CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT Symposium on the Scientific Basis for Nuclear Waste Management XXV
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DATE/PLACE: November 26–30, 2001
Boston, Massachusetts

AUTHORS: F.P. Bertetti, L. Browning, G. Cragnolino, R. Pabalan, Y.-M. Pan, D.A. Pickett, and L. Yang

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PERSON(S) PRESENT:

In addition to the CNWRA staff (authors), C. Greene, A. Henry, and D. Esh (NRC) participated. The symposium was also attended by scientists from various United States and foreign organizations.

BACKGROUND AND PURPOSES OF TRIP:

The purpose of the trip was to attend various sessions on nuclear waste management and to gather technical information that would be useful for Center for Nuclear Waste Regulatory Analyses (CNWRA) technical assistance activities in the U.S. Nuclear Regulatory Commission (NRC) high-level waste program. CNWRA technical staff also helped in administration of the symposium, presented papers, and conducted technical reviews of papers contributed by other authors. G. Cragnolino co-chaired the symposium, R. Pabalan co-chaired a session on contaminant transport, and D. Pickett co-chaired a session on natural analogs.

The following papers were presented by CNWRA staff in oral or poster sessions:

- R.T. Pabalan, L. Yang, and L. Browning. Deliquescence behavior of multicomponent salts: Effects on the drip shield and waste package chemical environment of the proposed nuclear waste repository at Yucca Mountain, Nevada.
- L. Yang, R.T. Pabalan, and L. Browning. Experimental determination of the deliquescence relative humidity and conductivity of multicomponent salt mixtures.
- Y.-M. Pan, S. Brossia, G. Cragnolino, D. Dunn, V. Jain, and N. Sridhar. Evolution of solution chemistry through interactions with waste package.
- G.A. Cragnolino, D. Dunn, and Y.-M. Pan. Localized corrosion susceptibility of Alloy 22 as a waste package container material.
- F.P. Bertetti and B.A. Werling. Studies of neptunium(v) sorption on calcite.

SUMMARY OF PERTINENT POINTS:

The 25th Scientific Basis for Nuclear Waste Management Symposium comprised four days of technical sessions on a variety of topics relevant to the scientific basis for nuclear waste management. The symposium attracted a large number of participants from 16 countries. A total of 77 oral and 50 poster presentations were made on many scientific and technical issues relevant to radioactive waste management in 15 well attended sessions. The session topics are (i) container materials and engineered barriers; (ii) cements in radioactive waste immobilization; (iii) ceramics—structure; (iv) ceramics—corrosion; (v) natural analogs; (vi) radiation effects; (vii) performance assessment (high-level waste and low-level waste); (viii) waste processing; (ix) glass and alternative waste forms; (x) glass structure and corrosion; (xi) spent nuclear fuel and transuranic chemistry; (xii) contaminant transport; (xiii) cement-based materials and waste containment; and (xiv) cladding and spent nuclear fuel.

The symposium was opened by a keynote lecture of Professor R. Ewing, a member of the Board of Radioactive Waste Management of the National Research Council. Professor Ewing summarized 25-years of materials research in nuclear waste, emphasizing the progress that has been made and the challenges that still confront investigators and technologists in materials science and performance evaluation. After providing a brief chronology of important events and a top 10 list of breakthrough papers in the field, Ewing predicted that fruitful research would provide a deeper level of understanding in the following subdisciplines: (i) prediction of long-term corrosion behavior, (ii) role of corrosion and alteration products in radionuclide release, (iii) formation and transport of colloids, (iv) materials and processes for separations technologies, and (v) performance assessment calculations. The lecture was followed by a session on Containers Materials and Engineered Barriers where Professor A. Sagüés, a member of the U.S. President-appointed Nuclear Waste Technical Review Board discussed the corrosion performance expected for the waste packages to be used in the proposed high-level waste repository at Yucca Mountain, Nevada. In his presentation, Sagüés emphasized that evaporation, salt formation and deliquescence humidities are likely to play an important role in affecting predictions of localized corrosion, and should therefore continue to be evaluated. In addition, he questioned the validity of using nucleation potential thresholds for localized corrosion processes in performance assessment calculations, because these threshold values may or may not be valid over a 10,000-year period. Invited talks on performance assessment and repository studies for different national programs were presented by speakers from the United States, Sweden, Japan, Belgium, Switzerland, Italy, and the United Kingdom. Developments in the United States were discussed in numerous papers on the proposed high-level waste repository at Yucca Mountain, on the Waste Isolation Pilot Plant in Carlsbad, New Mexico, which is now open and accepting transuranic wastes for disposal, and on low-level radioactive waste disposal facilities.

A large number of papers was presented on the structure, properties, and degradation of various waste forms such as glasses, ceramics (mostly for plutonium immobilization), cements, and spent nuclear fuel. For the second consecutive time, the number of papers on ceramics far exceeded papers on glass, which had been the dominant material discussed at this symposium over the prior 23 years. New studies on zirconates confirmed the recently discovered highly resistant nature of this material to radiation damage. The recently developing controversy over the role of protective surface layers and glass corrosion was discussed and received lively and interesting debate from the audience. Nuclear waste processing was the subject of several

papers from the United States and Russia. Dr. C. Jantzen presented an interesting paper showing how thermodynamic modeling in high ionic strength solutions was used to solve an evaporator fouling problem at the Savannah River site and is now being used in process control. There were several presentations devoted to contaminant transport, including radionuclide solubility, speciation, sorption, and migration, and to natural analogs, including uranium deposits and natural fission reactors. Overall, the symposium reflected the significant advances in processing, characterization, and analysis of a variety of materials and on understanding the effects of the environment on their degradation processes that have occurred over the past 25 years.

Abstracts of the papers presented at the symposium are available online at http://www.mrs.org/meetings/fall2001/abstracts/AbstractBookJJ.pdf.

Brief summaries of some of the papers presented at the symposium are given in the following paragraphs.

- G. Gdowski, of Lawrence Livermore National Laboratory (LLNL), presented a paper on the waste package environment at Yucca Mountain with co-authors T. Wolery and N. Rosenberg. Temperature and relative humidity projections were presented for both the low temperature and the high temperature operating modes, which will be used to define alternative conceptual models for predictions of water chemistry and deliquescence behavior in the future. In the current paper, Gdowski et al., used the geochemical code EQ3/6 to estimate the solubilities of mixtures of two-salt endmember compositions at room temperature, and to make qualitative predictions of evaporated Yucca Mountain porewater compositions based on the chemical divide theory. During informal discussions following the session, L. Browning (CNWRA) determined that T. Wolery is currently working to improve EQ3/6 capabilities to model high ionic strength activities at elevated temperatures using a modified Pitzer-type approach, and that the group has plans to evaluate the evaporative behavior of analytical porewater compositions recently collected by United States Geological Survey staff. In addition, it was determined that the Lawrence Livermore National Laboratory group does not have any immediate plans to evaluate the evaporative compositions of seepage waters that have interacted chemically with engineered materials.

- R. Pabalan (CNWRA) presented the results of thermodynamic calculations that were conducted to determine the deliquescence behavior of salt mixtures and to simulate the evaporation of Yucca Mountain groundwaters. The results show that the deliquescence points of salt mixtures are lower than that of individual salts. If the salt mixtures comprise NaCl and KCl salts, the deliquescence point of pure $NaNO_3$ salt is an appropriate lower bound for the deliquescence point of the salt mixture. However, mixtures containing magnesium and calcium salts have much lower deliquescence points than pure $NaNO_3$. If magnesium and calcium salts are deposited on waste package and drip shield surfaces, it could lead to earlier initiation and higher temperatures for aqueous corrosion than assumed by the DOE in its performance assessment abstractions. Such salt mixtures can be formed by evaporation of waters with compositions similar to some Yucca Mountain porewaters and would be characterized by low deliquescence relative humidity, high chloride concentration, and low concentrations of anions such as nitrate and sulfate that could mitigate against the

chloride-enhanced corrosion of the waste package. Evaporation of Yucca Mountain groundwaters also could lead to fluoride concentrations that are above the threshold for accelerated corrosion of the titanium drip shield.

- T. Summers (LLNL) discussed the influence of thermal aging on the mechanical and corrosion properties of gas tungsten arc-welding welds of Alloy 22. She noted that the as-welded sample has reduced corrosion resistance and impact toughness compared to the base metal, possibly due to formation of tetrahedrally close-packed phases along grain boundaries in the as-welded condition. Lowering of the impact toughness of welded specimens was also observed after short aging times at temperatures up to 760 °C.

- G. Cragnolino (CNWRA) presented updated results on the repassivation potential for crevice corrosion of welded and thermally treated specimens of Alloy 22 in chloride-containing solutions emphasizing the detrimental effects of these processes on localized corrosion susceptibility. The inhibiting role of nitrate both in terms of initiation and propagation of crevice corrosion was described and quantitatively evaluated through its effect on the repassivation potential.

- K. Mon (Duke Engineering) presented his work conducted with the WAPDEG code for the evaluation of waste package performance, and D. Shoesmith (University of Western Ontario) discussed the long-term stability of passive corrosion for the waste package and the drip shield. A. Pulvirenti (Catholic University of America) presented results of experimental investigations on the combined effect of chloride and fluoride on the corrosion of Titanium Grade 7 in concentrated groundwaters in which the case is made for very severe corrosion. Y.-M. Pan (CNWRA) presented a study on the evolution of solution chemistry in contact with waste package internal structural components. For this study, a test cell was designed to investigate changes in the in-package solution chemistry as a result of localized corrosion. High cation concentrations and a significant pH reduction were measured inside a simulated pit drilled in a type 316 L stainless steel plate above a critical potential, suggesting that in-package chemistry in localized areas may have a substantial effect on waste form corrosion.

- A. Pulvirenti and C. Marks (Catholic University of America) presented posters on the effects of heavy metal ions (e.g., Pb, Hg, and Cd) on corrosion of Titanium Grade 7 and Alloy 22 in concentrated groundwaters. Dissolution tests of Titanium showed that these ions do not significantly accelerate the general corrosion rates. For Alloy 22 no stress corrosion cracking was observed for U-bend tests of Alloy 22 in Pb- or Hg-containing solutions at temperatures up to 250 °C. However, the dissolution tests of Alloy 22 disks showed significantly enhanced dissolution rates due to the presence of Pb or Hg species, particularly at high Hg concentrations (~5,000 ppm as mercury acetate).

The session on performance assessment for high level waste has several invited presentations. Of particular interest was the presentation of R. Rechard (Sandia National Laboratories) where the approach and specific details of the performance assessment for the Waste Isolation Pilot Plant were discussed, in addition to information regarding the current operation of this first geological repository for transuranic residues.

W. Weber (PNNL), in an invited presentation, reviewed radiation effects arising from alpha decay in crystalline oxides used for immobilization of actinides. He discussed the results of computer simulations and experimental studies using short-lived actinides and ion-beam simulations. The radiation effects on zircon, apatite, zirconolite, and pyrochlore/fluorite structures were the main subject of this talk.

N. Bibler (Westinghouse Savannah River Co.) discussed leaching studies of actinides and U-235 fission products from high level waste glasses using the standard ASTM 1285 test. In the ASTM product consistency test, the soluble elements B, Li, and Na in the glass were chosen as indicators of glass durability, and release of radionuclides was not considered originally because radioactive glasses were not available at the time of adoption of the method. However, later radioactive glasses became available and the question arose, do any of the radionuclides have normalized releases greater than those for the soluble elements? Three radioactive glasses, two Defense Waste Processing Facility glasses and one Hanford glass, were tested to address this question in accordance with the product consistency test procedures. Experimental results indicated that normalized releases of B, Li, and Na are equal to or greater than those of actinides and U-235 fission products from the three radioactive glasses. In all three cases boron release rates are the highest.

S.-Y. Jeong (Argonne National Laboratory) presented information on corrosion of glass-bonded sodalite and its components as a function of pH and temperature. Glass-bonded sodalite is the ceramic waste form that is being developed to immobilize electrorefiner salt wastes from electrometallurgical treatment of sodium-bonded spent nuclear fuel. The ceramic waste form can be fabricated using either hot isostatic pressing or pressureless consolidation processes. The parameter values in the waste form degradation model were previously determined from the dissolution rates measured in MCC-1 tests conducted at 40, 70, and 90 °C. Sensitivity analyses were performed to evaluate the effects of leaching temperature, ceramic waste form fabrication method, and glass composition by conducting additional MCC-1 tests with sodalite, binder glass, and ceramic waste form in pH-buffered solutions in the pH range of 5-10 at temperatures of 20–90 °C. The leaching results showed that the model parameters measured over the temperature range of 40–90 °C can adequately predict the dissolution rate at 20 °C, and the rate expression is not sensitive to the ceramic waste form fabrication method and moderate changes in the glass composition.

J. Icenhower (PNNL) discussed the effect of radiation damage on dissolution rate of plutonium-and uranium-bearing ceramics. Titanate-based ceramics have emerged as the leading candidate for a matrix for disposal of excess weapons-grade plutonium. Concern persists, however, that accumulation of radiation damage will compromise the chemical durability of the titanate matrix. Single-pass flow-through experiments were performed with Pu-239 and U-238 bearing (11.8 and 23.9 mass % PuO_2 and UO_2, respectively) titanate ceramics over a pH interval of 2 to 10 at 90 °C. The ceramics consisted of pyrochlore-dominated compositions with minor amounts of zirconolite and Hf-rich rutile. In addition, a Pu-238 bearing ceramic of a similar composition was tested at pH 2 and 90 °C. Preliminary results indicated that steady state release rate of Pu and U is about 1,000 and 700 times faster, respectively, from a Pu-238 bearing specimen compared to a Pu-239 bearing specimen, probably due to amorphization of the Pu-238 bearing specimen as a result of accumulated radiation damage. It was mentioned that new materials that are resistant to radiation damage may be needed.

P. Bertetti (CNWRA) delivered a presentation summarizing recent results of experiments investigating the potential uptake of Np-237 by calcite under various solution conditions. Experiments were conducted over a pH range of 7 to 9 and in the presence of atmospheric CO_2. Solutions were all kept near saturation or slightly undersaturated with respect to calcite, in an effort to mimic conditions found in the saturated alluvium of Fortymile Wash. For the conditions studied to date, Np sorption onto calcite is strongly pH dependent. Moreover, Np sorption behavior on calcite is consistent with the speciation of Np in solution and the predicted speciation of Np on calcite. When compared to sorption values reported by DOE for the same system, it is evident that the limited conditions of study in the DOE investigations do not adequately represent the range of Np sorption behavior possible in Fortymile Wash. Some characteristics of the calcite sorption curve that differ from those observed for Np sorption on aluminosilicates are likely due to differences in surface speciation between carbonates and silicates. Additional work is underway to develop a detailed sorption model and further characterize Np sorption behavior under varying PCO_2.

J. Serne (PNNL) discussed results of column studies that examined the potential influences of organic complexing agents on the sorption and transport behavior of radionuclides. Serne's presentation included a subset of material to be published in an upcoming NUREG sponsored by NRC Research. Serne showed that some complexing agents (e.g, EDTA) are much more effective at reducing the sorption of divalent metals such as Ni and Co, but that competing cations and adsorption reactions result in the disassociation of many of the metal-organic complexes. Serne proposed that at complexing agent concentrations typical of waste disposal sites, these competitive effects would limit the potential for complexants to mobilize radionuclides. Serne did recommend that solution chemistry conditions, such as pH, must be considered because under certain conditions (e.g., EDTA at alkaline pH) radionuclide sorption onto soils could be significantly reduced. In another interesting result, Serne demonstrated that under certain conditions picolinic acid appeared to change the surface of the sorbing material (an Fe-oxide coated sand) causing a release of previously sorbed metals. This resulted in an effluent concentration of the metal (in this case Ni^{2+}) that exceeded input concentration by a factor of 4.

D. Jolley (Duke Engineering and Services) presented results of calculations designed to estimate the potential retention and transport of radionuclides by microbes within the engineered barrier subsystem. Jolley calculated the potential cumulative microbial biomass that could result from microbial growth given the nutrients available within the engineered barrier subsystem. Assuming microbial sorption and mineralization, as well as inhibited transport of microbes at the air-water interface of unsaturated materials, Jolley estimates that up to several hundred kilograms of uranium could be retained with each drift invert over a million-year time period. At the same time, microbial colloids could provide a mechanism for plutonium or Th transport. Jolley noted that quantitative inclusion of retardation credit is unlikely given the high degree of uncertainty in the calculations, but microbial based arguments could be used as a qualitative description of system transport characteristics. Jolley acknowledged that other effects of microbial growth on transport within the invert, such as potential changes in diffusion characteristics, were not addressed.

IMPRESSIONS/CONCLUSIONS

The multidisciplinary approach of the nuclear waste management symposium provided the opportunity to consider a variety of topics relevant to nuclear waste disposal. The symposium was very well attended by United States and foreign scientists.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

None.

RECOMMENDATIONS:

Continued participation in future Material Research Society nuclear waste management symposia is highly recommended.

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