sorption onto Colloidal Particles," by S. Kurosawa (Japan Nuclear Cycle Development Institute) and co-authors, experiments and models confirmed the importance of kinetic control of radionuclide attachment to colloids. The authors used the code COLFRAC to simulate colloid-facilitated transport. E. Buck (Pacific Northwest National Laboratory) and others, in "Partitioning of Uranyl Oxide Hydrate Colloids at Air-Water Interfaces," showed experimental evidence for the retention of colloidal metaschoepite during unsaturated corrosion tests of uranium oxide. This phenomenon, depending on flow conditions, could either facilitate or suppress radionuclide release.

M. Sutton (Lawrence Livermore National Laboratory) presented "Evaporative Evolution of Carbonate-Rich Brines from Synthetic Topopah Spring Tuff Pore Water, Yucca Mountain." This poster showed experimental results and attempts to match them with EQ3/6 simulations with modified high-temperature Pitzer ion-interaction parameters. While water chemistry evolution was generally understood, model matches were not always satisfactory and further model/parameter development is underway.

<u>Spent Fuel and UO_2 Studies II</u>

R. Finch (Argonne National Laboratory) began the symposium's final session with a summary, titled "The Roles and Fate of Actinides during Spent-Fuel Alteration: Expectation and Experiment" of the state of knowledge of transuranic element behavior during corrosion of spent fuel. Recent work on neptunium incorporation in secondary uranium phases such as studtite and U_3O_8 was summarized; earlier evidence for incorporation in uranophane is now called into question, but new work may support the process. Finch concluded, however, that evidence for neptunium retention under potential Yucca Mountain conditions remains "indirect and circumstantial." A recent paper by Buck and others (*Micron* 35:235) suggests a plutonium-rich, U_3O_8 surface layer on corroded spent fuel that may enhance colloidal plutonium release.

Two papers on neptunium incorporation in secondary uranium phases followed. J. Friese (Pacific Northwest National Laboratory) presented "Neptunium incorporation/sorption with uranium alteration products," which provided indirect evidence for neptunium incorporation in meta-schoepite and another U(VI) phase during spent fuel corrosion; however, co-precipitation versus sorption was not discerned. E. Buck presented new spent fuel corrosion results that suggest neptunium incorporation in uranophane and studtite, though with a higher degree of confidence in the latter.

IMPRESSION/CONCLUSIONS:

Attendance to the Symposium on the Scientific Basis for Nuclear Waste Management XXVIII was highly beneficial because the symposium provided an excellent opportunity to keep current with a variety of topics relevant to the NRC high-level radioactive waste program.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

None.

RECOMMENDATIONS:

Continued participation in future Scientific Basis for Nuclear Waste Management symposia is highly recommended because these symposia provide a valuable and up to date perspective on the relevant scientific issues with a significant international participation.

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