CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: National Cooperative for the Disposal of Radioactive Waste Workshop on Geochemistry in Performance Assessment (20.01402.871.018)

DATE/PLACE: October 29–30, 2001
Wettingen, Switzerland

AUTHORS: D.R. Turner

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PERSONS PRESENT: D.R. Turner (CNWRA) and about 30 representatives from National Cooperative for the Disposal of Radioactive Waste and other European agencies. See attachments 1 and 2 for a meeting agenda and list of attendees.

BACKGROUND AND PURPOSE OF THE TRIP:

The National Cooperative for the Disposal of Radioactive Waste is the group charged with investigating and evaluating radioactive waste storage options in Switzerland. National Cooperative for the Disposal of Radioactive Waste was created as a cooperative in 1972 and receives funding from both the Swiss federal government and nuclear power plant operators. National Cooperative for the Disposal of Radioactive Waste organized a workshop on the development and justification of geochemical data for performance assessment held in Wettingen, Switzerland on October 28–30, 2001. The main goals for the workshop included:

- To present the geochemical databases and the underlying approaches used for the safety assessment of the proposed high-level waste repository in the Opalinus Clay to an international audience;
- To have the geochemical approaches in safety assessment reviewed by internationally recognized experts and compare them with approaches from other radioactive waste programs;
- To set priorities for future geochemical research in the context of performance assessment;
- To promote collaboration for specific research topics.

A strong focus of the meeting was on "surprises" encountered in the course of preparing the National Cooperative for the Disposal of Radioactive Waste safety assessment. These included geochemical consistency, data gaps, and unresolved issues. The meeting was structured to provide sufficient time for discussions within plenary sessions and in working groups. Working groups were established to consider three specific topics:

- *In-situ* conditions
- Sorption/diffusion
- Solubility data

An additional plenary session was dedicated to general applications of geochemical information in performance assessment.

The workshop was attended by about 30 invited experts from National Cooperative for the Disposal of Radioactive Waste , France, Spain, Belgium, Sweden, Finland, Germany, Japan, the United States and Switzerland.

MEETING SUMMARY

The following is a brief summary of presentations made by the meeting participants. The author of this trip report has a copy of the materials presented by the participants in the workshop.

B. Schwyn (National Cooperative for the Disposal of Radioactive Waste)

B. Schwyn of National Cooperative for the Disposal of Radioactive Waste presented a brief overview of the proposed repository design in the Swiss high-level waste program and identified the places where geochemistry is considered within the Entsorgungsnachweis Performance Assessment. Key design attributes of the system that contribute to safety include a steel canister and bentonite backfill. Key aspects of the natural system include the reducing groundwater conditions (reduced solubility, corrosion) and the impermeable geologic barrier of the Opalinus Clay. Radionuclide transport is dominated by diffusion, and the sorption coefficient (K_d) is used to derive the effective diffusion coefficient (D_e). Geochemical databases include thermodynamic data, sorption/diffusion data, and information on mineralogy and water chemistry. The approach taken by the Swiss is more deterministic than the stochastic approaches adopted in the United States High-Level Waste program. Geochemical parameters are assigned best estimates, and in some cases bounding analyses are performed to support the safety assessment calculations. Of additional note, is the length of time considered in the Entsorgungsnachweis Performance Assessment. Calculations are run out to 10^6 years and more, in contrast to the much shorter 10^4 years considered in the United States High-Level Waste program.

<u>Plenary Session 1: *In-Situ* Conditions</u>

L. Johnson (National Cooperative for the Disposal of Radioactive Waste)

L. Johnson of National Cooperative for the Disposal of Radioactive Waste presented the current operational designs and conditions considered for the evolution of the near field in the Entsorgungsnachweis Performance Assessment. The current operations are designed to minimize disruption of the Opalinus Clay, and each emplacement drift is to be open for a maximum of 1–2 years. The current backfill design calls for compacted bentonite with an average dry density of 1.5 Mg/m^3 and a low moisture content of 2–3 percent, although this will saturate over time. Low thermal conductivity in the bentonite will lead to high initial temperatures at the waste package/bentonite contact in the range of 160 °C, with gradual cooling over 10^4 years to ambient. The outer half of the bentonite backfill is expected to remain unaltered because temperatures will not exceed 110 °C.

Porewater chemistry is expected to remain relatively constant over time. There will be some evolution of the redox conditions due to oxidation of pyrite in the Opalinus Clay, limited redox buffering capacity, and the large reducing capacity of the steel canisters and production of H_2

gas. It is expected that the conditions will be reducing in the near-field environment; any radionuclides will be present in reduced valence states [e.g., U(IV), Tc(IV), Np(IV), and Pu(III)]. This has the advantage of reducing radionuclide solubility, and enhancing retardation (high K_d).

A. Muurinen (VTT Technology–Finland)

A. Muurinen of VTT Technology discussed efforts in the Finnish High-Level Waste program to obtain water samples from compacted bentonite for chemical analysis. Several different methods were evaluated, including squeezing, leaching, centrifugation, and sintering. Each method has its own drawbacks, and does not necessarily give consistent results. This leads to significant uncertainty with regard to the porewater chemistry used in performance assessment. One additional complicating factor in determining porewater chemistry is the difficulty in discerning among the different types of water in the clay matrix. These include free porewater, electrostatically bound water, and interlayer water in the clay, each of which has a potentially different physical-chemical representation.

E. Curti (Paul Scherrer Institut)

E. Curti of Paul Scherrer Institut presented the results of using thermodynamic models to estimate key geochemical parameters in bentonite porewater. The thermodynamic model included a simplified representation of the bentonite mineralogy (smectite, quartz, gypsum, calcite, NaCl, and other trace minerals). Chemical equilibrium saturation was assumed for quartz, kaolinite, calcite, and gypsum. Redox was assumed to be controlled by equilibrium saturation with magnetite, an analog for steel corrosion products. Finally, the system was assumed open to CO_2 exchange by diffusion. Smectite was assumed to contribute to chemistry through exchange at amphoteric sites and internal cation exchange.

There are limited data available from squeezing to use to test the model results. In general, the model provided a reasonable simulation of major geochemical constituents as a function of bentonite density. Accounting for the electrostatic double layer does not have much effect on calculated major ion chemistry, but incorporation of water in the clay interlayers can increase concentrations by a factor of two to three.

<u>Plenary Session 2: Sorption-Diffusion</u>

M. Ochs (BMG Engineering)

M. Ochs of BMG Engineering presented an overview of sorption-diffusion modeling and reviewed the limits of the models. There are a number of concerns with the parameters contributing to the apparent diffusion coefficient (D_a) used in the Entsorgungsnachweis Performance Assessment. For example, the K_d that is used is typically measured under disperse conditions (low solid/water ratios on the order of a few kg/m^3). Using these values in Entsorgungsnachweis Performance Assessment diffusion models for clay, however, requires upscaling to compacted conditions where solid/water ratios can be in the range of 1 to 2 Mg/m^3 for compacted bentonite backfill. The validity of this upscaling where bound water may contribute significantly to water chemistry is one area of uncertainty in the diffusion models. Other parameters such as porosity, tortuosity, and effective diffusivity are also difficult to measure for clay. In constructing models, decisions must be made about whether the level of complexity included in the model is justified given the parameter uncertainty. Complexity that has been considered includes electrostatic effects, surface diffusion, and anion exclusion

through electrostatic layer constriction. These limitations notwithstanding, Dr. Ochs presented modeling results that provided a reasonable prediction of experimental results. Because the experimental dataset is limited, however, the "state-of-the-art" does not yet include a consistent dataset for D_a for all materials and radionuclides of interest in performance assessment.

B. Baeyens (Paul Scherrer Institut)

B. Baeyens of Paul Scherrer Institut presented a novel approach used to develop a sorption database for the Entsorgungsnachweis Performance Assessment. This approach presented a way to incorporate geochemical effects on sorption in a manner appropriate for performance assessment that takes into account data quality, selection criteria, and offers a consistent hierarchy of procedures to develop the necessary sorption database. Emphasis is placed on developing transparent, traceable, and technically justifiable procedures for populating a sorption database. This includes taking raw experimental sorption data, and using a combination of linear scaling factors to adapt these data to site specific mineralogy, pH, and speciation. Keeping in mind the deterministic nature of Entsorgungsnachweis Performance Assessment, the best estimates are selected and used in the database. A lower (conservative) bound is estimated based on dividing the selected value by an "overall uncertainty factor" that is approximately equal to five for the scaling factors used in the methodology.

As a test, Dr. Baeyens presented tests of the methodology for Ni(II) and Th(IV). The Ni(II) example provided excellent agreement between estimated and measured values. The Th(IV) example, however, did not provide good agreements, possibly due to uncertainties in Th(IV) speciation.

D. Turner [Center for Nuclear Waste Regulatory Analyses (CNWRA)]

I presented the results of efforts to abstract information from detailed sorption models for the U.S. Nuclear Regulatory Commission (NRC) Total-system Performance Assessment code. I included a brief overview of the United States High-Level Waste program, describing the statutory roles of the different federal agencies involved, and describing the conceptual model for a proposed repository at Yucca Mountain. The basic concept of defense-in-depth for long-term geologic disposal is similar to the Swiss model. The geology, hydrology, and geochemistry of the natural system are very different, however, and the probabilistic approach used in the NRC Total-system Performance Assessment is very distinct from the Entsorgungsnachweis Performance Assessment.

At the CNWRA, approaches have been developed to examine methods for including aspects of detailed sorption models into Total-system Performance Assessment calculations and addressing the effects of geochemical variability on radionuclide sorption. In one approach, parameter distributions are calculated based on variability in site-specific water chemistry from the Yucca Mountain vicinity. Model results are used to provide limits on K_d probability distribution functions as input into performance assessment. Under the groundwater chemical conditions observed at Yucca Mountain, calculated sorption parameters can range over many orders of magnitude. This approach has been implemented in the current version of Total-system Performance Assessment, and dose calculations were presented. Another approach is to calculate sorption behavior for a wide range in geochemical parameters and develop response surfaces for actinide sorption as a function of geochemistry.

M. Bradbury (Paul Scherrer Institut)

M. Bradbury of Paul Scherrer Institut presented an evaluation of the approach described by B. Baeyens (see previous discussion) for scaling K_d from disperse clay/water systems to compacted clays. Applying the scaling factors described previously, Dr. Bradbury compared K_d values derived from batch experiments for Cs(I), Ni(II), Am(III), Zr(IV), and Np(V) to those derived from laboratory diffusion experiments with compacted bentonite/montmorillonite. Within the limitations of the modeling approach, the agreement is good, within a factor of two to three. The agreement is noteworthy given that the sorption experiments were typically conducted at different laboratories under different conditions. This suggests that it is possible to scale sorption data from disperse systems to the compacted conditions of concern in the Swiss Entsorgungsnachweis Performance Assessment.

Plenary Session 3: Solubility Data

J. Bruno (EnvirosQuantisci)

J. Bruno of EnvirosQuantisci presented an overview of the use of natural analogs to constrain solubility limits for performance assessment. The behavior of 10 different trace metals (Ba, Sr, Sn, Pb, Se, Ni, Zn, Th, U, REE) was examined at six different analog sites:

(1) El Berrocal, Spain

(2) Palmottu, Finland

(3) Oklo, Gabon

(4) Cigar Lake, Canada

(5) Pocos de Caldas, Brazil

(6) Maqarin, Jordan

Based on this work, Th and U were determined to be controlled by individual solid phases. Sr, Ba, Zn, Se, REE, and U were also controlled by association with major components in the system. For example, Sr, Ba, and Zn were controlled by coprecipitation in Ca-phases. Analog data can be used to eliminate insignificant phases from thermodynamic databases used in performance assessment and identify mineralogical associations likely to affect radionuclide mobility. Analog research can also identify the best modeling approaches to use in geochemical calculations for performance assessment.

U. Berners (Paul Scherrer Institut)

U. Berners (Paul Scherrer Institut) presented the approaches used to construct the thermodynamic database used to calculate best estimates of solubility for Entsorgungsnachweis Performance Assessment. Starting with the thermodynamic data used for an earlier safety assessment, inconsistencies, gaps and differences in aqueous speciation equilibrium constants for trivalent (Np, Pu, Am, and Eu) and tetravalent actinides (Th, U, Np, and Pu) were identified. These gaps were filled in by a combination of fits to laboratory data, where available, and chemical analogy arguments where lab data were not available.

Complementing the database in this way produced significant changes in aqueous speciation, but this did not necessarily translate into differences in calculated solubility. For trivalent actinides, the exercise suggests that aqueous actinide-silicates are important, while for tetravalent actinides, mixed hydroxy-carbonate species may be of some significance. It is important to note, however, that calculated solubilities for each actinide are very different because different solubility limiting phases were chosen for different radionuclides.

S. Altmann (ANDRA)

S. Altmann (ANDRA) presented an overview of the French High-Level Waste program. The conceptual model under evaluation in France is very similar to that considered in the Swiss High-Level Waste program. The main contributor to performance in the natural barrier system is the thick impermeable Callovo-Oxfordien clay. The French have completed preliminary performance assessment calculations for 2001 and are scheduled to improve this for 2004, when a referendum will be held on the proposed conceptual design.

Working Groups

The following is a brief summary of the working groups. These comments are specific to the Swiss High-Level Waste program and conceptual designs and may not translate well to the proposed repository at Yucca Mountain, Nevada.

In-situ Conditions

There is a general need to evaluate different radionuclides under the redox conditions imposed by the relevant redox couples in the system. There is a need for kinetic studies to evaluate the transient behavior of redox evolution. It is important to include the effects of carbon dioxide in the system.

There still remains a great deal of uncertainty with regard to porewater chemistry in the clays and in compacted bentonites. There was no consensus reached on how to best distinguish among the different porewater types (bulk free water, electrostatically bound water, interlayer water), nor was there agreement on how important this is to performance assessment.

Sorption/Diffusion:

There was a general agreement that the approach of Baeyens and Bradbury shows promise, but additional work will be necessary to refine the scaling factors, particularly with regard to aqueous speciation. The generally good agreement between K_d values determined in batch and diffusion experiments is a good confidence builder, but it should be checked with different dry densities and extended to other radionuclides. The group also agreed that the remaining uncertainties in porewater composition affect the ability to use detailed geochemical modeling to simulate sorption, leading to conceptual model uncertainty.

Solubility

There is good field information available from analog sites to constrain uranium and thorium solubilities, and solid solutions with alkaline earth elements. There is remaining uncertainty in thermodynamic databases for trivalent and tetravalent actinides, and the significance of mixed hydroxy-carbonate and actinide-silica species remains to be examined in detail. The greatest

concern of the working group was the applicability of thermodynamic data for disperse systems to compacted clay systems, again tied to the uncertainty in porewater composition.

SUMMARY AND CONCLUSIONS:

On October 29–30, 2001, the Swiss National Cooperative for the Disposal of Radioactive Waste sponsored a workshop at Swiss National Cooperative for the Disposal of Radioactive Waste headquarters in Wettingen, Switzerland on the role of geochemistry in nuclear waste performance assessment. I presented an invited paper entitled "Radionuclide Sorption: Abstracting Information from Detailed Models for High-Level Waste Performance Assessment," summarizing work done to incorporate sorption modeling results in the NRC Total-system Performance Assessment code. The following is a brief summary of the meeting.

The geology considered in the Swiss performance assessment is very different from Yucca Mountain, Nevada. The site is in a clay unit (the Opalinus Clay) under hydrologically saturated, geochemically reducing conditions. The mineralogy of the clay is montmorillonite, calcite, and other trace minerals (including pyrite). The dominant radionuclide transport mechanism of concern is diffusion through the clay. The Swiss performance assessment differs from the approach taken in the U.S. High-Level Waste program in a number of key ways. A striking difference is the time frame of 1 million years as opposed to the 10,000 years regulatory time frame at Yucca Mountain. As opposed to the stochastic approaches adopted in the United States program, the Swiss performance assessment is deterministic, using best values for diffusion, solubility, and sorption derived from detailed geochemical modeling. In contrast to the oxidizing conditions assumed at Yucca Mountain, the Swiss program is very concerned about the redox behavior of the system, and relies on detailed geochemical modeling to establish which redox couples control localized reduction-oxidation. An additional concern is the scaling up of sorption experiments conducted under dispersed conditions, to high-density compacted clay. The situation for using geochemical models to derive performance assessment parameters is also complicated by the difficulty in obtaining water samples from the clay materials, where bulk water in a compacted clay system may be modified by electrostatically bound water and interlayer water.

The Swiss program and other European High-Level Waste programs seem to be reaching key decision points where feasibility studies and safety assessments are to be prepared in the next several years and presented for consideration by the public. Geochemical issues are considered more explicitly in the European performance assessment exercises, and it appears that basic research activities will be proposed to establish more firmly the necessary databases for simulating radioelement solubility and sorption under geochemically reducing conditions. Even though the United States High-Level Waste program is very different from the various European programs, the attendees expressed interest in continued United States participation in these efforts, particularly with regard to how to treat uncertainty in stochastic approaches to performance assessment.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

National Cooperative for the Disposal of Radioactive Waste is to provide a summary of the meeting for review and comment. D. Turner will review the summary and provide any necessary comments to the meeting organizers.

SIGNATURE

David R. Turner — Date: 11/21/2001

CONCURRENCE

English C. Pearcy — Date: 11/27/2001
Manager, Geohydrology and Geochemistry

Budhi Sagar — Date: 11/27/2001
Technical Director

ATTACHMENT 1

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A *In-Situ* Conditions	B Solubilities	C Sorption-diffusion
L. Johnson	P. Wersin	B. Schwyn
J.F. Pearson	J. Bruno	D. Turner
A. Muurinen	Th. Fanghänel	S. Altmann
T. Missana	K. Spahiu	P. de Cannière
H. Wanner	E. Giffaut	M. Ochs
N. Waber	M. Snellman	M. Cormensana
E. Curti	P. Hernán	M. Bradbury
B. Baeyens	U. Berner	J. Hadermann
A. Gautschi	W. Hummel	E. Wieland

17/10/01

ATTACHMENT 2

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Geochemistry Workshop:

The use of geochemical data for PA. Surprises, difficult issues and new opportunities encountered in the Swiss PA study «Entsorgungsnachweis»

October 28–30, 2001

Wettingen, Switzerland

REVISED PRELIMINARY PROGRAMME

Sunday, Oct 28

18:00 Arrival and common dinner in the Hotel du Parc, Baden

Monday, Oct 29

08:30	Welcome and introduction of participants	P. Zuidema, P. Wersin
08:45	Introduction to workshop, goals, expectations	P. Zuidema
09:00	Nagra's new geochemical databases: overview, lessons learnt, uncertainties....	B. Schwyn

Block I In-situ conditions in the near-field chairman: J. Pearson

09:15	Introduction, geochemical processes in near field, a holistic view	L. Johnson
09:35	Possibilities and limits of experimental data to derive porewater chemistry in compacted bentonite	A. Muurinen
09:55	Modelling porewater chemistry in compacted bentonite: conv. models and limits	E. Curti
10:15	Discussion	

10:45 Coffee break

Block II Sorption-diffusion part 1 chairman: M. Ochs

11:00	Introduction, current sorption-diffusion models and their limitations	M. Ochs
11:20	Sorption database for Swiss SF/HLW repository	B. Baeyens
11:40	Sorption data used for PA	D. Turner
12.00	Discussion 1 (sorption processes)	
12:40 - 14:00	Lunch	

Sorption-diffusion part 2

14:00	Comparison of distribution coeff. from sorption and diffusion experiments?	M. Bradbury

14:20 Sorption and solubility data derived from diffusion experiments P. de Cannière
14:40 Discussion 2 (sorption-diffusion modelling)
15:15 Coffee break
15:40 Formation of 3 working groups "solubilities" (Wersin) ", "in-situ conditions" (Johnson), "sorption-diffusion" (Schwyn)

18:30 - 19:45 Roman bath at Limmathof, Baden
20:00 - 22:00 Dinner at Restaurant Pavillon, Baden

Tuesday, Oct 30

Block III Solubility data chairman: T. Fanghänel
08:30 Challenges for solubility limits in PA: how include natural systems information? J. Bruno
08:50 Solubility database for Swiss SF/HLW repository U. Berner
09:10 Discussion
09:50 Coffee break

Block IV General applications chairman: K. Spahiu
10:10 Transport and retardation in the C-O formation, Andra's present thoughts for PA S. Altmann
10:30 Key messages related to geochemical approach for H-12 still open
10:50 Discussion
11:15 Continuing 3 working groups "solubilities", " in-situ conditions", "sorption-diffusion"
13:00–14:30 Lunch
14:30 Presentation of results from WG
15:30 Discussion of WG results chaired by J. Hadermann
16:00 General discussion on priorities & possibilities for possible collaboration areas P. Zuidema