

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES
TRIP REPORT

SUBJECT: 12th Annual V.M. Goldschmidt Conference (Goldschmidt 2002)
20.01402.561.012

DATE/PLACE: August 18–23, 2002
Davos, Switzerland

AUTHOR: Roberto T. Pabalan

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PERSON(S) PRESENT:

About 1,900 participants attended the symposium.

BACKGROUND AND PURPOSE OF TRIP:

The purpose of the trip was to participate in the 12th Annual V.M. Goldschmidt Conference (Goldschmidt 2002) that was held on August 18 through August 23, 2002, in Davos, Switzerland. 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 a U.S. Nuclear Regulatory Commission (NRC)-sponsored study on the effects of coupled processes on the environment of drip shields and waste packages at the proposed Yucca Mountain repository. In addition, the conference provided an opportunity to get feedback on NRC-funded work and to obtain information from the international community on geochemical issues relevant to nuclear waste management that may be useful in NRC reviews and analyses of U.S. Department of Energy (DOE) work.

SUMMARY OF PERTINENT POINTS:

The 2002 meeting had 10 general symposia and 49 special symposia designed to promote discussion on specific topics within geochemistry. Of the 59 symposia, the following had presentations of particular relevance to the NRC high-level waste program:

- (1) New Geochemical Approaches to Energy, Waste, and the Environment
- (2) Colloids: Their Nature, Reactivity, and Role in the Transport of Pollutants
- (3) Innovative Interpretations of Experimental and Field Geochemical Processes Using Reactive Transport Modeling
- (4) Geochemistry of Pollution
- (5) Novel Approaches and New Techniques in Dating Minerals, Rocks, and Geological Processes
- (6) Environmental Tracers for Groundwater Dating

- (7) Advances in Tracing Sources and Fates of Pollutants in Groundwaters
- (8) Small-Scale Processes in Heterogeneous Environments with Relevance to Environmental Biogeochemistry
- (9) Computational Geochemistry
- (10) Biogenic Substances and Their Effect on Trace Metal Cycling and Mineral Weathering.

I presented a paper titled "Effects of Salt Formation on the Chemical Environment of a High-Level Nuclear Waste Repository." The paper described the results of a modeling study bearing on the plausible range of deleterious chemical conditions that may occur on the drip shield and waste package surfaces. The study showed that Yucca Mountain groundwater could evolve through evaporation to compositions that may lead to an earlier onset and longer duration of aqueous corrosion of the drip shield/waste package than assumed by the DOE in its performance assessment calculations.

The conference abstracts were published by Elsevier Press in a special issue of *Geochimica et Cosmochimica Acta* and are also available at <http://www.goldschmidt-conference.com/2002/gold2002/>. Brief summaries of other pertinent papers follow.

C. Zhu (University of Pittsburgh), presented a paper titled "Groundwater Recharge in Late Pleistocene and Holocene at Yucca Mountain, Nevada". C. Zhu discussed the use of the chloride mass balance method to provide reliable estimates of groundwater recharge beneath the deep unsaturated zone at the Yucca Mountain site. Reliable estimates of recharge at the local scale are important because infiltrating waters provide a potential means for mobilization of radionuclides. Chloride mass balance is economic and effective, provided that the hydrological conditions for its applications are met and the modeling parameters are known. The study presented by C. Zhu shows that Cl^- deposition rates, estimated from Cl-36 data, were lower in late Pleistocene than Holocene at Yucca Mountain, Nevada, but higher in late Pleistocene than Holocene at Black Mesa, Arizona, another arid environment where hydrological data are abundant. The calculated average recharge estimates for Black Mesa are 9 mm/yr [0.35 in/yr] for Holocene and 35 mm/yr [1.4 in/yr] for late Pleistocene, whereas local recharge rates at Yucca Mountain estimated from the $\text{Cl-36}/\text{Cl}$ ratios and Cl^- concentrations in perched waters is 5 mm/yr [0.2 in/yr] for Holocene and 15 mm/yr [0.59 in/yr] for late Pleistocene. These estimates agree well with spatially and time-averaged net infiltration estimates for present-day and glacial transition climates {4.6 mm/yr [0.18 in/yr] and 15.6 mm/yr [0.61 in/yr], respectively} obtained from a watershed-scale infiltration model of Yucca Mountain.

O. Zaidan (St. Lawrence University) presented a paper titled "Computer Simulation of Uranyl Adsorption on Montmorillonite Clay." This paper discussed the results of computer simulations that were conducted to determine the adsorption characteristics of the aqueous uranyl ion on montmorillonite, a smectite clay that is an important sorbing phase in the Yucca Mountain groundwater flow path. The technique used in the study complements batch sorption experiments and surface complexation modeling and provides information on the mechanisms by which radionuclides are sorbed and their transport in groundwater retarded. The mechanistic information derived from these studies provides scientifically defensible bases for evaluating the appropriateness of DOE abstractions of radionuclide transport. The simulation results help explain why montmorillonite has higher K_d s compared to other minerals and

provides support for the parameters proposed for TPA code Version 5.0 using an "effective surface area" approach.

L. Newmark (USGS) discussed the extreme fractionation of U, Th, and Pb in fracture-coating minerals at Yucca Mountain, Nevada, as the basis for U-series and U-Pb dating and establishing the paleohydrologic history of the Yucca Mountain site. The next speaker, Y. Dublyansky (Russian Academy of Sciences) questioned the validity of the U-series and U-Pb dating work that was conducted by L. Neymark on the basis that, for minerals deposited in open cavities or large-aperture fractures, radon-derived Pb isotopes is taken up by the precipitating mineral resulting in enhanced Pb isotope concentration.

J. Zachara (PNNL) gave an overview talk on the mechanisms, significance, and needed conditions for colloid facilitated migration of radioelements, specifically with respect to the subsurface migration of Cs-137 in a high-level nuclear waste vadose zone plume at the Hanford site. At the site, alkaline, high-ionic strength Cs-137 solutions have migrated 30 m [98 ft] through the subsurface, yielding an anomalous distribution profile. Low ionic strength meteoric waters currently infiltrate the site. These waters dilute pore-water Na⁺ and increase adsorptive affinity and colloid migration potential. Waste-induced mineral dissolution and precipitation reactions have occurred, leading to the formation of fine-grained zeolitic phases including sodalite and cancrinite. These phases have comparable Cs-137 adsorptivity to phyllosilicates in local sediments and exhibit surface charge characteristics conducive to particle migration. Column studies performed with pristine and contaminated sediments demonstrate the potential for colloid migration of a portion of the adsorbed Cs-137.

L. Citeau (INRA, France) presented a study that looked at the role of colloids in Zn, Cd, Pb, and Cu mobilization from contaminated soils. Two years of study in which water was collected *in situ* by zero-tension lysimetry in various types of soils show that (i) the nature of mobile colloids depends on the nature of soils and (ii) not all metal transfers involve colloids. For example, while 70 to 80 percent of the Pb in soil water is present in colloidal forms, Zn, Cd, and Cu are found mostly in dissolved forms. Colloidal forms of metals are found to be either organic (bacteria) or mineral (phyllosilicates, Al- or Fe oxyhydroxides and phosphates).

J. Perigault (Stanford University) described adsorption and aggregation experiments that were conducted on a model system of hematite, background electrolyte (NaCl), and three different adsorbates (picolinic acid, pyromellitic acid, and lead). In the study, the triple layer surface complexation model was used to satisfactorily model all the adsorption data. The triple layer surface complexation model was used to evaluate the effect of adsorption on the electrostatic properties of the hematite surface and to estimate surface potentials for different chemical scenarios. The surface potentials were used to calculate interparticle forces between two approaching colloids. Based on these calculations, it was predicted that hematite stability was very sensitive to pyromellitic acid adsorption but indifferent to picolinic acid and lead adsorption, despite large differences between their adsorptive behavior. Experimental stability factors determined using dynamic light scattering data were consistent with the stability trends predicted by the estimated interparticle forces. The results of this work indicate that the triple layer surface complexation model description of the charge/potential relationships at the solid/aqueous interface provides useful information on particle stability.

G.A. Icopini (Pennsylvania State University) discussed the kinetics of silica nanocolloid formation from supersaturated solutions. The study looked at the evolution of silica colloids in simulated brine solutions (ionic strength = 0.25 M) ranging in pH from 3 to 7. Changes in monosilicic acid, nanocolloidal silica (<0.1 μm effective diameter), and silica precipitate concentrations were monitored in batch reactions. An analysis of the reaction kinetics governing the initial stages of transformation from monosilicic acid to nanocolloids reveals that the rate of decrease of dissolved monomeric silica with time, R , has a fourth order rate dependence: $R = k [\text{SiO}_2]^4$. The rate constant, k ($\text{mM}^{-1} \text{sec}^{-1}$) varies with pH according to $k = k_0 [\text{H}^+]^{-0.89}$, where k_0 is the rate constant at pH 0. The results are consistent with the well-known observation that a supersaturated fluid is more likely to create scale the longer it remains in the supersaturated state. This study quantitatively documents the very strong influence of time on scaling.

C.S. Kim (Stanford University) discussed the results of a study using extended x-ray absorption fine structure spectroscopy that looked at the initial species of mercury (Hg) present in contaminated mine wastes and the variables that may control or influence speciation in natural environments. Extended x-ray absorption fine structure speciation analysis of roasted Hg ore (calcines), waste rock, Hg condenser soot, gold mine tailings, distributed downstream sediments, and colloidal particles released from column experiments shows a variety of Hg-bearing phases present among the samples studied, with highly insoluble mercuric sulfides (cinnabar, metacinnabar) most common. Soluble Hg-chlorides, oxides, and sulfates were also identified in several samples and may represent more significant contributors of Hg to the environment. Hg concentration and speciation in mine wastes were found to correlate closely with factors such as the initial conditions of Hg ore deposition, the roasting and weathering processes to which the samples were subjected, and particle size. Most notably, Hg in all samples, even those far downstream from their sources, appears predominantly in the crystalline phase and not as Hg sorbed to sediment particle surfaces. This discovery extends to the colloidal phase, where discrete particles of cinnabar (HgS, hex) as small as 20 nm [7.9×10^{-7} in] in diameter were identified by transmission electron microscopy.

D. Langmuir (Hydrochem Systems Corp.) discussed a study conducted at the McClean Lake Mill in northern Saskatchewan, Canada, where grinding, acid leaching and oxidizing of uranium ore produces high arsenic (As) concentrations {140–2,400 mg/L [parts per million]} in resultant acid raffinate solutions. An extensive laboratory study showed that As levels can be reduced to <2 mg/L [parts per million] if the molar Fe/As ratio of the raffinates is increased (if necessary) to about 3 by adding ferric sulfate before lime addition to attain a nominal pH of 8. With increasing pH most of the As in raffinates precipitates as poorly crystalline Al scorodite and annabergite. Government regulators have questioned whether the lab results for As would be borne out in the Tailings Management Facility. To alleviate government concerns, in June 2001, after two years of operation, tailings and pore waters were sampled from six bore holes in the Tailings Management Facility. With increasing depth (and tailings age) As concentrations peaked at <5-6 mg/L [parts per million] at 10 ft, decreased to <2 mg/L [parts per million] at about 35 ft and to ~1 mg/L [parts per million] at 65 ft depth.

C. Tournassat (Université Joseph Fourier) investigated the sorption of ferrous iron onto clay minerals, an important engineered or natural barrier to radionuclide transport, to determine whether aqueous Fe^{2+} could outcompete radionuclides for sorption sites on the clay. In nuclear waste disposal, the dissolution of containers and reinforced concrete in anoxic conditions could lead to the release of a large amount of ferrous iron into solution. The study showed that Fe^{2+}

can strongly sorb onto smectite particles through cation exchange on the basal planes of the clay particles and by specific adsorption on the clay edge, similar to that for other cations (Zn^{2+} , Co^{2+} , Ni^{2+}). For sorption on clay edge sites, specific complexation constants are much higher for Fe^{2+} than those for Zn^{2+} and Ni^{2+} . Thus, sorption of Fe^{2+} clay particles may potentially have a strong impact on clay immobilization capacity for radionuclides.

E. Curti (Paul Scherrer Institut, Switzerland) described a study on the solubility of radium (Ra) in a radioactive repository environment. In performance assessments, solubilities are generally calculated for pure radionuclide phases. However, geochemical evidence indicates that many radionuclides are incorporated as trace elements in suitable host phases. This study adopted an ideal solid solution model with endmembers $RaSO_4$ and $BaSO_4$ to calculate Ra solubility. The calculations indicated that, compared to pure $RaSO_4$ solubility, solid solution formation with even small amounts of barite will reduce dissolved Ra by three to four orders of magnitude in the Swiss repository design. This substantially reduces calculated Ra fluxes to the geosphere and improves repository performance.

W. Schüßler (Institute for Nuclear Waste Management, Germany) discussed a geochemically based source term assessment for the Asse salt mine, where low- and intermediate-level radioactive wastes were emplaced from 1972 to 1976. The author discussed the application of buffer and backfill materials for closure of the mine. The selection of these materials is based on geochemical modeling taking into account the corrosion of cemented waste forms, degradation of organic matter and the presence of different types of complexing ligands in salt brine. The study led to the conclusion that only cement, $Mg(OH)_2$ -based material and crushed salt should be used as buffer and backfill materials. A Mg-based buffer material provides a long-term stable and robust geochemical milieu. The calculated thermodynamic solubilities of Th, Pu and U are lower than their inventory based concentrations. Maximum concentrations of fission products and other actinides are limited by their inventories.

H. Yoshida (Nagoya University, Japan) presented a study of a redox front migration process in sedimentary rock and its implication for long-term behavior of nuclide migration relevant to near-field processes in radioactive waste disposal. The long-term behavior of redox front migration is considered one of the key processes to evaluate the barrier function of the near-field geological environment. As an analog of long-term redox front migration, a study was conducted on a redox front up to several meters below the ground surface in Tertiary sedimentary rock in central Japan. Detailed microscopic observations and geochemical analysis by XRF, EPMA, ICP-MS and SEM-EDS showed that the redox front has accumulated concentrations of major and minor elements that are at least several times more than the background levels. In particular, transition elements such as Zn, Co and Ni as well as HREE are co-precipitated within a band where Fe and Mn oxide are concentrated at the front. Microscopically, aggregations of spheroidal amorphous ferric iron grains with diameters of a few micrometers are identified in the pore spaces of the sedimentary rock. This suggests that the migration of the redox front might occur at the same time as these amorphous iron oxide grains move through the rock matrix scavenging the dissolved elements during their migration, probably due to their high effective surface area which is available for ionic adsorption.

F. Gauthier-Lafaye (Centre de Géochimie de la Surface, France) reviewed studies about the natural nuclear reactors in Gabon. About two billions years ago, the particular geochemical conditions (low REE and contents which are "poison" for neutrons) and the accumulation of high-grade uranium ores at Oklo initiated fission reactions that were sustained for 100,000 to

500,000 years. These reactors are now considered to be good natural analogues for nuclear waste disposal sites. In the natural reactors and their vicinity, the occurrence of many chemical elements with abnormal isotopic compositions give the unique opportunity to trace in detail the behavior of fission products and actinides during various geochemical processes.

J. Icenhower (PNNL) discussed the results of experimental studies to determine the effects of ion-exchange kinetics on glass degradation. Single-Pass Flow-Through experiments were conducted to evaluate the reaction kinetics of sodium aluminosilicate and borosilicate glasses. The data show that the rates of boron and sodium release become independent of solution composition at high activities of $\text{SiO}_2(\text{aq})$, which is not predicted by transition state theory-based models. The author concluded that ion-exchange reactions exert a governing influence on element release in solutions approaching saturation, therefore, transition state theory models must be modified to accommodate the existing database on glass degradation rates.

E. Pierce (Tulane University) presented the results of flow-through experiments on the dissolution kinetics of UO_2 at pH 8.5, $[\text{HCO}_3^-]=0.1 \text{ M}$, and $T=30 \text{ }^\circ\text{C}$ [86 $^\circ\text{F}$] and $60 \text{ }^\circ\text{C}$ [140 $^\circ\text{F}$]. The results indicate that the elemental release rate of uranium is not only dependent on temperature but also flow rate and surface area. The rates obtained in this study are 1 to 2 orders of magnitude faster than previously reported and may reflect the dependence of rates on the ratio of flow rate to surface area.

K. Mayer (The University of British Columbia) discussed the use of mineralogical data to constrain reactive transport models. Using two examples, one on acid mine drainage from mine tailings and another from a reactive permeable barrier, the authors showed that using mineralogical data as a constraint can improve model reliability, and increases the usefulness of reactive transport models for hypothesis testing. In particular, secondary mineral accumulations can be used to minimize model nonuniqueness.

A number of people asked questions about the status and future of the Yucca Mountain repository program, and whether the NRC will continue to support process level geochemical studies (experimental or modeling). In connection with nuclear waste issues, Dr. V. Dolin (Institute of Environmental Geochemistry, National Academy of Sciences of Ukraine) expressed interest in collaborative work with CNWRA staff on remediation and radionuclide transport issues pertaining to nuclear waste sites at Chernobyl. Dr. Dolin stated that contaminated materials from the Chernobyl nuclear power plant have been disposed in numerous unlined, shallow burial grounds, which could lead to contamination of groundwater.

Dr. R. Blake, Assistant Professor, Department of Geology and Geophysics, Yale University, was awarded the 2002 Clarke Medal of the Geochemical Society. The F.W. Clarke Award is awarded to an early-career scientist for a single outstanding contribution to geochemistry or cosmochemistry, published either as a single paper or a series of papers on a single topic. Dr. Blake is a former CNWRA undergraduate summer intern who worked in the geochemistry laboratory.

IMPRESSIONS/CONCLUSIONS

The symposium was very well organized and attendance exceeded that of all previous Goldschmidt conferences. The conference provided an opportunity to interact with other

scientists on nuclear waste and radionuclide transport issues that may be useful in NRC reviews and analyses of DOE work.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

None.

RECOMMENDATIONS:

Continued participation in future Goldschmidt conferences is highly recommended.

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