

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES
TRIP REPORT

SUBJECT: 13th Annual V.M. Goldschmidt Conference (Goldschmidt 2003)
DATE/PLACE: September 8–12, 2003
Kurashiki, Japan
AUTHOR: Roberto T. Pabalan
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AUTHOR: R.T. Pabalan

PERSON(S) PRESENT: R.T. Pabalan (CNWRA)

BACKGROUND AND PURPOSE OF TRIP:

The purpose of the trip was to participate in the 13th Annual V.M. Goldschmidt Conference (Goldschmidt 2003) that was held on September 8 through September 12, 2003, in Kurashiki, Japan. The conference is an international forum held every year to discuss issues of interest to the geochemical community. The trip was undertaken to present a paper discussing the results of an U.S. Nuclear Regulatory Commission (NRC)-sponsored experimental and modeling study designed to determine the deliquescence relative humidity of salt mixtures that may form on the surfaces of drip shields and waste packages at the proposed Yucca Mountain geologic repository for high-level wastes. In addition, the conference provided an opportunity to obtain information from international scientists on geochemical issues relevant to nuclear waste management that may be useful in NRC reviews and analyses of U.S. Department of Energy work.

SUMMARY OF PERTINENT POINTS:

The 2003 meeting had 9 general symposia and 55 special symposia designed to promote discussion on specific topics within geochemistry. Participants from various countries presented about 900 papers in oral and poster sessions.

The conference had a special symposium on Geochemical Immobilization and Long-term Isolation of Waste, in which papers were presented on recent developments in designing, characterizing, and testing of geochemical barriers for the confinement of long-lived waste materials and contaminants. A keynote paper was presented by T. Eighmy (University of New Hampshire) on the use of orthophosphate (PO_4^{3-}) as a chemical stabilization agent for wastes, including contaminated soils, sediments, groundwaters, industrial wastewaters, smelter dusts and slags, wire chopping wastes, mine tailings, and incineration residues. The technology is based on the known strong interaction of PO_4^{3-} with 26 cations and four oxyanions, notably U(IV,VI), Pb(II), Cd(II), Cu(II), Zn(II), Ni(II), and As(V), to form stable and insoluble solids, analogous to the approximately 300 naturally-occurring phosphate-bearing minerals. The technology is applied in waste processing lines; within *in-situ* treatment systems; and within reactive caps and reactive permeable barriers. T. Eighmy discussed the geochemical basis for the use of orthophosphate with a focus on the generally wide pH distribution, pH-pE predominance, and redox stability of reaction products within the context of typical cation/anion-Ca-Al-P-S-C-Cl-H₂O geochemical systems. The theoretical and observed stabilization

mechanisms in solutions (precipitation, Ostwald ripening, and solid solution formation), as well as on phosphate mineral (typically apatite) surfaces (sorption, surface precipitation, precipitation) were also presented.

In another keynote paper, N. Chapman (NAGRA, Switzerland) presented an overview of the geochemical issues pertinent to deep underground disposal of nuclear wastes. N. Chapman stated that a thorough understanding of the key geochemical processes that control waste evolution in deep rock-groundwater systems is necessary in the evaluation of the long-term performance of underground disposal facilities. His paper reviewed the relative importance of key geochemical processes and the circumstances under which they have strong controls on disposal safety. The paper also assessed the circumstances under which processes are likely to be of less or little concern in estimating safety impacts. The topics discussed include: (i) products of waste degradation and their complexation with groundwater ligands, (ii) sorption and precipitation of mobile waste species, (iii) microbially enhanced processes, (iv) quality of and uncertainties in geochemical databases used in predictive safety evaluations, (v) generation and dispersion of gases from solid wastes, (vi) mobility of waste components in deep groundwater and brine systems, (vii) chemical degradation of engineered materials used to contain wastes, (viii) appropriate indicators of toxicity for evaluating the performance of waste repositories at different times, and (ix) natural and chemical analogues for some of the above processes.

F. Gauthier-Lafaye (Centre de Géochimie de la Surface, EOST-ULP, France) presented a paper on the role of secondary minerals in retention of fission products and actinides in natural environments. Studies of the Cigar Lake uranium deposit and the natural nuclear fission reactors of Gabon show similar phenomena of hydrothermal alteration of the ore-containing sandstones as well as of clay formation around the uranium ore. The clay halo provided effective redox buffering, and significant amounts of Ca, Sr, and LREE were found to be coprecipitated by Al-phosphates in the clay halo. Clay minerals and Ti-oxide have significant amounts of sorbed uranium, and sorption was followed by the formation of coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$). Uraninite crystals retain most of the actinides produced by the fission reactions. When uraninite becomes hydrothermally altered or transformed during supergene weathering, the reduced conditions in the close vicinity of the uranium ore allows its precipitation in newly formed Si-P-REE uranium minerals. The author suggested that the formation of coffinite and U-bearing phosphate minerals can be an important factor for the long-term preservation of radioactive material because it retards the mobility of actinides and fissionogenic lanthanides.

J. Tits (Paul Scherrer Institute, Switzerland) presented an experimental study on the immobilization of Eu(III) and Cm(III) by calcium silicate hydrates. Calcium silicate hydrate phases are major components of the cement used to condition the radioactive waste and as backfill and construction material, and could play an important role in retarding the migration of radionuclides in the near field and the altered far field of a cementitious radioactive waste repository. Retention of Eu(III) and Cm(III), two analogs for Am(III), by calcium silicate hydrate phases was investigated using batch sorption experiments and time-resolved laser fluorescence spectroscopy. Calcium silicate hydrate phases with different compositions were synthesized in the presence of varying Eu(III) and Cm(III) concentrations. The distribution of both elements between solid and liquid phase was determined by radiochemical analysis. The coordination of Cm(III) in the solids was probed using time-resolved laser fluorescence spectroscopy. The radiochemical data and the time-resolved laser fluorescence spectroscopy data show that in both the sorption and co-precipitation experiments, practically all the Eu(III) and Cm(III) is taken

up by the calcium silicate hydrate-phases, independent of the calcium silicate hydrate composition. The calculated distribution ratios (R_d) are very high, on the order of $(6 \pm 3) \times 10^5 \text{ L kg}^{-1}$. Higher R_d values were found in the desorption experiments, suggesting that the uptake of these elements is at least partially irreversible. Time-resolved laser fluorescence spectroscopy revealed that in both the coprecipitation and sorption experiments the same Cm(III) species are associated with the solid. Two different incorporated Cm(III) species could be detected: one species replacing Ca(II) in the interlayer space of the calcium silicate hydrates phases, and the other replacing Ca(II) in the octahedral layer of the calcium silicate hydrates phases.

S. Stipp (University of Copenhagen, Denmark) presented a study of the uptake of Eu(III) in calcite. Calcite is known to incorporate divalent cations within its atomic structure, thus immobilizing them as long as the calcite remains stable, but little is known about calcite's ability to immobilize trivalent ions, including trivalent actinides. Eu(III) was used in the study because it serves as a safe analogue for the trivalent actinides, especially curium and americium, and its ionic radius is almost the same as calcite. In the study, more than 100 calcite samples from various geological environments were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) to determine the relative abundance of Eu(III) in natural calcite. In addition, precipitation experiments using the constant addition method were conducted to determine how much Eu(III) could be accommodated in the calcite structure. The latter experiments showed that much more Eu(III) could be accommodated within the calcite structure than is found in natural samples. A distribution coefficient for Eu-calcite solid solution of about 800 was derived from these experiments. The results indicate that Eu(III), or elements with similar behavior, are strongly sequestered in the solid phase and suggest that low Eu concentrations in natural samples result from low solution concentrations rather than the inability of the structure to accommodate it.

Several oral and poster papers were presented relevant to the Tono uranium mine in Japan. T. Iwatsuki (Japan Nuclear Cycle Development Institute) described a study dealing specifically with the baseline groundwater chemistry at an Underground Research Laboratory (URL) in Mizunami, Japan before construction. Groundwater samples were collected from sedimentary rocks and basement granite at depths of up to approximately 175 m below ground level. Analytical results show that the groundwaters can be divided into two types: Si-Na-Ca-SO₄-HCO₃ ions dominate water in the shallow part of the sedimentary rocks and Na-Cl ions dominate fresh water in the deeper part of the sedimentary sequence and in the basement granite. Chemical evolution processes are most likely weathering of silicate minerals, and dissolution of marine sulfide/sulfate and carbonate minerals in the shallow part, and mixing between high and low salinity Na-Cl dominate water in the deeper part. The study suggested that hydrochemical changes caused during and after URL construction can be evaluated by a numerical model that assumes mixing among multiple components of groundwater. R. Arthur (Monitor Scientific, Denver, USA) presented a study on the geochemical constraints of uranium mobility within the Tono uranium deposit. Uranium-series isotope data indicate that some remobilization of uranium has occurred within the deposit, albeit over scales of space and time that are not well constrained at present. The study examined whether this apparent mobility could result from local variations in the geochemical environment, and from associated effects on the aqueous-speciation and solubility behavior of uranium. Geochemical constraints on uranium mobility within the Tono deposit were evaluated assuming that an amorphous to incipiently crystalline UO₂(s) solid that is metastable with respect to uraninite is solubility controlling. The solubility of this phase was calculated to vary by up to two orders of magnitude over a range of conditions [pH ~ 7.5 – 10; Eh ~ -250 to -400 mV; log PCO₂(g) ~ -2.5 to -5 bar]

believed to be representative of porewaters in the deposit. The results suggest that plausible local variations in environmental conditions within the Tono deposit could induce mass transfer of uranium among solid and aqueous phases, and that this could explain the uranium-series isotope data if such mass transfer is accompanied by mass transport on a local-to-regional scale. K. Hama (Japan Nuclear Cycle Development Institute) described investigations of oxidation-reduction (redox) around a drift in the Tono uranium mine. The study was undertaken because redox fronts are important geochemical boundaries that need to be considered in any safety assessment for a future deep repository for radioactive waste. During construction and operation of an underground facility, air will be introduced into the geological formation and an oxidized zone will be generated around the facility which will potentially have a strong influence on the mobility of redox sensitive elements. For the redox study, a cored borehole was drilled from a drift wall. Core samples were treated under anaerobic conditions to avoid additional oxidation. Activities of uranium-series nuclides (U-238, U-234, Th-230, Ra-226, Pb-210) and thorium-series nuclides (Th-232, Th-228) were determined and ratios of Fe(II)/Fe(III) and aerobic/anaerobic bacteria were also measured. The results showed evidence of an Fe²⁺/Fe³⁺ redox front between 40 and 50 cm from the drift wall and also evidence for oxidation of U⁴⁺ throughout the core. Decreased uranium contents were observed at less than 70 cm from the drift wall, with U-234/U-238 and Th-230/U-238 activity ratios suggesting that this section of rock had experienced recent, rapid removal of uranium.

J. Davis (U.S. Geological Survey, Menlo Park) described a semiempirical, site-binding generalized composite modeling approach to modeling of metal sorption. This approach is a compromise between the simple constant-K_d approach and more complex surface complexation modeling that are difficult to apply. The generalized composite modeling approach is preferable to empirical approaches because the important linkage between surface and aqueous species (and associated thermodynamic data) can be retained in geochemical or reactive transport models. A study was conducted of uranium(VI) sorption on natural and U-contaminated sediments in the laboratory and in the field environment. The location of the study and the source of sediments was the uranium mill tailings site near Naturita, Colorado, which has a well characterized uranium(VI) contaminant plume in a shallow alluvial aquifer. It was shown in laboratory batch and column experiments with uncontaminated Naturita sediments that the sorption and retardation of U(VI) transport by the Naturita sediments was strongly influenced by the dissolved bicarbonate concentration (alkalinity). A surface complexation model was developed to describe U(VI) sorption measured in the laboratory on the uncontaminated sediments. For the range of chemical conditions observed in the Naturita aquifer, variable bicarbonate was more important than either variable pH or U(VI) concentration in influencing U(VI) mobility. Surface complexation modeling-predicted U(VI) sorption agreed to within a factor of 2 to 3 with estimates of U(VI) sorbed on contaminated sediments from the Naturita aquifer.

E. Trueman (University of Reading, U.K.) described a study of the alteration of depleted uranium metal. Depleted uranium contamination now exists in diverse environments, for example, agricultural land in Kosovo, and desert in Kuwait due to its use in munitions, and also in the sea following weapons testing. However, the environmental fate of depleted uranium following corrosion and oxidation of fragments is not well known. To date, the only documented secondary mineral formed as a result of the alteration of depleted uranium metal is schoepite [(UO₂)₈O₂(OH)₁₂(H₂O)₁₂], which is a relatively unstable phase. In the study, discs of depleted uranium metal from unfired penetrators were reacted over six months with ultra high quality water, as a control, a calcium phosphate-rich solution representing agricultural soils and a silica-

rich solution representing desert conditions. XRD results show that the first phase formed in ultra high quality water is UO_2 followed after one week by schoepite and, after four months, studdite ($\text{UO}_4 \cdot 4\text{H}_2\text{O}$). Surface analysis of the depleted uranium in the calcium phosphate solution detected uranyl phosphate hydrate [$(\text{UO}_2)_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$] after one week with schoepite after eleven weeks. The discs in this solution showed little visible sign of corrosion and the mass did not change significantly during the experiment, suggesting passivation of the surface. XRD analysis of depleted uranium in the silica-rich solution detected a range of uranyl oxides from UO_2 to UO_3 . Corrosion of depleted uranium in the silica solution was more rapid and after six months 20 percent of the original mass had been lost.

A. Richter (Institute of Radiochemistry, Germany) described the development, implementation, and application of the Rossendorf Expert System for Surface and Sorption Thermodynamics (RES3T), a digitized thermodynamic sorption database utilizing surface complexation models. It is mineral-specific and can therefore also be used for complex models of solid phases such as rocks or soils. This is the first such digital thermodynamic database for surface complexation equilibria in the world. Data records comprise mineral properties, specific surface area values, characteristics of surface binding sites and their protolysis, sorption ligand information, and surface complexation reactions. An extensive bibliography is also included, providing links not only to the above listed data items, but also to background information concerning surface complexation model theories, surface species evidence, and sorption experiment techniques. An integrated user interface helps users access selected mineral and sorption data, extract internally consistent data sets for sorption modeling, and export them into formats suitable for other modeling software. It assists the identification of critical data gaps, the evaluation of existing parameter sets, consistency tests and the establishment of selected reference data sets. RES3T is implemented as a relational database under MS ACCESS. The database is intended for an international use and is currently converted into a WWW-based version.

I presented a poster paper titled "Deliquescence Relative Humidity of Salt Mixtures: An Experimental and Thermodynamic Study" co-authored with L. Yang and M. Juckett. The paper discussed the results of experiments and modeling designed to determine the deliquescence relative humidity of salt mixtures. The deliquescence relative humidities of salt mixtures in the system Na-K-Ca-Mg-Cl- NO_3 were measured as a function of temperature (-20 to 85°C) using two methods, one using a hygrometer and the other using conductivity cells inside a controlled temperature/humidity chamber. To facilitate the calculation of the deliquescence relative humidities of multicomponent mixtures, a thermodynamic approach based on the Pitzer ion interaction model was used, with model parameters derived from the literature. The modeling results are generally in good agreement with experimental data, except for nitrate-bearing salt mixtures with very high salt concentrations. An alternative model will be investigated in future work. The results of the study will be used to evaluate the chemistry of water contacting the drip shields, waste packages, and ground support materials in the potential Yucca Mountain repository and the time and temperature during which corrosion of the metallic materials initiates.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

The author will acquire a copy of the Rossendorf Expert System for Surface and Sorption Thermodynamics (RES3T) sorption database for evaluation and possible use in Radionuclide Transport Key Technical Issue resolution activities.

RECOMMENDATIONS:

Continued participation in future Goldschmidt conferences is highly recommended. The conference facilitates interaction and collaboration between international experts on various aspects of geochemistry, including nuclear waste management.

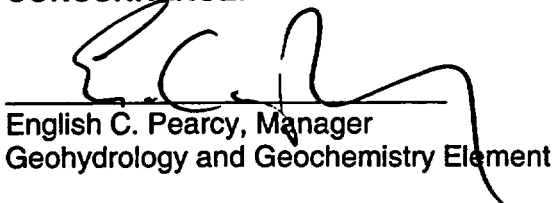
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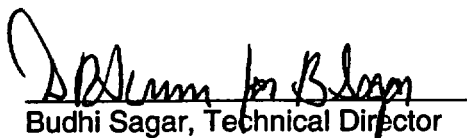
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