ATTACHMENT 2

LR-287-7
7/15/85

LETTER REPORT

TITLE: Concerns Relative to the Applicability of the Yucca Mountain Radionuclide Sorption Information for Site Performance Assessment Purposes

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PROJECT TITLE: Technical Assistance in Geochemistry

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SUMMARY

We are concerned that the information on radionuclide sorption and retardation available for the Yucca Mountain candidate repository site may prove to be inappropriate or inadequate for utilization in site characterization and repository licensing activities due to the use of potentially nonconservative or inaccurate experimental methodology, and that application of the sorption information may not meet the regulatory criteria of reasonable assurance. We suggest that it could be productive to address some of the specific concerns listed below through interaction between the Nuclear Regulatory Commission/Office of Nuclear Material Safety & Safeguards (NRC/NMSS), Oak Ridge National Laboratory (ORNL), Nevada Nuclear Waste Storage Investigations (NNWSI), and Los Alamos National Laboratory (LANL).

1. PURPOSE

The purpose of this letter report is to document some of our concerns relative to the radionuclide sorption information that has been developed by LANL for the NNWSI project. We have assumed that the NNWSI plans to use this information in performance assessment calculations both during characterization of the Yucca Mountain candidate repository site and in a repository license application. Our concerns have evolved both from an extended review, conducted on this NRC/NMSS project, of the sorption information published by LANL and from some initial results of our experimental evaluation of the LANL sorption methodology which we have recently started under a companion NRC/NMSS project (#B0290).

2. SPECIFIC CONCERNS

2.1 Lack of Sorption Information Compilation and Synthesis

The LANL has been conducting extensive experimental measurements of various radionuclide sorption values relative to the Yucca Mountain site since about 1979. The results of this work have been described in detail (see Section 3) in progress reports, topical reports, summary reports, and papers at Department of Energy (DOE) contractor meetings, Materials Research Society meetings, and other meetings. This reportage represents over 1000 pages of text and contains several thousand individual sorption values. Unfortunately, we have been unable to find any single report or paper that attempts to compile and synthesize this mass of data to yield a coherent and consistent understanding of radionuclide sorption and retardation in either the engineered facility or the site far field at Yucca Mountain. Much of the reporting has been limited to a description of the experimental methods employed and documentation of the values measured without further explanation of the potential relevance or application of the values in performance assessment calculations. We do not understand how NNWSI plans to model sorption for the Yucca Mountain site. Also, we can not tell which of the many published values are the key or important ones that may be utilized in the site characterization and repository licensing process. Therefore, it is difficult for us to assess questions such as the applicability, relevance, or completeness of the published sorption information with respect to regulatory requirements for the Yucca Mountain candidate site.

2.2 Timeliness of Reporting

In order for the NRC and its contractors to evaluate information in a timely manner consistent with regulatory schedules, it is desirable that the NRC remain current with the conceptual approach and the experimental or calculational results being conducted at the DOE projects. Unfortunately, in the case of the Yucca Mountain sorption information, most reports available to us are over a year behind the LANL activities. The most recent report received in the ORNL library is LA-10154-PR, the quarterly progress report for January-March 1984 of all the NNWSI activities at LANL. In our meeting with LANL staff at the USGS Core Library at Mercury, Nevada, in February 1985, we heard interesting topics peripherally discussed that have not yet appeared in publications available to us. Of particular interest to the subject of this letter report were comments that LANL had not been able to correlate measured sorption values and experimental parameters for many radionuclides, and that a computer regression program was being written to attempt to establish such correlations. We suggest that it could be beneficial to the NRC/NMSS goals if some means of more rapid and frequent interaction could be established between ORNL and LANL to facilitate information transfer.

2.3 Absence of a Performance Assessment Strategy for Sorption Modeling

The NNWSI or LANL has not revealed the performance assessment strategy to be employed for the Yucca Mountain site, therefore, we are unable to evaluate the relevance to site assessment activities of the sorption methodology employed or the values measured. The NNWSI has not indicated how, or even if, credit for sorption and retardation will be taken at Yucca Mountain in the performance assessment of the engineered facility and/or the site far field. Thus, we cannot evaluate their position on sorption since it is unknown. We suggest that it may be desirable for the NRC to attempt to explore the strategy planned by NNWSI for Yucca Mountain; at least qualitative knowledge of the performance assessment strategy is essential in order for the NRC to evaluate many types of information including sorption information.

The release pathway for groundwater from emplaced waste to the accessible environment and the important sorptive minerals along the pathway have not been completely identified for the Yucca Mountain repository. Much of the thrust of the LANL sorption information effort (for example, LA-9328-MS and LA-9846-PR) has been aimed at correlating radionuclide sorption with tuff sample mineralogy. Good correlations were only obtained for Sr, Cs, and Ba sorption onto clinoptilolite [LA-9328-MS]. However, until the release pathway mineralogy is defined, the completeness or applicability of the measured sorption value/tuff mineralogy correlation for even these few radionuclides must be considered unknown.

Many of the sorption values reported by LANL for Yucca Mountain are for fission product radionuclides such as Sr, Cs, Ba, etc. Some of these have relatively short half-lives and might be expected to decay prior to canister failure and availability for migration. Release scenarios that could make migration of these radionuclides to the accessible environment a potential problem have not been published, thus we are uncertain as to the relevance of the short-lived fission product sorption information to the repository assessment modeling. It is desirable to determine whether NNWSI plans to explore other key radionuclides, and which ones.

2.4 Uncertain Applicability of Distribution Coefficient Values Measured with Crushed Rock Samples to Model Fracture-Flow Geologic Systems

Sorption ratios measured in batch contact tests are often assumed, as NNWSI has done [DOE (1984)], to be equivalent to distribution coefficients and used to calculate retardation factors for solutes such as radionuclides in groundwater. This calculation assumes that the radionuclides in groundwater will exhibit conventional ion exchange chromatographic behavior during migration through the geologic media. This assumption is valid only if: (1) the sorption and desorption reactions are rapid and reversible, (2) the bulk of the geologic media is available for sorption, and (3) saturated conditions exist. These conditions are often, but not necessarily, met for migration of trace metal contaminants in soil, but can not be satisfied for radionuclide migration in fractured impermeable media. These constraints on the application of batch contact methodology were recognized in the earliest LANL publication [LA-7216-MS], but seem not to have been addressed in more recent reports.

A good discussion of the problems involved in calculating the retardation of radionuclides due to sorption in a fractured dense host rock is given in Neretnieks (1980) or McKinley and Hadermann (1984). The simplifying approach inherent in the treatment reported by NNWSI [DOE (1984)] assumes that the entire bulk of the host rock is available for sorption. Neretnieks (1980) shows that the calculated retardation factors obtained by this method are both inaccurate and non-conservative because the rate of diffusion of radionuclides into the rock is slow compared to the groundwater migration rate. Neretnieks (1980) develops sound arguments for determining the accessibility of the rock matrix to the radionuclides and using this information in transport equations to estimate retardation due to sorption. We suggest that such an approach to retardation in the Topopah Spring tuff could yield more defensible retardation factor values than those obtained using the simplified non-conservative assumptions in DOE (1984).

A limited amount of work has been reported by LANL to compare radionuclide retardation measured by column chromatographic techniques with the retardation factors calculated from batch contact distribution coefficient values [LA-9329-MS]. Poor agreement resulted in some cases; plutonium behavior was different in flow-through column tests vs batch contact tests and the batch contact values proved to be non-conservative [LA-9793-PR]. This disagreement suggests that some experimental parameter(s) for the batch contact tests is(are) not representative of dynamic systems. In any case, this column work still involved the use of crushed rock material. A few experiments to measure radionuclide sorption by tuff rock wafers have also been described [LA-9577-PR], but this information apparently was not utilized in the performance assessment in DOE (1984).

We suggest that interaction with NNWSI and LANL on this fundamental concern relative to sorption methodology may be particulary desirable since every indication is that LANL is continuing to give emphasis to batch contact experiments employing crushed rock material. If this concern should be upheld after additional scrutiny, then most of the radionuclide sorption information for the Yucca Mountain site may be unacceptable for licensing purposes.

2.5 Unevaluated Batch Contact Methodology Test Protocol and Parameters

The batch contact methodology employed with crushed tuff to measure sorption and desorption ratios appears to have been established by LANL in 1977 for experimental work with Yucca Flat soils [LA-7216-MS], and then used without substantial alteration of the test protocol or parameters in subsequent work with argillite [LA-7455-MS], granite [LA-7456-MS], and finally in the extensive tuff work from 1979 through the present time.

None of the reports describe how the protocol or parameters were selected or optimized for the material under investigation. We were surprized to see that geologic materials as dissimilar as soil, shale, granite, and tuff were treated identically in experiments. A discussion of the sensitivity of the measured sorption or desorption values to the methodology is not generally included in the reports. This deficiency may render questionable the precision, accuracy, and, therefore, the applicability of the reported values for modeling purposes.

A careful description of the batch contact methodology is given in LA-9328-MS. This methodology is very similar to that given in LA-7216-MS and LA-7455-MS, or the sorption methodology handout given to us at the meeting in February, 1985 (Bayhurst, et al., unpublished). No justification or optimization of the important parameters used such as crushed rock/groundwater ratio, rock particle size, contact temperature, contact time, method of recovering groundwater after contact, etc. is given. We are concerned that the protocol and parameters used may not be optimized and that the information obtained could be biased or inaccurate.

2.6 Groundwater Instability During Experiments

Most of the sorption and desorption experiments conducted by LANL, and the resulting tables of sorption ratio values [LA-9328-MS, LA-9846-PR, DOE (1984)], have been carried out with radionuclide-traced water from well J-13, which is adjacent to Yucca Mountain. The natural pH of this groundwater is 6.7 to 7.0. This pH has been extensively documented in LANL reports (for example, LA-9328-MS). We have recently received two samples of J-13 well water and have measured similar pH values. On standing with exposure to air, we have observed that the pH rises to considerably higher values, probably due to loss of dissolved CO§2. In most of the LANL batch contact experiments, the final pH after contact was reported to be from 8 to 9 when the test atmosphere was air. In tests involving an inert atmosphere of nitrogen, the final pH was even higher. We are concerned that pH changes of this magnitude during the sorption experiments could result in changes in both the rock/groundwater system and the measured sorption ratios to conditions or values which would not be representative of repository conditions. Many fission product and actinide radionuclides exhibit speciation changes with increases of pH from near neutral to pH 8 to 10 and the concomitant changes in bicarbonate/carbonate concentrations. Reactive minerals present in the tuff samples might also be altered by such pH changes. We are concerned that the Yucca Mountain sorption information obtained under test conditions that allowed the pH to range so far from the natural system pH may be of questionable relevance to the repository. We know the LANL staff are now aware of this concern about CO_2 loss and pH change since we heard some discussion of this point during the February meeting at Mercury, Nevada. However, the new LANL work under a CO_2/air atmosphere has not yet appeared in published reports available to us. We suggest that it may be important to pursue this concern with LANL because the bulk of the sorption ratio information was measured under experimental conditions that allowed this pH increase and, therefore, may be of uncertain applicability for the repository analysis activities.

A second aspect of groundwater instability during the tests involves the recent discovery by LANL that the well water contains microorganisms which grow when exposed to light [LA-10006-PR, LA-10032-PR]. LANL has reported that bacterial growth is occurring in the batch contact tests and that the presence of bacteria increased the measured plutonium sorption ratio values [LA-10154-PR]. We have not seen results from tests that explore the effect of bacterial growth on the sorption information for the other radionuclides. Bacteria might be expected to scavenge a number of the transition elements and actinides from solution. We have confirmed that microorganisms grow in the J-13 well water on exposure to light. This recent discovery by LANL brings into question all their previous sorption work with this water. We can only assume that similar growth occurred in all previous LANL experiments with J-13 well water involving all radionuclides. This previously unrecognized biological activity brings into question the validity of much of the published Yucca Mountain sorption information for use in repository performance assessment calculations. As with the pH changes discussed in the previous paragraph, we suggest that this subject should be a topic for NRC interaction with NNWSI and LANL.

3. SORPTION INFORMATION REPORTS

The reports published by LANL that contain sorption methodology descriptions or sorption information related to Yucca Mountain are given below in chronological order. Additional papers presented at DOE contractors meetings, Material Research Society meetings, or other meetings in general repeated the information contained in these LANL reports and are not listed.

LA-7216-MS, K. Wolfsberg, Sorption-Desorption Studies of Nevada Test Site Alluvium and Leaching Studies of Nuclear Test Debris, April 1978.

LA-7455-MS, B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, P. Q. Oliver, and K. Wolfsberg, Sorption-Desorption Studies on Argillite: I. Initial Studies of Strontium, Technetium, Cesium, Barium, Cerium, and Europium, March 1979.

LA-7456-MS, B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, C. J. Duffy, F. O. Lawrence, S. Maestas, P. Q. Oliver, and K. Wolfsberg, Sorption-Desorption Studies on Granite: I. Initial Studies of Strontium, Technetium, Cesium, Barium, Cerium, Europium, Uranium, Plutonium, and Americium, February 1979.

LA-7480-MS, K. Wolfsberg, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, B. P. Erdal, F. O. Lawrence, A. E. Norris, and J. R. Smyth, Sorption-Desorption Studies on Tuff: I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada, April 1979.

LA-8110-MS, E. N. Vine, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, P. Q. Oliver, J. L. Thompson, and K. Wolfsberg, Sorption-Desorption Studies on Tuff II. A Continuation of Studies with Samples from Jackass Flats, Nevada, and Initial Studies with Samples from Yucca Mountain, Nevada, January 1980.

LA-8747-MS, K. Wolfsberg, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. P. Erdal, F. O. Lawrence, S. Maestas, A. J. Mitchel, P. Q. Oliver, N. A. Raybold, R. S. Rundberg, J. L. Thompson, and E. N. Vine, Sorption-Desorption Studies on Tuff: III. A Continuation of Studies with Samples from Jackass Flats and Yucca Mountain, Nevada, May 1981.

LA-9327-PR, Compiled by W. R. Daniels, B. R. Erdal, D. T. Vaniman, and K. Wolfsberg, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, January 1-March 31, 1982, October 1982.

LA-9328-MS, W. R. Daniels, K. Wolfsberg, R. S. Rundberg, A. E. Ogard, J. F. Kerrisk, C. J. Duffy, T. W. Newton, J. L. Thompson, B. P. Bayhurst, D. L. Bish, J. D. Blacic, B. M. Crowe, B. R. Erdal, J. F. Griffith, S. D. Knight, F. O. Lawrence, V. L. Rundberg, M. L. Skyes, G. M. Thompson, B. J. Travis, E. N. Treher, R. J. Vidale, G. R. Walter, R. D. Aguilar, M. R. Cisneros, S. Maestas, A. J. Mitchell, P. Q. Oliver, N. A. Raybold, and P. L. Wanek, Summary Report on the Geochemistry of Yucca Mountain and Environs, December 1982.

LA-9329-MS, E. N. Treher and N. A. Raybold, The Elution of Radionuclides Through Columns of Crushed Rock from the Nevada Test Site, October 1982.

LA-9484-PR, Compiled by K. Wolfsberg, W. R. Daniels, B. R. Erdal, and D. T. Vaniman, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1-June 30, 1982, October 1982.

LA-9577-PR, Compiled by W. R. Daniels, B. P. Erdal, and D. T. Vaniman, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1-September 30, 1982, March 1983.

LA-9666-PR, Compiled by A. E. Ogard, W. R. Daniels, and D. T. Vaniman, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, October 1-December 31, 1982, May 1983.

LA-9691-PR, Compiled by W. R. Daniels, Laboratory and Field Studies Related to the Radionuclide Migration Project, October 1, 1981-September 30, 1982, May 1983.

LA-9793-PR, Compiled by K. Wolfsberg, D. T. Vaniman, and A. E. Ogard, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, January 1-March 31, 1983, June 1983.

LA-9846-PR, Compiled by A. E. Ogard, K. Wolfsberg, and D. T. Vaniman, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1-June 30, 1983, December 1983.

LA-10006-PR, Compiled by E. A. Bryant and D. T. Vaniman, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1-September 30, 1983, July 1984.

LA-10032-PR, Compiled by K. Wolfsberg and D. T. Vaniman, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, October 1-December 31, 1983, August 1984.

LA-10154-PR, Compiled by B. M. Crowe and D. T. Vaniman, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, January 1-March 31, 1984, February 1985.

4. ADDITIONAL REFERENCES

The following references were also cited in the text:

B. P. Bayhurst, W. R. Daniels, S. D. Knight, B. R. Erdal, F. O. Lawrence, E. N. Treher, and K. Wolfsberg, A Batch Method for Determination of Sorption Ratios for the Partition of Radionuclides Between Groundwaters and Geologic Materials, unpublished LANL document, personal communication from K. W. Thomas, February 1985.

DOE (1984), Department of Energy, Draft Environmental Assessment; Yucca Mountain Site, Nevada Research and Development Area, Nevada, DOE/RL-0012, December 1984.

I. G. McKinley and J. Hadermann, Radionuclide Sorption Database for Swiss Safety Assessment, EIR-Bericht Nr. 550, October 1984.

I. Neretnieks, J. Geophys. Res. 85, 4379-4397 (1980).

ATTACHMENT 3

ORNL WS-41350

CONCERNS RELATIVE TO THE APPLICABILITY OF THE YUCCA MOUNTAIN SORPTION INFORMATION FOR SITE PERFORMANCE ASSESSMENT PURPOSES

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PRESENTED AT
ORNL PROGRAM REVIEW
(FIN No. B0287/B0290)

SEPTEMBER 18–19, 1985
OAK RIDGE, TENNESSEE

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ORNL WS-41351

OUTLINE OF CONCERNS*

1. LACK OF SORPTION INFORMATION COMPILATION AND SYNTHESIS
2. TIMELINESS OF REPORTING
3. ABSENCE OF A PERFORMANCE ASSESSMENT STRATEGY FOR SORPTION MODELING
4. UNCERTAIN APPLICABILITY OF DISTRIBUTION COEFFICIENT VALUES MEASURED WITH CRUSHED ROCK SAMPLES TO MODEL FRACTURE-FLOW GEOLOGIC SYSTEMS
5. UNEVALUATED BATCH CONTACT METHODOLOGY TEST PROTOCOL AND PARAMETERS
6. GROUNDWATER INSTABILITY DURING EXPERIMENTS

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*DETAILED IN LETTER REPORT LR-287-7, JULY 15, 1985.

ORNL WS-41352

LACK OF COMPILATION AND SYNTHESIS

- EXTENSIVE REPORTAGE BY LANL OF INDIVIDUAL SORPTION VALUES HAS APPEARED IN QUARTERLY PROGRESS REPORTS
- WE HAVE NOT IDENTIFIED ANY REPORT THAT COMPILES AND SNYTHESIZES THESE VALUES TO YIELD AN UNDERSTANDING OF RADIONUCLIDE SORPTION IN EITHER THE ENGINEERED FACILITY OR IN THE FAR FIELD
- WE CANNOT TELL:
  - WHICH OF PUBLISHED SORPTION VALUES ARE "KEY" VALUES
  - HOW NNWSI PLANS TO MODEL SORPTION AT YUCCA MOUNTAIN
- THUS WE CANNOT ASSESS QUESTIONS SUCH AS:
  - APPLICABILITY OF SORPTION INFORMATION TO ENGINEERED FACILITY OR YUCCA MOUNTAIN FAR FIELD
  - RELEVANCE OF SORPTION INFORMATION TO REPOSITORY LICENSING PROCESS
  - COMPLETENESS OF SORPTION INFORMATION TO SATISFY REGULATORY REQUIREMENTS

ORNL WS-41353

TIMELINESS OF REPORTING

- MOST RECENT REPORT OF SORPTION INFORMATION RECEIVED AT ORNL IS LA-10299-PR, THE NNWSI QUARTERLY FOR JULY–SEPTEMBER 1984
- WE HEARD INTERESTING TOPICS DISCUSSED IN OUR MEETING IN FEBRUARY 1985 AT THE CORE LIBRARY IN MERCURY, NV, WHICH HAVE YET TO BE AVAILABLE TO US IN PRINT
- IT MAY BE DESIRABLE TO ESTABLISH A MORE RAPID INFORMATION EXCHANGE SYSTEM BETWEEN ORNL AND LANL

ABSENCE OF PERFORMANCE ASSESSMENT STRATEGY FOR THE YUCCA MOUNTAIN SITE

- NNWSI HAS NOT INDICATED (OTHER THAN IN DRAFT EA) HOW, OR EVEN IF, CREDIT FOR SORPTION/RETARDATION OF VARIOUS RADIONUCLIDES WILL BE ESTIMATED IN THE ENGINEERED FACILITY OR FAR FIELD AT YUCCA MOUNTAIN
- RELEASE PATHWAY FROM EMPLACED WASTE TO THE ACCESSIBLE ENVIRONMENT, AND THE SORPTIVE MINERALS AND GEOCHEMICAL CONDITIONS ALONG THE PATHWAY, HAS NOT BEEN COMPLETELY DEFINED
- MUCH OF PUBLISHED SORPTION INFORMATION IS FOR Sr, Cs, Ba; THESE ELEMENTS HAVE SHORT HALF-LIVES AND MAY BE EXPECTED TO DECAY PRIOR TO CANISTER FAILURE AND RELEASE AT 1000 YEARS
- Am > Pu > Tc ARE PROBABLY KEY ELEMENTS AT 1000 YEARS AFTER EMPLACEMENT; THESE ARE NOT WELL ADDRESSED IN PUBLISHED SORPTION INFORMATION
- *WE CANNOT EVALUATE NNWSI'S POSITION ON SORPTION SINCE IT IS UNDEFINED*

ORNL WS-41355

UNCERTAIN APPLICABILITY OF SORPTION INFORMATION FOR MODELING FRACTURE-FLOW GEOLOGIC SYSTEM

- ION-EXCHANGE BEHAVIOR AS CONCEPTUAL MODEL OF RADIONUCLIDE REACTIONS WITH SORBENT (K_d CONCEPT)
- CHROMATOGRAPHIC BEHAVIOR AS MATHEMATICAL MODEL OF RADIONUCLIDE RETARDATION IN GROUNDWATER (R_f CONCEPT)

$$R_f = 1 + K_d\left(\frac{\rho}{\theta}\right)$$

- THIS METHOD WAS DEVELOPED FOR SOIL/GROUNDWATER SYSTEMS
- THIS METHOD HAS BEEN USED PRIMARILY TO DESCRIBE FISSION PRODUCT MIGRATION

UNCERTAIN APPLICABILITY (CONT'D)

- K_d (EQUILIBRIUM DISTRIBUTION COEFFICIENT) ASSUMES:
  - SORPTION REACTIONS ARE RAPID AND REVERSIBLE
  - ONLY ONE FORM OF THE RADIONULCIDE IS PRESENT (NO MULTIPLE SPECIES OR COLLOIDS)
  - TEST MATERIALS AND CONDITIONS MODEL IN SITU MATERIALS AND CONDITIONS (ROCKS, GROUNDWATER, RADIONUCLIDE SPECIES, Eh, pH, etc.)
- R_f (CHROMATOGRAPHIC RETARDATION FACTOR) ASSUMES:
  - K_d INDEPENDENT OF RADIONUCLIDE CONCENTRATION
  - BULK ROCK AVAILABLE FOR SORPTION
  - SATURATED CONDITIONS EXIST
  - TEST MATERIALS AND CONDITIONS USED IN K_d MEASUREMENT REPRESENT GEOLOGICAL SYSTEM

ORNL WS-41357

UNCERTAIN APPLICABILITY (CONT'D)

- RELIANCE ON K_d AND R_f CONCEPTS LEADS TO INACCURATE AND NONCONSERVATIVE PREDICTIONS OF RADIONUCLIDE RELEASES TO THE ENVIRONMENT FOR FRACTURE-FLOW SYSTEMS
- USE OF FRESHLY CRUSHED ROCK IS NOT REPRESENTATIVE OF FRACTURE-FLOW MINERALS
- USE OF SATURATED CONDITIONS DOES NOT MODEL YUCCA MOUNTAIN REPOSITORY
- KEY RADIONUCLIDES HAVE NOT BEEN EMPHASIZED IN PUBLISHED INFORMATION

ORNL WS-41358

UNEVALUATED METHODOLOGY

- BATCH CONTACT METHODOLOGY ESTABLISHED FOR USE WITH YUCCA FLAT SOILS
- FAILURE OF REPORTS TO DESCRIBE HOW PROTOCOL OR PARAMETERS FOR BATCH TESTS WERE SELECTED OR OPTIMIZED FOR YUCCA MOUNTAIN MATERIALS; IDENTICAL METHOD USED WITH SOIL, ARGILLITE, GRANITE, AND TUFF
- PARAMETERS NOT OPTIMIZED OR SENSITIVITY EXPLORED:
  - CRUSHED ROCK/GROUNDWATER RATIO
  - ROCK PARTICLE SIZE
  - CONTACT TEMPERATURE
  - CONTACT TIME
  - METHOD OF RECOVERING GROUNDWATER AFTER CONTACT
- *PROTOCOL AND PARAMETERS USED MAY GENERATE BIASED OR INACCURATE INFORMATION*

ORNL WS–41359

GROUNDWATER INSTABILITY

- ACTUAL J-13 WELL WATER USED IN MOST PUBLISHED SORPTION EXPERIMENTS
- IN MOST PUBLISHED EXPERIMENTS, ELEVATION OF pH FROM ~7 TO ~9 DUE TO CO_2 LOSS DURING TEST
- MICROORGANISMS GROW IN J-13 WATER DURING TESTS
- *GROUNDWATER IN TESTS, THEREFORE, NOT REPRESENTATIVE OF IN SITU CONDITIONS*

ORNL WS-41360

CONCLUSIONS

- PUBLISHED YUCCA MOUNTAIN SORPTION INFORMATION MAY BE BOTH INACCURATE AND NONCONSERVATIVE
- INFORMATION MAY NOT BE ACCEPTABLE FOR PERFORMANCE ASSESSMENT PURPOSES FOR SITE CHARACTERIZATION OR LICENSE APPLICATION

ORNL-WS 41476

APPLICATION OF RADIONUCLIDE SORPTION INFORMATION FOR PREDICTION OF RETARDATION IN FRACTURE-FLOW GEOLOGIC SYSTEMS

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Presented at

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ORNL-WS 41477

OUTLINE

1. Review assumptions underlying K_d and R_f concepts for modeling radionuclide sorption and migration
2. Identify limitations/inaccuracies in applying K_d and R_f concepts to fracture-flow systems and actinide elements
3. Review some recent European publications
4. Summary

CONVENTIONAL METHOD OF DESCRIBING RADIONUCLIDE MIGRATION IN A GEOLOGIC SYSTEM

- Ion-exchange behavior as conceptual model of radionuclide reactions with sorbent (K_d concept)
- Chromatographic behavior as mathematical model of radionuclide retardation in migrating groundwater (R_f concept)

$$R_f = 1 + K_d\left(\frac{\rho}{\theta}\right)$$

- Good review of history of development of this method given by Lester et al., in Zwiebel and Sweed, AIChE Symposium **71**, 202–213 (1975)
- Developed for soil/groundwater systems
- Primarily used to describe fission product migration

ASSUMPTIONS UNDERLYING K_d AND R_f MODELING

- K_d (equilibrium distribution coefficient) assumes:
  - — Sorption reactions rapid and reversible
  - — Only one form of the radionuclide is present (no multiple species or colloids)
  - — Test materials and conditions model in situ materials and conditions (rocks, groundwater, radionuclide species, Eh, pH, etc.)
- R_f (chromatographic retardation factor) assumes:
  - — K_d independent of radionuclide concentration
  - — Bulk rock available for sorption
  - — Saturated conditions exist
  - — Test materials and conditions used in K_d measurement represent geologic system

ORNL-WS 41480

SORPTION REACTIONS

(KINETIC ASPECTS OF K_d APPROACH)

Reaction	Often Rapid and Reversible
Ion Exchange	Yes
Surface Adsorption	Yes
Chemisorption — Redox change — Interstitial substitution	No
Precipitation/Filtration	No

Conclusion: Only YES reactions can be modeled by K_d concept.

ORNL-WS 41481R

SELECTION OF KEY RADIONUCLIDES

- Selection of key radionuclides based on:
  - Those where NRC 10^{-5} release rate from waste package exceeds EPA release to environment amounts:

    Am > Pu > Tc ¦ > Np

    Source: Virginia Oversby, LLNL, personal communication, July 1985.
  - 99% of 1000-year activity in Am (53.6%), Pu (44.4%), and Tc (0.8%)

    Source: HEDL-TME-84-30, 1985.

KEY RADIONUCLIDES (MULTIPLE SPECIES/COLLOID ASPECTS OF K_d APPROACH) (CONTINUED)

Forms of Radionuclides Possible Under Repository Conditions

Key Radionuclides	Multiple Valences	Multiple Species	Colloids
Am		X	X
Pu	X	X	X
Tc	X		
Np	X	X	?

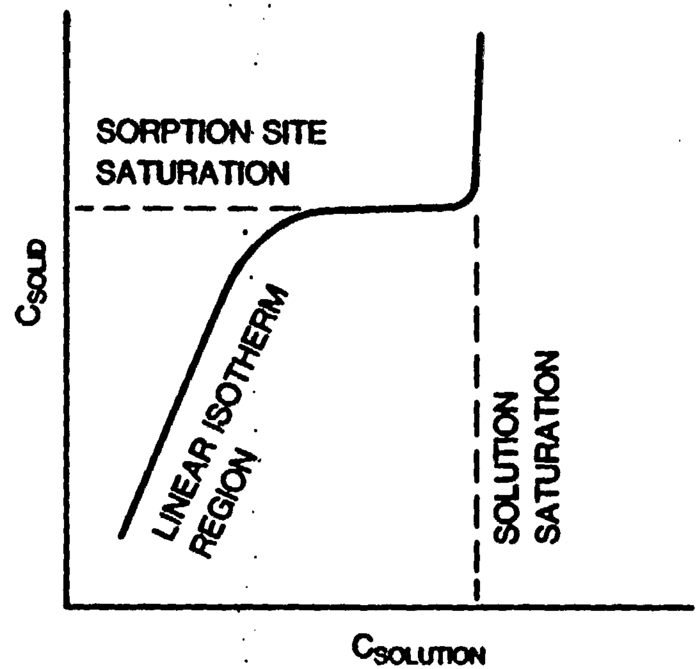
Conclusion: No key radionuclides unambiguously meet single-form assumption.

ORNL DWG 85-1087

SORPTION ISOTHERMS

(K_d INDEPENDENT OF CONCENTRATION ASPECT OF K_d APPROACH)

- Typical sorption isotherm (C = concentration)



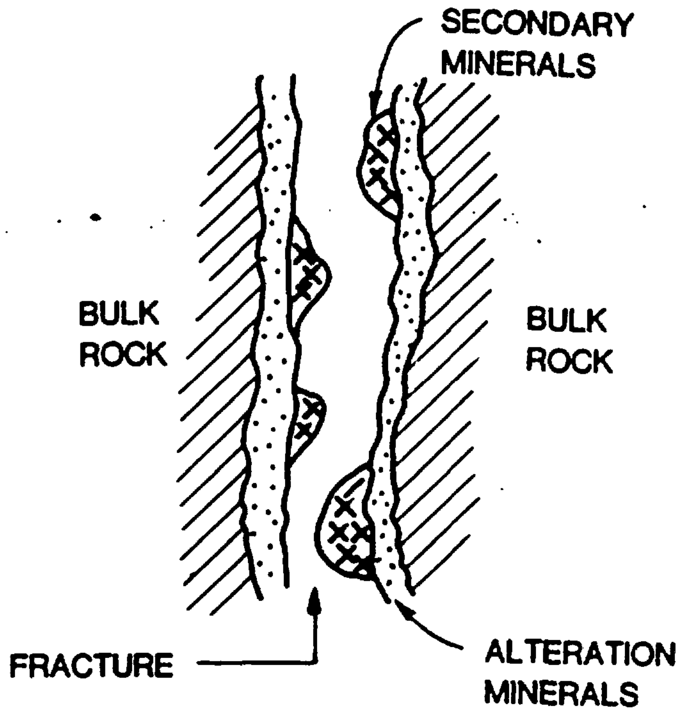
- K_d may be relatively independent of radionuclide concentration only at very low concentrations

Conclusion: K_d approach valid only if it can be shown that radionuclide concentration cannot be higher than linear region.

ORNL DWG 85-1088

IDEALIZED FRACTURE-FLOW SYSTEM

(BULK ROCK AVAILABILITY AND TEST MATERIALS REPRESENTATIVE ASPECTS OF R_f APPROACH)



Conclusions:

- Groundwater velocity probably much greater than rate of diffusion of radionuclides into bulk rock, thus K_d nonconservative.

- Freshly crushed bulk rock surfaces used in test probably not representative of fracture minerals, thus test may not be representative of in situ behavior.

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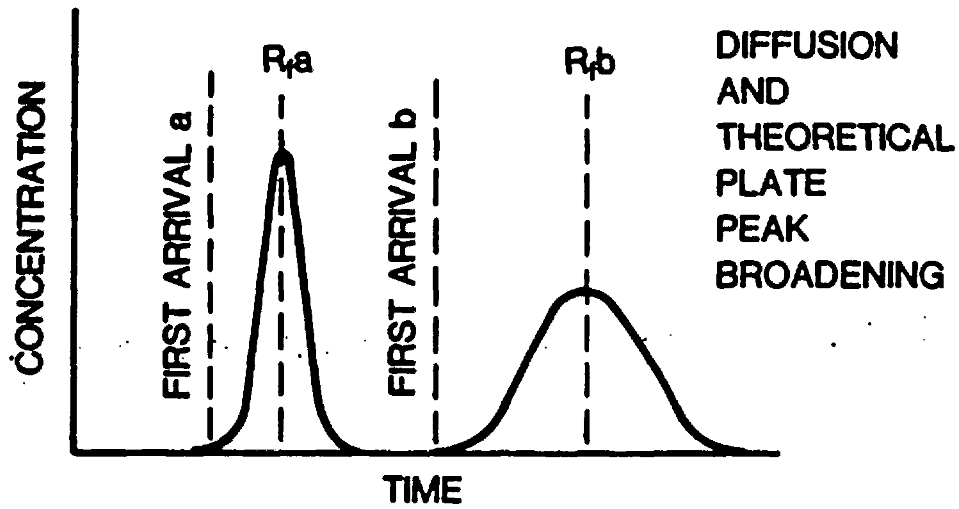
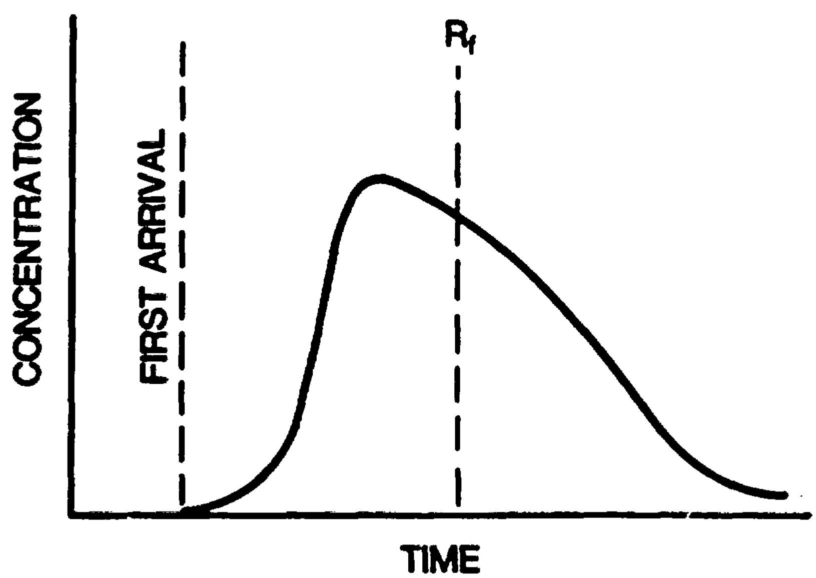
INACCURACIES IN R_f CHROMATOGRAPHIC PEAK CALCULATIONS FOR RADIONUCLIDE MIGRATION

- R_f calculated is for mid-point of idealized chromatographic peak, not time of first arrival or peak concentration.

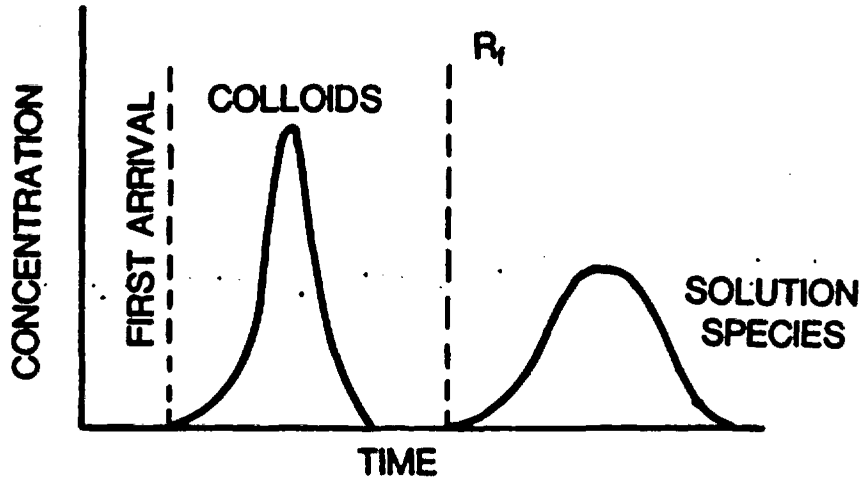


- Nonlinear sorption isotherm results in skewed peak.

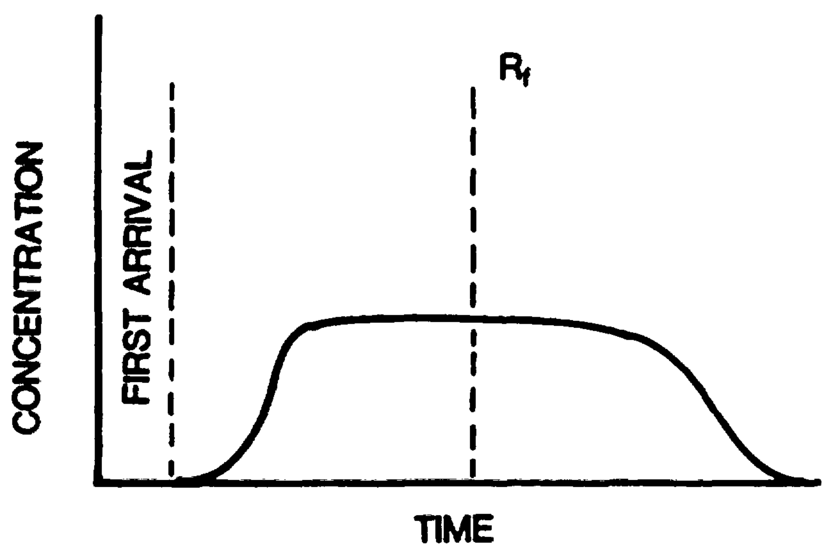


INACCURACIES (CONTINUED)

- Presence of multiple species/colloids can greatly alter chromatographic peaks.



- Two species—no interconversion.



- Two species—rapid conversion.

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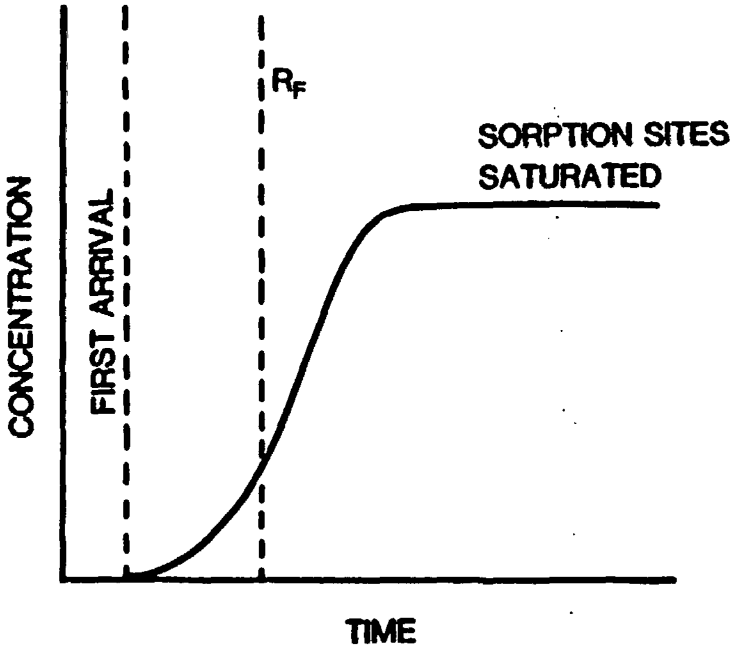
INACCURACIES (CONTINUED)

- Continuous release of radionuclide from waste form eventually would produce continuous release to environment.



Conclusions:

- R_f concept does not predict concentration released to environment as a function of time
- R_f concept cannot deal with competition for sorption sites (displacement chromatography)

ORNL-WS 41483

NRC DISCUSSION OF UNCERTAINTIES IN SORPTION INFORMATION

- Problems in extrapolating laboratory sorption measurements to repository behavior over geologic times:
  - Groundwater/rock ratio
  - Reactions of primary, secondary, and accesory minerals
  - Reaction kinetic limitation on time extrapolation
  - Radionuclide speciation effects
  - Groundwater/host-rock reactions
  - Thermal and radiation pulse effects

Source: Nuclear Regulatory Commission, NUREG-0960, Appendix T, 1983

ORNL-WS 41484

WASTE ROCK INTERACTION TECHNOLOGY (WRIT) PROGRAM RECOGNIZED PROBLEMS INHERENT IN BATCH CONTACT METHODOLOGY

- Relyea et al., PNL-3349, 1980:
  - Reversible ion exchange or surface adsorption is mechanism underlying batch test methodology.
  - Study of fracture-flow systems needed (p. 22).
- Serne and Relyea, PNL-3997, 1982:
  - All existing computer migration codes rely on K_d concept.
  - Traditional use of K_d assumes linear isotherm.
  - Unresolved problem—absence of scaling factors to convert lab results with disaggregated rock to model in situ fractured rock with low matrix porosity (p. 34).

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INITIAL LANL REPORT RECOGNIZED UNDERLYING ASSUMPTIONS FOR BATCH CONTACT METHODOLOGY

- Wolfsberg, LA-7216-MS, 1978, p. 2:
  - Sorption—desorption ion exchange reactions basis for chromatographic work with equilibrium distribution coefficient (K_d).

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BWIP SORPTION WORK ALSO BASED ON K_d AND R_f APPROACH

- Salter et al., RHO-BWI-LD-43, 1981, p. 1:

  $$R = 1 + (\rho/\theta)K_d$$

- Salter et al., RHO-BWI-LD-48, 1981, p. 1:

  $$R = 1 + (\rho/\theta)K_d$$

  — Noted equation valid only for equilibrium sorption where sorption can be described as a linear isotherm.

ORNL-WS 41487

NEXT VIEWGRAPHS SUMMARIZE SOME INTERESTING FOREIGN PUBLICATIONS

- Canadians, Swiss, and Swedes plan repositories in granite.
- Radionuclide release pathway will be fracture flow through relatively impermeable bulk rock.
- Modeling efforts under way to describe radionuclide migration in such a system.

ORNL-WS 41488

NERETNIEKS, *J. GEOPHYS. RES.* 85, 4379 (1980)

- Paper discusses migration in bed rock surrounding a repository.
- Considers both sorption and matrix diffusion.
- Sorption mechanism assumptions make conventional extrapolation of laboratory-measured data inaccurate for calculation of radionuclide migration in bed rock.

ORNL-WS 41489

NERETNIEKS (CONTINUED)

Two limiting sorption conditions:

1. Bulk reaction (K_d concept)
   - Water is assumed to flow evenly through porous bed rock and bulk of rock will be equilibrated with radionuclides.
   - Overestimates the radionuclide retardation capacity of the rock if all parts not accessed by water.
2. Surface reaction (K_a concept)
   - Assumes water flows only in the macrofissures and radionuclides react only with fissure surface.
   - Underestimates the radionuclide retardation capacity of the rock since diffusion into microfissures and pores not considered.

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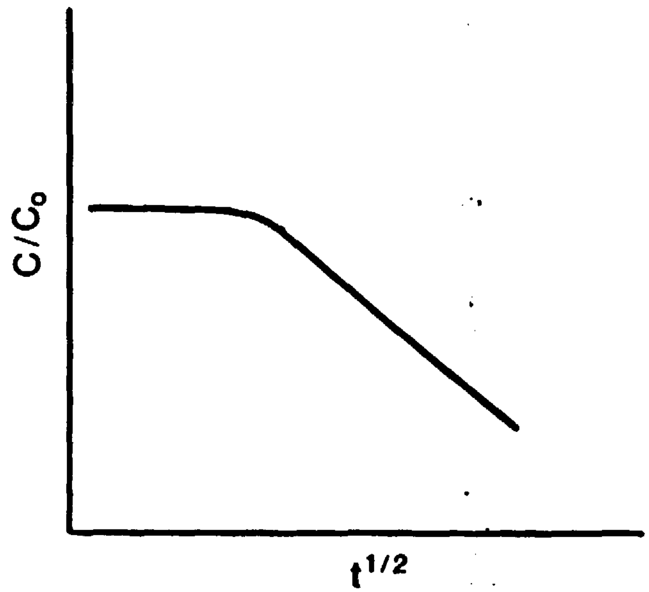
NERETNIEKS (CONTINUED)

- Discourages use of either K_d or K_a since both are particle size dependent.
- Recommends combination of matrix diffusion and sorption phenomena.
- Experimental support for diffusion into granite seen in published sorption experimental results.



From data of Seitz (1978), Allard (1978), and Erdal (1979) for granite.

NERETNIEKS (CONTINUED)

Conclusions of Neretnieks studies:

- Radionuclide diffusion into rock is important.
- Largest fractures will dominate radionuclide transport due to $(2b)^3$ half-width term. 2 × larger fracture = 64 × earlier arrival.
- Tests with crushed rock inappropriate since rock stressed beyond breaking point and new microfissures have been introduced.

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CHAPMAN AND SARGENT, AECL-8361, 1984

- Critizes existing solute transport models since:
  - — Only equilibrium controlled sorption reactions are considered.
  - — Assume fluid flow independent of chemical changes in system.
- Recommends including more realistic chemistry:
  - — Direct coupling of transport equations for reacting species.
  - — Coupling geochemical reaction models to a flow modes.
- Identified need to deal with:
  - — Speciation.
  - — Slow kinetics.

ORNL-WS 41492

MORENO, NERETNIEKS, AND ERICKSEN
***WATER RESOURCES RES.* 21, 951(1985)**

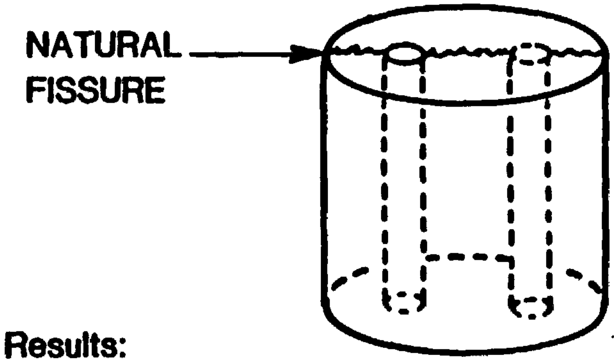
- Performed analysis of laboratory tests of radionuclide migration in natural fissure by two models.

- Models:
  - — Hydrodynamic dispersion–diffusion
    - Assumes radionuclides flow in single parallel wall fissure.
  - — Channeling dispersion—diffusion
    - Assumes transport takes place in parallel channels of different widths.
    - Velocity different in each channel.

ORNL DWG 85-1093R

MORENO ET AL. (CONTINUED)

- Experimental setup



Nonsorbing tracers I^-, Br^-
Sorbing tracer Sr^{2+}

- Results:
  - — Both models gave good agreement for nonsorbing tracers.
  - — Essential to include matrix diffusion term.
  - — Fair agreement with Sr^{2+} batch data when both sorption and matrix diffusion considered.
  - — Tests needed with longer fractures.

McKINLEY AND HADERMANN, SWISS TR 84-40, 1985

- Good review of approaches taken to describe sorption in geologic media.

  — Ideal solution

  a. Langmuir isotherm, assumes:

  — Ideal solution behavior.

  — Radionuclide sorbed as monolayer.

  — Sorption surface homogeneous.

  — No interaction between sorbed species.

  — Sorbed species fixed on surface.

  Poorly describes most geologic systems.

  b. Freundlich isotherm, assumes:

  — Ideal solution behavior.

  — Surface affinity decreases exponentially as amount sorbed increases.

  Frequently gives good fit of experimental data. Cannot be extrapolated beyond data.

  c. Dubinin-Radushkevich isotherm:

  — Describes sorption of sparingly soluble solutes.

  — Amount sorbed is function of sorption potential.

  — Thermodynamically derived equation, but usually used for curve fitting.

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McKINLEY AND HADERMANN (CONTINUED)

— Empirical

— In real world neither solution or sorbed phase exhibit ideal behavior.

— Usually collect data and fit curve.

— Cannot be extrapolated beyond data.

— Thermodynamic

— Could be extrapolated.

— Work under way.

— Data base small.

— Mineral systems not at equilibrium.

ORNL-WS 41405

McKINLEY AND HADERMANN (CONTINUED)

- Identified problem areas, or aspects of radionuclide sorption not considered by existing approaches:
  - — Kinetics (slow reactions)
  - — Reversibility (chemisorption)
  - — Colloids (real or pseudo)
  - — Microbiological activity (big unknown)
- Report also contains good summary of radionuclide geochemistry in granite systems.

ORNL-WS 41496

HADERMANN AND ROESEL, SWISS TR 85-40, 1985

- Develops mathematical model for radionuclide chain transport in inhomogeneous rock.
- Model includes surface sorption and matrix diffusion.
- Conclusions of Hadermann and Roesel:
  - Width of zone of altered rock adjacent to flowing water is most important parameter.
  - Radionuclide transport in altered rock zone and in pores in intact rock differ strongly.
  - Mechanical dispersion in the water conducting zones is relatively unimportant.
  - Sorption capacity of altered rock zones is important.
  - Transport by colloids needs more attention.
  - Nonlinear sorption is the rule; isotherms must be used, not single K_d values.

ORNL-WS 41407

SUMMARY OF CONCERN RELATED TO CONCEPTUAL MODEL OF RADIONUCLIDE SORPTION UNDERLYING BWIP OR LANL MEASUREMENTS

- Method—batch or column contact of crushed rock with excess volume of radionuclide-traced groundwater.
- Assumption—ion-exchange chromatographic behavior describes radionuclide sorption in geologic systems.
- Conditions necessary for assumption to be valid:
  - — Sorption reactions rapid and reversible.
  - — Bulk of geologic media accessible for sorption.
  - — Single radionuclide species exists.
  - — Freshly crushed rock representative of in situ sorbent.
- *Conclusion*: Conditions not well satisfied in basalt or tuff.

SUMMARY OF CONCERN RELATED TO NNWSI AND BWIP MATHEMATICAL MODEL OF RADIONUCLIDE RETARDATION

- Simplified chromatographic retardation factor expression used:

$$R_f = 1 + K_d\left(\frac{\rho}{\theta}\right) ,$$

where

K_d = equilibrium distribution coefficient;
ρ = bulk density;
θ = porosity.

Sources: DOE/RW-0012 (Sects. 6.3.1.2.3 and 6.4.2.1.2), 1984; DOE/RW-0017 (Sect. 6.3.1.2.7), 1984.

ORNL-WS 41521

- Use of this expression may be inaccurate and nonconservative for fracture-flow systems since:
  - — K_d model requires—
    - a. Thermodynamically reversible reactions.
    - b. Sorption independent of radionuclide concentration.
    - c. Only one radionuclide species exists.
    - d. No colloids present.
  - — Assumes bulk rock accessible for sorption.
  - — Assumes crushed rock (fresh surfaces) represent fracture-filling minerals.
  - — Assumes saturated conditions exist.
- *Conclusion:* These requirements and assumptions not well satisfied in basalt or tuff.

ORNL-WS 41522

SUMMARY OF GENERAL CONCLUSIONS

- Reliance on K_d and R_f concepts leads to inaccurate and nonconservative predictions of radionuclide releases to the environment for fracture-flow systems.
- Use of freshly crushed rock not representative of fracture-flow minerals.
- Interesting modeling work in Europe to take credit for matrix diffusion.
- No migration models deal with nonequilibrium sorption reactions or multiple radionuclide species; unfortunately, these conditions may predominate for key radionuclides.