CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: 2003 Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management XXVII
Project Numbers 20.06002.01.071 and 20.06002.01.081;
AIs 06002.01.071.004 and 06002.01.081.313

DATE/PLACE: June 15–19, 2003
Kalmar, Sweden

AUTHORS: Roberto T. Pabalan and Gustavo A. Cragnolino

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PERSONS PRESENT:

The symposium was attended by 227 participants from 19 countries. Among the attendees there were three members of the Nuclear Waste Technical Review Board (NWTRB)—D. Bullen, P. Nelson, and R. Parizek, and a technical staff of the NWTRB—D. Diodato.

BACKGROUND AND PURPOSE OF TRIP:

The Symposium on the Scientific Basis for Nuclear Waste Management XXVII, as part of the 2003 Materials Research Society symposia was held this year in Kalmar, Sweden with the financial support of Svensk Kärnbränslehantering AB (SKB). The purpose of the trip was to attend the Symposium and present two papers on issues related to the near field environment and container corrosion. A further purpose was to facilitate contact with scientists and technologists working on high-level nuclear waste management, mainly from Europe, where several national programs are moving forward.

SUMMARY OF PERTINENT POINTS:

The symposium comprised three days of technical sessions on a variety of topics relevant to the scientific basis for nuclear waste management, in addition to the presentations of issues related to site selection and public involvement. The fourth day comprised a visit to SKB facilities, including the Hard Rock Laboratory at Äspö, the Canister Laboratory in Oskarshamn, and the M/S Sigyn, a transport ship specially designed to transport radioactive freight. A total of 66 oral and 102 poster presentations were made on many scientific and technical issues relevant to radioactive waste management in 21 well attended sessions. The topics in the 16 oral sessions and 5 poster sessions were (i) site selection, investigation, and public involvement; (ii) spent fuel studies; (iii) geologic characterization and modeling; (iv) radionuclide solubility; (v) microbial effects; (vi) glass waste forms; (vii) performance assessment; (viii) alternative concepts; (ix) canister corrosion issues; (x) modeling of groundwater flow and chemistry; (xi) ceramic waste forms, (xii) radiation effects; (xiii) field tests and natural analogs; (xiv) colloids and sorption; (xv) gas migration; and (xvi) uranium disequilibria studies.

The plenary section, which initiated the symposium, was devoted to presentations on site selection, investigation, and public involvement. After welcoming remarks by the Governor of Kalmar County in which the nuclear related activities in the county were described, there were

three interesting presentations on site investigation programs by authors from Sweden, Finland and Japan, followed by a detailed presentation by P. Wikbergg on the site investigation studies conducted in Oskarshamn. The session was closed with a presentation from M. Silva (EEG, USA) on the public oversight of the Waste Isolation Pilot Plant (WIPP) repository.

The session on spent fuel studies had several interesting presentations. It was initiated with a overview presented by C. Poinsott (Commissariat à l'Énergie Atomique [CEA], France) in which the most important aspects of spent fuel evolution during prolonged dry storage and disposal were examined. An important conclusion is that no credit is given to the performance of cladding as a barrier beyond a 50-yr period, even though the criterion for failure due to creep was increased to 2–4 percent strain instead of the commonly accepted value of 1 percent strain. C. Ferry (CEA, France) presented a quantitative assessment of the instant release fraction of fission gases (Xe, Kr) and volatile elements (I, Cs) as a function of burnup and time under disposal conditions, in which the possible contribution of fission products in the highly restructured rim zone of fuels was emphasized. A. Loida (Institut für Nuckleare Enstorgung, Germany) discussed the corrosion of preoxidized high burnup spent fuel in salt brine. It was reported that the rate of dissolution, based on Sr release, was ten times higher in a 5 molal NaCl solution for a fuel preoxidized by air during a 7-year storage than that of non-preoxidized fuel. In the presence of iron powder more than 99.5 percent of the reacted Pu, Am, U, and Tc inventory was found retained in the iron corrosion products, and the container walls. M. Jonsson (Royal Institute of Technology, Sweden) presented a paper in which the effects of radiolysis on UO_2 dissolution were modeled using results of a recent experimental study.

In the session on geologic characterization and modeling, G. Lodha [Atomic Energy of Canada, Ltd. (AECL), Canada] described the geological, geophysical, and geotechnical studies that have been conducted by AECL in several areas of Canada, including Atikokan, Chalk River, and Whiteshell, Manitoba, that are underlain by plutonic rocks. The objectives of the work were to study the character and distribution of fractures in several types of plutonic rocks and to develop ways to use this information to infer conditions at depth, particularly with respect to repository characteristics required for hydrogeological modeling and for rock stability studies. Detailed airborne, surface, and borehole geophysical surveys were done to identify fractures and understand groundwater flow conditions. Hydrogeological monitoring and testing of over 75 inclined boreholes, some of which were drilled to depths of 1 kilometer, were performed. N. Marcos (Helsinki University of Technology, Finland) described a study designed to understand the change and evolution of the hydraulic properties of fractures in bedrock due to excavation of tunnels and other open spaces. The study used natural decay series isotopes—U-234/U-238, Th-230/U-234, and Th-228/Th-232—to obtain evidence of very recent changes in groundwater flow conditions caused by excavations in rock. J. Autio (Saanio and Riekkola Oy, Finland) presented a study on microfracturing and porosity changes in the excavation damage zone adjacent to experimental deposition holes in the Prototype Repository Tunnel in the Äspö Hard Rock Laboratory using ^{14}C-PMMA method and scanning electron microscopy (SEM). The results show that the porosity of the damaged rock zone is clearly higher than the porosity of undisturbed rock. The thickness of the crushed zone with significantly higher porosity is a few millimeters and the average depth of the damaged zone is from 10 to 20 mm. The apertures of the inter- and intragranular microfractures in the crushed zone varied from 5 to 30 micrometers, based on SEM examination.

In the session on solubility, G. Kallvenius (Chalmers University of Technology, Sweden) described experiments on the solubility of Np(IV) under alkaline and reducing conditions. This

work is pertinent to the Swedish repository program. The planned Swedish repository will be under reducing conditions, and some of the waste forms will include concrete, which could raise the pH to above 13. Previous studies on Np(IV) solubility used liquid scintillation as the analytical method, which has a detection limit of 10^{-8} M, and reported solubilities were at or below this limit, resulting in a high degree of uncertainty in the reported Np(IV) solubility. In this study, the solubility of Np(IV) in the form of NpO_2 was measured in (Na^+, OH^-, ClO_4^-) media at eight different pH values in the range of 10 to 14. Reducing conditions were ensured by using hydrogen atmosphere with a platinum catalyst. The neptunium concentration was determined using ICP-MS, which lowered the detection limit by several orders of magnitude compared to liquid scintillation analysis. The results were used to determine the hydrolysis stability constants of Np(IV). A. Odegaard-Jensen (Chalmers University of Technology, Sweden) presented a paper on the solubility of plutonium in carbonate-bearing water under reducing conditions. Plutonium hydroxide and carbonate were synthesized and reacted with 1 M NaClO4 solution in a vessel with a small piece of platinum wire and under an atmosphere of either H_2(g) or a mixture of H_2 and 0.03 percent CO_2. The results show that the plutonium concentration in solution reached a value between 10^{-9} and 10^{-8} M.

In the session on glass waste forms, R. Ewing (University of Michigan) presented a paper on the effect of ionizing radiation on alkali aluminophosphate glasses in which electron beam irradiation was used simultaneously with microstructural and microchemical characterization performed with the analytical electron microscope. It was found that this glass has a lower resistance to radiation damage compared to iron phosphate and alkali iron phosphate glasses. A very interesting paper was presented by P. Frugier (CEA, France) in which the interpretation of P. McGrail regarding the failure of the affinity rate law to describe the alteration kinetics of borosilicate glasses was questioned. The author emphasized the importance of using high surface/volume ratio in the experimental measurements and concluded that the formation of amorphous silica spheres in the alteration layer is a controlling factor in the kinetic law. B. Grambow (Ecole des Mines de Nantes, France) reported the results of 14-yr corrosion tests of borosilicate glass using inactive simulated compositions in $MgCl_2$ and NaCl solutions at 110 and 190 °C. The results show a square root of time dependence indicating a diffusion controlled mechanism. The final incremental fractional dissolution rates were found to be lower than 10^{-5} /yr even in the aggressive $MgCl_2$ solution at 150 °C, which extrapolates to values lower than 10^{-6} /yr at 50 °C based on an activation energy of 50 kJ/mole. B. Luckscheiter (FZK, Germany) presented an interesting paper discussing the effect of dissolving elements from glass besides Si that affect the dissolution rate. It was found that Mg, Al or Nd added separately to water decrease initially the release rate of Si compared with deionized water but not that of B. Only after Si saturation is attained at longer times that B release rate decreases with respect to pure water. The presentation of S. Gin (CEA, France) dealt with the validation, through experiments in humid clay, of the kinetics expressions derived from a model of glass dissolution developed by Ribet (2001) in which several empirical parameters are used as a variation of the affinity law. One of the parameters is the diffusion coefficient of Si in the gel alteration layer using Fick's law to account for the diffusional process and another one is related to the retention of Si in the gel.

In the session on performance assessment, two complementary papers regarding the Swiss repository program were presented. In the first paper, A. Gautschi (NAGRA, Swtizerland) provided an overview of the evaluation procedure used to narrow down potential siting options for a Swiss repository. In 1994, the Opalinus Clay (a marine claystone formation) was identified as the priority sedimentary host rock option and the Zürcher Weinland as the first-priority area

for site-related studies. Detailed characterization of the host rock and the potential siting area followed after 1994, which included a 3D seismic survey, experiments at the Mont Terru Rock Laboratory, regional studies on the Opalinus Clay including deep boreholes in the near and far vicinity of the siting area, and comparisons with clay formations that are under investigation in other countries for geologic disposal. In the complementary paper, L. Johnson (NAGRA, Switzerland) presented the results of safety assessment calculations of the proposed Swiss repository. The paper discussed the nature of the assessment cases considered and how they illustrate the robustness of the disposal system. The results of the calculations indicate that doses will be two orders of magnitude or more below the regulatory limit over the assessment time frame of one million years.

The opening paper in the session on canister corrosion issues was presented by L. Werme (SKB, Sweden). He described summarily the results of the corrosion studies conducted by the SKB program during the last 25 years in conjunction with results from Finland and Canada to assess the long-term performance of the copper canisters used in the Swedish design. He concluded that the life of the canisters will exceed 100,000 yr under the reducing conditions that would prevail in the proposed design of the Swedish repository in agreement with preliminary assessments. This paper was complemented by a study on corrosion of copper in the Äspö Hard Rock Laboratory reported by C. Taxen (Swedish Corrosion Institute, Sweden). Copper coupons were tested at 450 m in depth in a humid sulfide atmosphere and also with either bentonite or bentonite and a heating coil to raise the temperature to 75 °C. After 3-yr exposure a fraction of the coupons were examined and only those coupons exposed to the higher temperature were found to be covered with a dull greenish layer whereas the ones at room temperature remained shiny. T. Saario (VTT, Finland) presented a paper in which an online corrosion sensor and a reference electrode for repository conditions were described. The reference electrode is based on an external pressure balanced Ag/AgCl electrode. In this session one of the authors of this trip report presented a paper titled "Evaluation of corrosion processes affecting the performance of Alloy 22 as a proposed waste package material," co-authored by G. Cragnolino, D. Dunn, and Y. Pan. The paper discussed recent work evaluating localized corrosion and stress corrosion cracking of Alloy 22 (58Ni-22Cr-13Mo-3W-4Fe). It was found that both welded and thermally aged materials are more susceptible to localized corrosion in chloride solutions at temperatures above 60 °C than the mill-annealed material. This observation suggests that welding and certain post-welding operations may decrease the estimated life of the waste packages. However, no stress corrosion crack growth was observed in concentrated chloride solutions and in simulated, concentrated groundwater at 95 °C when precracked compact tension specimens were tested under both constant and cycling loading. B. Kursten (SCK-CEN, Belgium) presented a study on pitting of AISI 316L and UHB 904L stainless steels, the candidate container materials for the Belgium HLW disposal in argillaceous formations. Although values of pit nucleation potential and pit repassivation potential were reported to be higher than the corrosion potential, the authors emphasized that pitting may occur because the corrosion potential could become greater than the repassivation potential in the long term. The last paper in this session was presented by N. Smart (Serco Assurance, UK). In this paper, prepared in support of the Swedish waste package design, Smart discussed the corrosion of carbon steel in contact with bentonite clay under anaerobic conditions at two water–bentonite ratios and two temperatures (30 and 50 °C). The corrosion rate was measured through the generation of hydrogen gas and it was concluded that bentonite increases the corrosion rate with respect to that in artificial groundwater. It was emphasized that hydrogen was able to permeate through compacted bentonite.

In the session on groundwater flow and chemistry, L. de Windt (Ecole des Mines de Paris, France) described the modeling of radionuclide source terms in an underground spent fuel disposal system. The reactive transport models CHEMTRAP and HYTEC were used to simulate the release of radionuclides from spent fuel packages and their migration in the near-field environment. The behavior of three elements with long half-lives, cesium, nickel and uranium, was studied. U. Kuhlman (TK Consult AG, Switzerland) described a study involving local- and repository-scale hydrodynamic modeling for geoscientific characterization of a candidate intermediate level waste (ILW)/HLW repository in northern Switzerland. The study examined the consistency of the general hydrogeological conceptualization with hydraulic and geochemical data, the impact of the backfilled repository structures on the natural flow field, the time-scale and flow pattern during the re-saturation phase after repository construction and operation, and the long-term evolution of hydrogeological conditions at the site.

In the session on radiation effects, three papers discussing the effect of α-radiation on the dissolution rate of spent fuel were presented. The most interesting one was the paper by C. Jegou (CEA, France) in which UO_2 pellets doped with α-emitters showed an increase in the dissolution rate in deaerated, deionized water, measured through the U release rate, proportional to the α-radiation flux at the reaction interface. It was noted, however, that the rate was significantly lower than that reported before for aerated water. On the other hand, γ-radiation at a dose rate of 650 Gy/hr induced a significant increase in the dissolution rate (170 times higher) with respect to that in the absence of irradiation. In addition, the effect of α-radiation in deaerated water was found negligible compared to that of γ-radiation in aerated water. A code, CHEMSIMUL, was used to calculate water radiolysis and uranium release into solution.

In the session on colloids and sorption, K. Traexler (University of Michigan) presented a paper (co-authored by Rod Ewing) that criticized the Department of Energy abstraction of colloid transport of radionuclides, as presented in the DOE analysis model reports (AMRs). The paper pointed out that, in most cases, the AMRs use bounding limits for input parameters related to colloid generation, stability, and sorption reactions based on laboratory experiments, field data, or natural system studies, but some of the assumptions in the AMRs are not supported by data. For example, the AMRs assume that colloids expected at the repository can be represented by either smectite or iron-(hydr)oxides, but due to the limited number of colloid samples, there is insufficient data to determine whether these phases are dominant in the Yucca Mountain groundwater system. The authors state that the lack of data regarding other possible types of pseudocolloids expected to be present within the nuclear waste repository prevents the DOE AMRs from being fully conservative and bounding. T. Missana (CIEMAT, Spain) described experiments on the sorption of Pu(IV) onto two different steel corrosion products: goethite and magnetite. The experiments were done in the pH range 2 to 10 under nitrogen atmosphere and ionic strengths from 0.001 to 0.1 $NaClO_4$. The results show that the sorption edge of plutonium on goethite occurs between pH 3 and 4, and between 4 and 5 for magnetite. No significant effect of ionic strength on Pu(IV) sorption was observed. The data were modeled using a surface complexation model with no electrostatic term. For magnetite, the model invoked a reduction process of Pu(IV) to Pu(III), whereas no reduction reaction was included in the model for Pu(IV) sorption onto goethite. B. Kienzler (Institut für Nuckleare Enstorgung, Germany) described experiments on actinide sorption onto granite and weathered material from the Äspö Hard Rock Laboratory. Slices of Äspö rock and of weathered material (altered fracture filling) were reacted with Äspö groundwater containing Pu-238, Np-237, and U-233 in a glove box at anoxic conditions. The spatial pattern of actinide distribution on the surface was determined by

α-radiography. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical valence state of some elements on the surface, such as neptunium and iron. The results show that neptunium sorption is correlated with the presence of Fe(II) in the minerals. Np(V) was reduced to Np(IV) and retained in the tetravalent state. Areas of the slices with the minerals chlorite, epidote, titanite, and apatite showed high neptunium sorption.

The second paper from CNWRA staff was a poster paper titled "Chemical evolution of in-drift waters at the proposed Yucca Mountain, Nevada, nuclear waste repository," co-authored by R. Pabalan, L. Yang, and L. Browning. The poster paper discussed the results of thermodynamic simulations of the chemical evolution of in-drift waters resulting from evaporation and condensation processes. The objective of the study was to determine the types of brines that may form and the ranges of brine chemistry that may contact the surfaces of drip shields, waste packages, and ground support materials. Such information will be useful in evaluating the potential degradation of those materials. The thermodynamic calculations were supplemented by an alternative approach based on the concept of chemical divides. The results of the study showed that evaporation and condensation of in-drift waters at the proposed Yucca Mountain repository would lead to a wide range of chemistry of waters contacting the drip shield, waste package, and ground support materials. Some of the in-drift water could evolve into brines characterized by high concentrations of corrosive species, such as Cl^-, F^-, and Br^-, and low concentrations of corrosion inhibitors such as NO_3^-. Condensate waters can be acidic but have low ionic strengths, whereas residual brines have high ionic strengths but mildly acid to alkaline pH.

At the end of the conference, Pabalan and Cragnolino participated in the meeting of the Steering Committee, composed of previous Symposia chairs, to plan future Symposia. L. Browning of the CNWRA will be a co-chair of the next symposium to be held in San Francisco, CA, on April 12–16, 2003.

Cragnolino visited the facilities of the Chemical Engineering and Technology Department at the Royal Institute of Technology, Stockholm, on June 20, following an invitation by Luis Moreno, a collaborator and coauthor of many papers with I. Neretnieks on solute transport in fractured rock and porous media.

IMPRESSION/CONCLUSIONS:

The attendance to the Symposium on the Scientific Basis for Nuclear Waste Management XXVII 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. The symposium was well attended particularly by European scientists. One of the most valuable aspects of this trip was the opportunity to visit several SKB facilities relevant to the HLW program. The Äspö Hard Rock Laboratory was visited and information was provided on different testing stations for near field parameters, borehole corrosion, etc. In the Canister Fabrication Laboratory we had the opportunity to examine welded canisters and equipment for electron beam welding and stir friction welding, and non-destructive examination equipment such as a powerful X-ray machine, and ultrasonic and eddy current testing instruments. Above all, it was very interesting to learn that all these facilities are toured by thousands of visitors per year and many of them are from the Oskarshamn area, where two nuclear power plants are located. A brief tour of M/S Sigyn, a transport ship specially designed to transport radioactive freight was also conducted. This ship also is used extensively in Sweden for public awareness exhibits.

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.

REFERENCES:

The program with the list of the conference papers is attached to this trip report. A book of conference abstracts was published by the organizers and is available from the authors upon request.

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