UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

JAN 09 1991

MEMORANDUM FOR: Margaret Federline, Chief
Hydrology and Systems Performance Branch
Division of High-Level Waste Management

FROM: John Bradbury
Hydrologic Transport Section
Hydrology and Systems Performance Branch
Division of High-Level Waste Management

SUBJECT: OCTOBER 14-18, 1991, NEA SORPTION WORKSHOP IN INTERLAKEN, SWITZERLAND; OCTOBER 21-25,1991, THE THIRD INTERNATIONAL CONFERENCE ON CHEMISTRY AND MIGRATION BEHAVIOR OF ACTINIDES AND FISSION PRODUCTS IN THE GEOSPHERE

Enclosed is an abstract and a detailed trip report which contains a summary of some of the more important observations that I made as a result of my participation in the two subject meetings.

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Enclosures: As stated

cc: BJYoungblood
JTaylor, EDO
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GPA/IP

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/s/

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Date: 1/9/92

TRIP REPORT ABSTRACT
DATE OF REPORT
1/6/92

| | |
|---|---|
| OFFICIAL TRAVELER:<br>John Bradbury | TRAVEL TO:<br>Interlaken, Switzerland and<br>Jerez de la Frontera, Spain |

BEGINNING ON: 10/14/91 UNTIL: 10/25/91

OFFICE: NMSS
Division of High-Level Waste Management
Hydrology and Systems Performance Branch

MEETING TITLE AND/OR AFFILIATION:

October 14 - 18, 1991, NEA Sorption Workshop

October 21 - 25, 1991, The Third International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '91

ORGANIZED BY: NEA (the workshop)

CIEMAT, CEC, and ENRESA (the conference)

ABSTRACT AND/OR SUMMARY OF MEETING RESULTS

The objectives of NEA Sorption Workshop were to evaluate critically the way sorption processes are incorporated in performance assessment models, to document the current status of application of sorption processes, to identify open issues of high priority, and to propose future activities to resolve these issues. The workshop was divided into two parts; the first part was devoted to an Intercalibration Exercise organized in 1989-1990 by Finland under the auspices of the NEA; the second part concentrated on the comparisons of existing sorption databases used in performance assessments, the methods used to develop such databases, and the experimental techniques employed to measure sorption parameters. Position papers were prepared during the workshop and will be published by the NEA in 1992 along with papers prepared for presentation at the workshop.

The Intercalibration exercise involved nine laboratories from six countries. The United States did not participate in this exercise. The sorption experiment involved cesium and uranium on crushed granite in a synthetic groundwater. Two sets of experiments were to be done - one was supposed to utilize a standardized recipe concocted by the Finns, the other could be methods preferred by the individual laboratories. As it turned out, most of the laboratories did not follow the standardized recipe to the letter. As a

result the Kd values varied by up to about twenty percent. There was much discussion about the cause for this range in experimental uncertainty. It was suggested that given the "uncontrolled" characteristic of batch sorption experiments involving multicomponent systems, better precision should not be expected. The draft position paper presented at the end of the session contained no thoughts that are at odds with the NRC views on sorption experimentation and modeling.

In the second the Canadian approach to modeling a nuclear repository in granite was discussed. Of interest was the recognition that the system will change with time, and thus complicate greatly the modeling effort. At the present time, due to lack of data and computational limitations, the Canadians must assume time-invariant sorption parameters to model the performance of the site.

Also, it was suggested that iron oxyhydroxide may coat all the surfaces of the silicates and control sorption reactions. Apparently, this phase is ubiquitous and is a very strong sorbant. The possibility also exists that organics may coat surfaces of the iron oxide/hydroxide, effectively changing the surface charge from positive to negative. As techniques for surface characterization improve, we should become more concerned with the actual mechanisms of sorption.

A mechanistic approach to sorption was described. The importance of considering competition of major cations for sorption sites was demonstrated. This is important when changes in bulk chemistry are encountered. The need for research modelling to support the separate performance assessment modelling was strongly endorsed. This approach is comparable to our IPA effort which includes the auxillary analyses.

Migration '91

The most common concerns echoed at the Third International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere concerns were those dealing with the problems of differentiating between dissolved and particulate (colloidal) material, redox reactions in aqueous solution and on surfaces, and the effects of microbes and organic complexation on radionuclide migration.

One session dealt with new analytical techniques applied to actinide chemistry. An analytical technique called time-resolved laser-induced spectroflourometry (TRLIS) was applied to organocomplexes of curium to 1E-8 M. Differential pulsed voltammetry was used to determine Pu(IV) speciation. Cyclic voltammetry was used to study Pu(IV) and Pu(V) chemistry. Kinetic phosphorescence analysis was used to analyze a solution for uranium. Laser resonance ionization mass spectroscopy was used to analyze uranium, neptunium, and plutonium down to 1E7 atoms in the sample. Continuous electrophoretic ion focusing has been used for the identification of oxidation states of neptunium and plutonium in ultra-trace amounts.

The 1D migration of C-14 in the unsaturated zone at Yucca Mountain was modeled taking into account temperature changes with time and partitioning the chemical components among the solid (calcite), liquid and vapor. Due to the mobility of the gas phase, drastic excursions in groundwater chemistry can occur.

The papers will be published in Radiochimica Acta and in Journal of Contaminant Hydrology.

DETAILED TRIP REPORT OF:

John W. Bradbury
Hydrologic Transport Section
Hydrology and Systems Performance Branch
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards

SUBJECT: TRIP REPORT ON NEA SORPTION WORKSHOP AND MIGRATION 91 CONFERENCE

The NEA Sorption Workshop was held in Interlaken, Switzerland from October 14-18, 1991. The objectives of this workshop were to evaluate critically the way sorption processes are incorporated in performance assessment models, to document the current status of application of sorption processes, to identify open issues of high priority, and to propose future activities to resolve these issues. The workshop was divided into two parts; the first part was devoted to an Intercalibration Exercise organized in 1989-1990 by Finland under the auspices of the NEA; the second part concentrated on the comparisons of existing sorption databases used in performance assessments, the methods used to develop such databases, and the experimental techniques employed to measure sorption parameters. Position papers were prepared during the workshop and will be published by the NEA in 1992 along with papers prepared for presentation at the workshop.

The Intercalibration exercise involved nine laboratories from six countries. These were AECL (Canada), HY (Finland), VTT (Finland), FUB (Germany), GSF (Germany), SFG (Germany), JAERI (Japan), RIVM (The Netherlands), and PSI (Switzerland). The United States did not participate in this exercise. The sorption experiment involved cesium and uranium on crushed granite in a synthetic groundwater. Two sets of experiments were to be done - one was supposed to utilize a standardized recipe concocted by the Finns, the other could be methods preferred by the individual laboratories. As it turned out, most of the laboratories did not follow the standardized recipe to the letter. As a result the Kd values varied by up to about twenty percent. There was much discussion about the cause for this range in experimental uncertainty. It was suggested that given the "uncontrolled" characteristic of batch sorption experiments involving multicomponent systems, better precision should not be expected.

Some discussion on the rationale for filtering the solutions after the sorption experiment occurred. The assumption is that the filtrate represents that which is mobile. Pore size of the filters ran from 0.45 to 0.20 micrometers. Theory states that particles and colloids from 0.10 to 0.30 micrometers can be carried by the flowing fluid for some distance. Particles larger than 0.30 micrometers would settle out quickly, whereas particles less than 0.1 micrometers would diffuse quickly, maybe to a pore wall, where they would attach due to electrostatic attraction. By removing particles greater than 0.45 micrometers from the solution by filtration, the experimentalist has prepared a solution that could transport radionuclides. He could also argue that since he did not remove the particles that were less than 0.10 micrometers, he has prepared a mobile phase whose radionuclide concentration exceeds that which he expects in the repository. The resulting Kd would be conservative as long as the filter has not sorbed any radionuclide.

The argument against filtration is that since particles greater than 0.3 micrometers should settle out quickly. Thus, there should be no reason to filter at 0.45 micrometers. If needed, centrifugation should suffice to enhance the settling rate. Likewise, based on the theory, it is inappropriate to filter at 0.2 micrometers, as this would remove some of the mobile radionuclide from consideration. Discussions with Julie Canepa from LANL revealed that they do not filter.

At Paul Scherrer Institute, researchers are using dialysis bags to keep the particulate matter separate from the solution. Although this technique raised some eyebrows, as it was more innovative than the usual batch technique, I think it's another step removed from nature. (While writing this trip report, I got distracted and started reading an old NUREG published in 1984 describing the work of R. Meyer at Oak Ridge. Apparently, he was using dialysis bags back in 1983. So much for the scientific community's memory!)

The conclusions of the Intercalibration Exercise are that: 1) there was better agreement between the laboratories than previous intercalibation exercises, although everyone's memory was a little fuzzy when it came to particulars of the previous exercise; 2) the improved agreement was probably due to the extra care taken in preparing the solids; 3) a statement to the effect that the results are good enough for performance assessment was later withdrawn due to a lack of concensus; 4) there is still not 100% agreement; 5) nobody is able/willing to follow instructions; 6) poor overall response; 7) nobody measured the cesium concentration; 8) there was incomplete chemical analysis; and 9) thus, there were limitations on statistical treatment of the data. It was agreed that a position paper be published by NEA describing the results of the exercise. The draft position paper presented at the end of the session contained no thoughts that are at odds with the NRC views on sorption experimentation and modeling.

The second session began with the T. T. Vandergraaf describing the Canadian approach to modeling a nuclear repository in granite. The Canadians are characterizing a site which may or may not be the repository for the nuclear waste. Of interest was his recognition that the system will change with time, and thus complicate greatly the modeling effort. At the present time, due to lack of data and computational limitations, they must assume time-invariant sorption parameters to model the performance of the site.

Vandergraaf also discussed the problems with using sorption parameters derived from experiments with crushed material to model retardation in fractured rock. He stated that it is incorrect to apply bulk sorption coefficients, obtained on crushed rock, to contaminant transport in consolidated material, using measured porosities of the consolidated material in order to determine the retardation coefficient. The sorption coefficient and the porosity must apply to similar states of aggregation. However, he then provided an example where the retardation factor did not vary as a function of consolidation. Apparently, in his example the change in the consolidation of the samples cancelled out the change in the bulk sorption coefficient. I am not yet convinced that this observation is applicable to all systems.

B. Allard discussed two aspects of sorption experimentation that I thought were noteworthy. First, the size of particles in a batch test often exceed grain size, so the particles consist of multiple mineral grains with a coexisting interstitial porosity. In a sorption experiment, radionuclide sorbant diffuses slowly into the particle. Given the short duration of sorption experiments, this diffusion into the particle will continue even after the experiment has stopped and the desorption experiment has begun. As a result, the concentration of radionuclide leached from the solid in a desorption experiment should be less than that in the solution of a sorption experiment. Thus, the one of the processes is not the reverse of the other.

Second, he suggested that goethite may coat all the surfaces of the silicates and control sorption reactions. Apparently, goethite is ubiquitous and is a very strong sorbant. R. Rundberg agreed that this may be taking place in many sorption experiments. The possibility also exists that organics may coat surfaces of the iron oxide/hydroxide, effectively changing the surface charge from positive to negative. As techniques for surface characterization improve, we should become more concerned with the actual mechanisms of sorption. He pointed out that all minerals exhibit similar hydrolyzed surfaces with notable exceptions.

M. Bradbury (the first unrelated Bradbury I ever met) described a mechanistic approach to sorption of neptunium. He demonstrated the importance of considering competition of major cations for sorption sites. This is important when changes in bulk chemistry are encountered. He strongly endorsed the need for research modelling to support the separate performance assessment modelling. This approach is comparable to our IPA effort which includes the auxillary analyses.

I listened to talks on expert elicitation for choosing retardation factors to be used in the modelling of WIPP but came away with an empty feeling. The speakers professed no special knowledge of sorption which bothered me since I wondered how good the selection process of experts could be. It is noteworthy that not all the experts agreed with the ground rules established for assuring compatible values to retardation factors.

R. Rundberg described a multifaceted approach to characterizing sorption processes involving pure minerals, crushed, and rock. With pure minerals, investigations can include adsorption isotherms, thermodynamic and spectroscopic characterization. (He mentioned that Los Alamos is currently setting up an atomic force microscope to look at mineral surfaces.) With crushed rock, investigations can include batch tests and column elutions. With intact rock, the possibility exists that column elutions can be performed along with diffusion experiments.

Of interest was Rundberg's discussion of multiple sorption sites in the zeolites. Sodium ion which is associated with waters of hydration fits preferably in the largest site whereas potassium ion which has fewer waters of hydration can fit into smaller sorption sites. The distinct sites correspond to crystallographic locations. This is noteworthy because the contractors for the State of Nevada were focussing on this aspect of sorption last year. It was their contention that zeolites plastered to fractures would expose crystallographic sites that were less effective sorbers than the average sorption capability determined using crushed material.

Rundberg also reiterated some aspects of retardation experiments at Los Alamos that remain unexplained. First, plutonium (V) and (VI) elute from a crushed tuff column unretarded. This does not correspond to the Kd determined from batch tests. The other point of interest was that some of the pertectnetate hangs up in the first 15 cm of the column. This could be due to an experimental artifact such as bacterial growth of some trace mineral concentrated in that region.

P. Wikberg described laboratory Eh simulations of redox conditions of waters expected around a nuclear waste repository in granite. Of note was the length of time (2 weeks) required for equilibrium to be reached for the Pt electrode with the Fe(II) - Fe(III) couple. And the iron couple appears to be the only one that has ever worked well with the Pt electrode. It was suggested that to control redox conditions in an experiment, nails should be thrown into the reaction vessels. Since Lindberg and Runnells showed that the various electroactive couples in natural waters are normally not in equilibrium with one another, it makes no sense to assume that by attempting to control redox conditions in an experiment we will be able to simulate the oxidation states of the electroactive radionuclides in natural waters. Why bother?

I. Neretniek talked about problems of modeling retardation in systems with constrained geometries. He stated that the pores and crevices can be on the scale of the surface complexation models. Thus, these models might need to be adjusted to simulate reactions in systems of constrained geometry where the liquid unaffected by the solid-liquid interface is absent.

I. McKinley brought up the topic of competing radionuclides in sorption experiments. He stated that a number of years ago he studied a system involving three radionuclides and found to his dismay that he could not sort out the interactions between the radionuclides and the solid phase. This is interesting to me because although the NRC had raised the concern of radionuclide interactions earlier, I had always heard from DOE that due to the fact that the radionuclides will occur in trace amounts, interactions between radionuclides would not be expected. The argument seemed logical to me, so I did not pursue it. Here, then, is evidence to the contrary.

## Migration '91

The Third International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere was held in Jerez de la Frontera, Spain on October 21-25, 1991. This conference involved scientists from twenty countries.

J. Kim began the conference by asking the question, "Why is the migration of actinides and fission products important to us since their concentrations in the geosphere are so small?" He answered his own question by rhetorically asking another question, "Which is more dangerous, an elephant or a virus?"

W. Stumm, famous for his classic textbook on aquatic chemistry, presented the inaugural lecture on metal ion sorption. Although he admitted to his limited exposure to actinide chemistry, his talk covered most of the problemmatic aspects of analytical chemistry that were echoed thoughout the conference. These included problems with differentiating between dissolved and particulate (colloidal) material and redox reactions in aqueous solution and on surfaces. He strongly endorsed the use of surface complexation models.

J. Brainard described the interaction of siderophiles with actinides. In the terms of a nonbiologist, a siderophile is a microbe that can chelate Fe extracellularly, i.e., these microbes excrete a chemical which reacts with iron for the benefit of the cell. It turns out siderophiles can also chelate actinides. Furthermore, siderophiles can solubilize actinides.

K. Pedersen described the effects of bacteria on trace element migration in crystalline bedrock. In this study 12E9 bacteria were found in a cubic meter of groundwater, and the about 1E5 times that are attached to the surfaces. Those attached to surfaces appear to be predominantly sulfate-reducing bacteria. Actinides can sorb onto the surfaces of mobile bacteria, sorb onto immobile bacteria which takes the form of films and slime, or be complexed by chemicals formed by the bacteria. Fast flowing systems supply more nutrients to bacteria. Thus, here is another reason why fractures are different from the matrix.

J. Thompson described the results of field tests on the Nevada Test Site to characterize radionuclide migration in geologic media. The radionuclides were introduced into the geologic environment by underground nuclear tests. He described the Cambric site where groundwater has been analyzed for H-3, Kr-85, Sr-90, Ru-106, Sb-125, Cs-137, Ce-144, and Pu-239. Apparently H-3 has moved with 92% of it being pumped out. The pumping has gone on for 17 years, but was stopped two months ago. Other radionuclides which have been observed in the pumped water, and thus are considered mobile, are Kr-85 and Ru-106. The Kr-85 is inert and consequently moves unretarded. Observing Ru-106 was a surprise, since sorption batch tests indicated Ru should be strongly retarded. It was later determined that Ru could occur as an anion species as well as a cationic species. It was the anionic species that was relatively mobile.

He described another site that was studied for radionuclide migration. This site, U7ag, was fired in fractured zeolitized tuff in 1977. Holes were subsequently drilled around the site to test for radionuclide movement. Ruthenium was observed 650m from the site and it was suggested that its presence was due to fracture flow. Cesium was observed 300m from the site. This observation was unexpected considering the results of batch sortion tests. Thompson suggested that this material was forcibly injected. I talked to him after the presentation about this process. I wondered if there was other chemical evidence to support this hypothesis. He said no, that Cs was in high concentrations and easily detected; other evidence is not so detectible or it decays before the analysis.

J. Kim talked about actinide interactions with groundwater colloids. The colloids were predominantly humic and fulvic acids. He described analytical techniques such as laser fluorescence spectroscopy and photoacoustic detection of light scattering (PALS). Throughout the conference he made it clear that he thought colloids were ubiquitous and important.

P. Vilks discussed colloids at Cigar Lake. Suspended particles consist of fracture-lining minerals such as quartz, micas, clays, chlorite, and Fe-Si oxyhydroxide. Colloids consist of organics, carbonates, iron oxides, and aluminosilicates. From uranium series data on dissolved and suspended material, it was suggested that uranium can be transported as particulates.

H. Nitsche described the solubilities of key radionuclides in J13 and UE25p1 well water. Neptunium solubilities ranged from 1E-3 to 1E-5 m; plutonium solubilities ranged from 1E-6 to 1E-7 m; americium solubilities ranged from 1E-6 to 1E-9. These solubilities were determined approaching equilibrium from supersaturation. These values are essentially the same as reported in the SCP.

R. Killey discussed studies at Chalk River where 80% of the Co-60 is anionic and complexed with high molecular weight organics which are unstable in light. (I wonder if the sorption tests at Los Alamos are done in the dark.) One percent of the cobalt elutes with no retardation. Zr-85, Ru-106, Sb-125, and Cs-144 are also anionic, whereas Fe-55 is both cationic and anionic. Plutonium is 2% cationic and 98% anionic. Americium and curium are both cationic.

An interesting aspect of this study was that Cs content in the water was related to the bacteria content. Irradiation killed the bacteria and the Cs content dropped. However, the bacteria grew back with a corresponding Cs content increase. Repeated irradiation killed off some types of bacteria which were replaced by other types.

One session dealt with new analytical techniques applied to actinide chemistry. C. Moulin described an analytical technique called time-resolved laser-induced spectroflourometry (TRLIS). The technique was applied to organocomplexes of curium to 1E-8 M. Marx used differential pulsed voltammetry to determine Pu(IV) speciation. Capdevila used cyclic voltammetry to study Pu(IV) and Pu(V) chemistry. Waite used kinetic phosphorescence analysis to analyze a solution for uranium. Trautmann used laser resonance ionization mass spectroscopy to analyze uranium, neptunium, and plutonium down to 1E7 atoms in the sample. Continuous electrophoretic ion focusing has been used for the identification of oxidation states of neptunium and plutonium in ultra-trace amounts.

G. Choppin described the role of natural organics in radionuclide migration. He mentioned that organic colloids shrink as ionic strength increases. Also he had evidence that suggested the species that is responsible for charge transfer was repulsed by anionic form of U(VI)(CO3)(OH).

R. Guillaumont discussed environmental plutonium at very low concentrations. The distribution of plutonium in various regions of the geosphere and biosphere is remarkably homogeneous, especially in terrestrial waters in which the concentration is 1E-17M within one order of magnitude. In small volume systems like isolated pores, the concentrations can be 100 atoms/cc. At these concentrations, classical thermodynamics may not apply. For example, from statistical mechanics, the calculation of the energy of a system requires the use of Stirling's approximation. At small numbers of atoms, this approximation becomes invalid. Thus, classical thermodynamics may not apply to systems involving only hundreds of atoms.

R. Codell and W. Murphy coauthored a paper on the migration of C-14 in the unsaturated zone at Yucca Mountain. This 1D modeling effort simulated temperature changes with time and partitioned the chemical components among the solid (calcite), liquid and vapor. Changes in water saturation due to changes in temperature are simulated. Due to the mobility of the gas phase, drastic excursions in groundwater chemistry can occur.

I have the abstracts and list of participants. If you would like to see them or have questions for me, please call me at 504-2535.

DOCUMENT NAME: EURO-PM

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