

**REPORT ON THE PEER REVIEW OF THE
SORPTION MODELING FOR HIGH-LEVEL WASTE
PERFORMANCE ASSESSMENT RESEARCH PROJECT**

Prepared for

**Nuclear Regulatory Commission
Contract NRC-02-93-005**

Prepared by

**Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas**

September 1995



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Roberto T. Pabalan

**Center for Nuclear Waste Regulatory Analyses
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ABSTRACT

An independent panel of five experts in sorption studies reviewed ongoing radionuclide sorption research conducted by the Center for Nuclear Waste Regulatory Analyses (CNWRA) under the Sorption Modeling for High-Level Waste (HLW) Performance Assessment Research Project. The goals of the review were to (i) critically review the objectives and approaches of the CNWRA Sorption Research Project and its application to licensing issues at the proposed Yucca Mountain HLW repository site; (ii) recommend improvements to the research scope and methodologies, and identify new issues that may not be part of the original research plan; (iii) evaluate interpretations of the available data and explore alternative hypotheses; and (iv) help prioritize future activities taking into consideration resource and time constraints imposed on the project and anticipated programmatic schedules. The panel consisted of Drs. Laurent Charlet (University of Grenoble), James A. Davis (U.S. Geological Survey), David A. Dzombak (Carnegie Mellon University), John C. Westall (Oregon State University), and John M. Zachara (Pacific Northwest Laboratories). The panel members reviewed CNWRA documents and attended a 1½-day meeting in San Antonio, Texas. This report discusses the procedure used in selecting the review panel members, includes an outline which the panel used as a guide for the review process, and summarizes the comments and recommendations of the review panel. A copy of the panel report is included as an appendix. The review results and the panel recommendations will be used in revising the future direction and scope of the Sorption Research Project, as well as in developing compliance determination methods and procedures for reviewing the Department of Energy's license application for a proposed HLW repository at Yucca Mountain.

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This report was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the Nuclear Regulatory Commission (NRC) under Contract No. NRC-02-93-005. The activities reported here were performed in behalf of the NRC Office of Nuclear Regulatory Research, Division of Regulatory Applications. This report is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

David Turner and F. Paul Bertetti made substantial contributions to the preparation for and conduct of the peer review meeting. Britt Hill provided valuable guidance for the expert-panel elicitation process. Arturo Ramos provided logistical support for the review meeting and assisted in the preparation of this report. Technical and programmatic reviews by English Percy, James Prikryl, and Wes Patrick improved the content of this report.

1 INTRODUCTION

1.1 BACKGROUND

A fundamental concern in evaluating the suitability of Yucca Mountain (YM), Nevada, as a repository for high-level nuclear waste (HLW) is the possibility of radionuclide migration from the repository to the accessible environment as dissolved constituents in groundwaters. An important mechanism for attenuating radionuclide migration is sorption of radionuclides on minerals encountered along flow paths. Sorption is specifically referred to in 10 CFR 60.122(b) [(Nuclear Regulatory Commission, (NRC), 1992)] as a favorable geochemical condition that will tend to inhibit radionuclide migration and "favorably affect the ability of the geologic repository to isolate the waste." Conversely, geochemical processes that "would reduce sorption of radionuclides" are listed [10 CFR 60.122(c)(8)] as a potentially adverse condition that could reduce the effectiveness of the natural barrier system.

To support the NRC HLW program, the Center for Nuclear Waste Regulatory Analyses (CNWRA) is conducting research activities under the Sorption Modeling for HLW Performance Assessment (PA) Research Project. The broad objective is to develop sufficient understanding of radionuclide transport issues so that timely prelicensing guidance can be provided to the Department of Energy (DOE) and a sound basis is available for evaluating the DOE license application. The results will be used to support development and implementation of the NRC License Application Review Plan (NRC, 1994), particularly sections 3.2.3.2, 3.2.3.3, and 3.2.3.5 pertaining to favorable and potentially adverse geochemical conditions and processes at a potential repository site, and section 3.4, which addresses the effectiveness of natural barriers against the release of radioactive material to the environment. Laboratory and modeling studies of radionuclide sorption, retardation, and transport, which are central to the Sorption Research Project, will provide independent bases for addressing Key Technical Uncertainties, including: (i) identity and magnitude of the effects of geochemical processes that reduce radionuclide retardation, (ii) parametric representation of retardation processes, (iii) capacity of alteration mineral assemblages to inhibit radionuclide migration, and (iv) the effect of degree of saturation on radionuclide sorption and transport. In addition, development of Compliance Determination Methods for assessing DOE compliance with the regulatory requirements will utilize data and models generated from this research project. Results arising from this project will also be integrated with those from other CNWRA activities such as those of the Geochemical Natural Analog Research Project, PA Research Project, and the Iterative Performance Assessment.

1.2 REVIEW OBJECTIVES

The CNWRA is committed to providing the NRC with the highest possible quality technical assistance and research products. External peer reviews of ongoing research projects provide a mechanism to ensure that scientifically defensible research is being conducted. Thus, an external review of the CNWRA Sorption Research Project was desired. The primary goals of the review were to:

- Critically review the objectives and approaches of the CNWRA Sorption Research Project and its application to licensing issues at the proposed YM HLW repository site
- Recommend improvements to the research scope and methodologies, and identify new issues that may not be part of the original research plan

- Evaluate interpretations of the available data and explore alternative hypotheses
- Help prioritize future activities of the Sorption Research Project taking into consideration resource and time constraints imposed on the project and anticipated programmatic schedules

2 REVIEW METHODS

2.1 REVIEW PANEL SELECTION PROCESS

The procedure used to select experts for the Sorption Research Project review panel was patterned after that used for the CNWRA volcanism research peer review (Hill, 1995), which was based on a self-selection process and involved soliciting nominations for panel members from recognized experts in the appropriate field. The nominations received were compiled, and the leading nominees were invited to join the review panel, provided that they met certain criteria (e.g., scientific discipline representation, freedom from conflict of interest, etc.). The above procedure is considered to be the most objective and practical method of selecting review panel members (DeWispelare et al., 1993, 1994).

For the CNWRA Sorption Research Project review, an initial set of letters soliciting nominations for review panel membership (Appendix A) was sent out in October, 1994, to 62 active researchers in sorption/transport studies. These researchers are employed at U.S. and international academic, government, or private institutions. Based on responses to the initial solicitation, 41 additional letters were sent to individuals who were not on the initial list. Of the 103 solicitation letters sent out, 73 responses were received resulting in the nomination of 120 review panel candidates.

The distribution of the number of nominations that the candidates received is shown in Figure 2-1. Of the top seven candidates (represented in Figure 2-1 by bars at $n \geq 11$), one was unavailable and another had an obvious conflict of interest. Four of the remaining five were sent letters of invitation (Appendix B) to participate in the review panel and all four accepted the invitation. A fifth candidate, who received a smaller number of nominations ($n=4$) than a few others, was selected based on his expertise in a specialized area of research, to avoid duplicating the technical disciplines of the other four panel members.

2.2 SELECTED REVIEW PANEL MEMBERS

Subsequent to approval by the CNWRA/NRC Conflict-of-Interest Evaluation Committee, the expert panel members were hired as CNWRA consultants or subcontractors for this review. In alphabetical order, the panel members were:

- Dr. Laurent Charlet, Professor of Water Geochemistry, Department of Geophysics, University of Grenoble, France. Dr. Charlet received his Ph.D. in Soil and Environmental Sciences from the University of California at Riverside in 1986. His research has been in the sorption of heavy metals on (hydr)oxides, silicates, and carbonates, and he has published several papers and a book chapter on the application of x-ray absorption spectroscopy to the study of sorption processes.
- Dr. James A. Davis, Research Hydrologist, Water Resources Division, U.S. Geological Survey, Menlo Park, California. Dr. Davis received a Ph.D. in Environmental Sciences from Stanford University in 1977. His research for the past 18 yr has been in the general area of mineral/water interface geochemistry, including coupling of hydrologic and biogeochemical models in solute transport models, optimization of aquifer remediation, spectroscopic characterization of amorphous mineral phases and mineral surfaces, biogeochemical kinetics and mechanisms, redox reactions, environmental chemistry of soils,

Results of the Peer Review Panel Solicitation

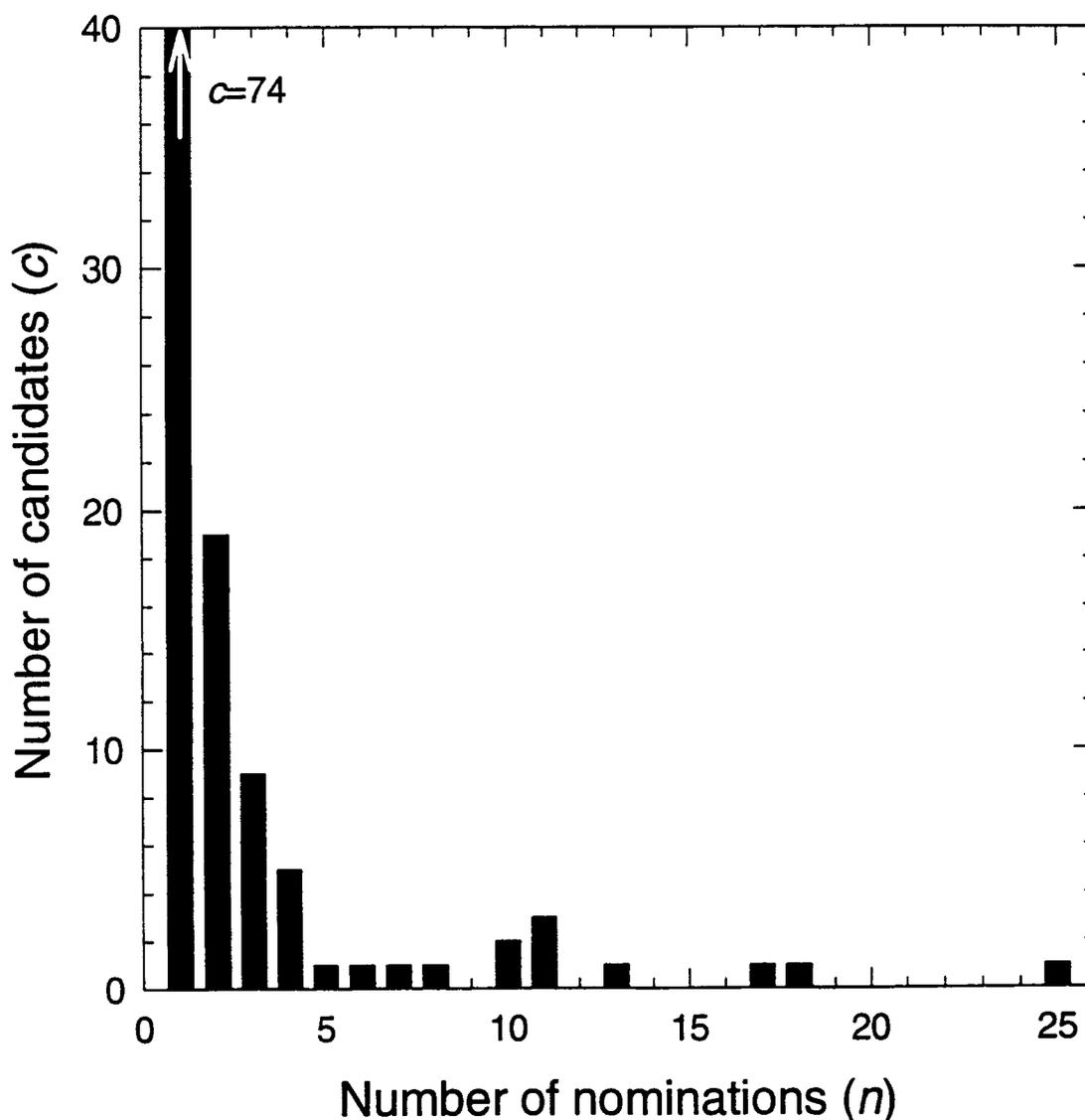


Figure 2-1. Compilation of nominations for the peer review panel. Recommended candidates are grouped by the number of nominations they received.

sediments and aquifers, and mobility of radionuclides. He has published over 60 reports and articles and has organized several symposia at national and international meetings of the Geochemical Society and the American Chemical Society. He has also co-edited a book on "Geochemical Processes at Mineral Surfaces" published in 1986.

- Dr. David A. Dzombak, Associate Professor, Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania. Dr. Dzombak received his Ph.D. in Civil-Environmental Engineering from the Massachusetts Institute of

Technology (MIT) in 1986. He has published extensively in the area of aquatic chemistry, particularly on interactions of aqueous chemical species with mineral surfaces, fate and transport of organic and inorganic chemicals in surface and subsurface waters, water and wastewater treatment, *in-situ* and *ex-situ* soil treatment, and hazardous waste site remediation. He has published a book with Dr. F.M. Morel (MIT) "Surface Complexation Modeling: Hydrous Ferric Oxide" (1990) and has co-organized several workshops or conferences on hazardous waste site remediation and management.

- Dr. John C. Westall, Professor, Department of Chemistry, Oregon State University. Dr. Westall received his Ph.D. in Chemistry from MIT in 1977. His research has focused on experimental and modeling study of sorption of inorganic and organic substances, including surfactants, on natural materials, and on partitioning of organic and inorganics between aqueous-nonaqueous phases. He has co-organized symposia for the American Chemical Society and several times has been a visiting professor at the Swiss Federal Institute of Technology.
- Dr. John M. Zachara, Chief Scientist, Earth and Environmental Sciences Center, Battelle, Pacific Northwest Laboratories, Richland, Washington. Dr. Zachara received his Ph.D., in Soil Chemistry from Washington State University in 1986. His research is mainly in the field of environmental geochemistry, including organic and inorganic transport processes and contaminant biogeochemistry. He has published at least 40 papers in the peer-reviewed literature. He has achieved the highest scientific level in his organization (Pacific Northwest Laboratories), and he serves as the principal scientist and research coordinator for the DOE Co-Contaminant Chemistry Subprogram, which is a national program involving principal investigators from over 12 universities and national laboratories. He is currently an associate editor of the *Journal of Contaminant Hydrology* and a member of the Stanford University Synchrotron Radiation Laboratory proposal review panel.

2.3 REVIEW MATERIALS

In preparation for this review, the panel members were sent an outline and a scope of work for the review (Appendix C), and copies of CNWRA documents, including project plan and work plans, CNWRA reports, peer-reviewed literature publications, abstracts of conference presentations, and draft manuscripts. A few DOE reports, study plans, and viewgraphs relating to DOE sorption studies were included to provide the panel members some perspective on how NRC/CNWRA research activities relate to DOE work and help them make recommendations regarding priorities and future activities in the Sorption Research Project. It was clearly communicated to the panel members that they were not tasked to review or evaluate DOE's sorption studies.

2.4 PEER REVIEW MEETING

The review meeting was held in San Antonio, Texas, on June 19-20, 1995. Staff from the CNWRA participated in the meeting, and staff from the NRC Division of Regulatory Applications and NRC Division of Waste Management participated by teleconference. The meeting agenda is given in Appendix D. The expert panel elected Dr. John Westall as Chair of the meeting. The Chair was responsible for keeping the discussion focused and ensuring that adequate time was allotted to discuss the main topics of the CNWRA Sorption Research Project. Although the discussions were led by the review

panel, the meeting generally followed the proposed agenda (Appendix D). The major points of discussion during the review are contained in the panel's report, which is attached as Appendix E and summarized in the following section.

3 EXPERT PANEL REVIEW RESULTS

Overall, the tone of the review was critical, focusing on the weaknesses and skipping over the strengths without much comment. As stated in the panel report, "there are some exceptionally positive aspects of this program that are barely mentioned in the review. Thus, the review should be taken in the spirit of 'many things have been done very well, and we'll recognize that without much comment, and focus our efforts on areas in which we recommend modifications.'"

An executive summary for the report was not prepared by the panel members because they felt that many of the recommendations and ideas expressed are complex and should be seen in the proper context. However, eight of the most significant issues were identified by the panel and were discussed, briefly due to time constraints, during the closeout session of the peer review meeting. After the meeting, the panel members sent detailed comments to the Chair, who collated each panel member's contributions and submitted the panel report (Appendix E) to the CNWRA. The eight major issues identified by the panel, and their recommendations to address these issues, are in Part 1 of the panel report and summarized below. Additional comments from individual reviewers are in Part 2 of the panel report.

3.1 GOALS, OBJECTIVES, AND SCIENTIFIC APPROACH OF THE CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES PROJECT

Although the general objectives of the CNWRA Sorption Research Project were clear to the reviewers, it was not clear to them (i) what knowledge, capability, or data the CNWRA research team wanted to have in hand by what date; and (ii) how this knowledge, capability, or data would be put to use in evaluating the DOE's license application. The panel recommended the CNWRA researchers develop a plan describing how they are likely to evaluate the relevant sections of the license application and how the database and models developed by the project would be utilized in this process. Because financial resources are tight and the magnitude of the technical challenge is high, the review panel recommended that the scientific objectives and approach be developed with rigor and detail and formally articulated in report form.

3.2 SELECTION OF RADIOACTIVE ELEMENTS FOR STUDY

The DOE has selected 15-20 radioactive elements of concern; however, it was not clear to the review panel that the elements chosen for detailed study by the CNWRA team (U, Np, Pu) will yield information sufficient to draw conclusions about the sorption behavior of all 15-20 elements of interest. The panel recommended that the CNWRA perform a critical review of the methods used by the DOE to develop groupings of radionuclides of concern, and that the CNWRA adopt or develop a set of groupings based on quantities, chemical properties, reactivity, migration potential, and/or other relevant factors. The panel also recommended that CNWRA researchers document their rationale for selecting U, Np, and Pu, for their detailed study.

3.3 RELATION OF CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES WORK TO DEPARTMENT OF ENERGY WORK

The review panel concluded that there is sufficient uncertainty in current understanding of sorption processes and in basic knowledge of geochemical and hydrologic conditions at the proposed HLW repository such that the CNWRA should continue conducting independent research instead of only

conducting confirmatory tests designed to check DOE's results. However, the panel believes the project plan should clearly state the relation of the CNWRA work to the DOE work.

3.4 ANALYSIS OF DOMINANT FLOW PATHS AND SURFACE MINERALOGY

Identification of relevant sorbing phases requires that groundwater flow paths be understood. The degree of confidence the CNWRA has in understanding hydrogeological conditions at the proposed repository was unclear to the review panel. The panel recommended that the CNWRA sorption team consult and collaborate with CNWRA hydrogeologists to decide upon the dominant flow scenario and the mineralogy along the dominant flow path and, hence, identify the most important surface mineral phases to study with respect to sorption processes.

3.5 STUDY OF REFERENCE MINERALS VERSUS ROCKS FROM THE SITE

The review panel emphasized the need for experiments and modeling of radionuclide sorption to rocks and mineral assemblages from YM because they believe the sorption behavior of natural mineral composites may be far different from that anticipated based solely on the sorption behavior of reference minerals. They recommended that the CNWRA obtain samples from YM or, if YM samples were not available, obtain the most relevant material possible from the tunnels in Rainier Mesa. These materials could be used for sorption experiments. The panel also encouraged the use of experimental data on site-specific materials to test the predictive capability of surface-complexation models developed previously by CNWRA investigators based on sorption data on reference minerals. Similar to issue 3.4 above, the peer review panel emphasized the need to determine the most likely flow/transport scenario (fracture or matrix flow) so that relevant samples can be collected for study.

3.6 EFFECT OF WATER COMPOSITION ON ADSORPTION BEHAVIOR

The panel recommended that future activities consider the following three solution parameters and their possible consequences on reactivity of mineral surfaces: (i) dissolved organic carbon, (ii) silicic acid and high-pH waters, and (iii) ionic strength and cation exchange processes.

3.7 MODELING APPROACH

The review panel provided a very detailed set of comments and recommendations with respect to modeling sorption. In brief, the panel recommended the CNWRA: (i) continue using the diffuse layer model for sorption on pristine reference minerals, but discontinue using the triple layer and constant capacitance models; (ii) ensure that sorption data used in model development have surface coverages broad enough to be applicable to field conditions; (iii) initiate the use of nonelectrostatic sorption models; and (iv) ensure that all sorbed species are chemically plausible. The rationale for (i) was discussed during the peer review meeting. Basically, there is a consensus among the panel members that any of the surface-complexation models (DLM, TLM, and CCM) can adequately represent experimental sorption data. Because the DLM is the simplest among the three and because CNWRA investigators have already developed an extensive database of parameters for the DLM, the panel believed further modeling effort using either the TLM or CCM is not needed. The panel also made specific recommendations for modeling approaches to relate information from reference minerals to rocks from the proposed repository site. There were some disagreements among the panel members about the best modeling approach to use

(e.g., multiple site types versus multiple surface species). There was also some discussion about adapting a more detailed mechanistic modeling approach versus a conservative approach that more closely follows the approach of DOE. However, the reviewers agreed that it is far more important to collect experimental data over a wide range of experimental conditions—or conditions relevant to the problem being studied—and then take care of the modeling in the most logical way.

3.8 CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES PLANS FOR FURTHER WORK

The panel commented upon the list of further work that the CNWRA proposed. Basically, the reviewers felt some of the proposed activities could not be completed in the limited timeframe to yield benefits to the practical problems of the project. Thus, the panel reiterated some of the recommendations listed previously, including development of a comprehensive conceptual model of transport in the unsaturated zone and the use of site specific samples in the experimental and modeling work. Experimental work on Pu was also recommended with a caveat on the potential experimental difficulties caused by the redox activity of this element.

A number of the main issues listed above suggests that some information regarding the CNWRA and NRC HLW program was not adequately conveyed to the expert panel in the time available for the review. For example, the panel recommendations for Issue 3.1 are already being addressed by CNWRA and NRC activities related to development of the NRC License Application Review Plan (NRC, 1994), Compliance Determination Strategies, and Compliance Determination Methods. Some of these activities were briefly discussed by D. Turner during the peer review meeting (see Appendix D). The rationale for the selection of important radionuclides (Issue 3.2) has been articulated in three CNWRA reports (CNWRA, 1994a,b; Jarzempa and Pickett, 1995), although developing groupings of radionuclides which exhibit similar sorption behavior as the panel suggested would be useful. The dominant flow paths for groundwater at YM (Issue 3.4) are still unknown, particularly in light of currently unspecified thermal loading. Analysis of dominant flow paths is an area of current active research by DOE, NRC, and CNWRA, and sorption researchers at the CNWRA will certainly keep abreast of developments in this area.

A few of the panel recommendations were implemented immediately after the peer review meeting. For example, new experiments were initiated to evaluate the effect of ionic strength and cation exchange processes on Np sorption on montmorillonite. Experimental protocols were also changed to include monitoring the dissolution of sorbent phases and its possible effect on radionuclide sorption. In addition, the use of the triple-layer and constant-capacitance surface complexation models for radionuclide sorption was discontinued as suggested by the panel. Most of the other comments and recommendations require further thought and deliberation to ensure their proper incorporation into modifications of the Sorption Research Project plan and their use in other CNWRA activities.

4 CONCLUSIONS

The expert panel review of the CNWRA Sorption Research Project met all its objectives successfully. Five independent experts in sorption research examined the CNWRA program in detail, made recommendations on how to improve the research methodologies, and identified new issues which were not part of the original research plan. The panel also provided useful recommendations with respect to future activities and priorities. The review results and panel recommendations will be used in revising the future direction and scope of the CNWRA Sorption Research Project, as well as in developing compliance determination methods, procedures, and acceptance criteria for reviewing the DOE license application.

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APPENDIX A

NOMINATION ELICITATION LETTER

Center for Nuclear Waste Regulatory Analyses

SOUTHWEST RESEARCH INSTITUTE • 6220 CULEBRA ROAD • SAN ANTONIO, TEXAS, U.S.A. 78238-5166
(210)-522-5160 • FAX (210) 522-5184

Date

Address

Dear:

The Center for Nuclear Waste Regulatory Analyses (CNWRA) is a federally-funded research and development center that supports the Nuclear Regulatory Commission (NRC) High-Level Nuclear Waste (HLW) Repository Licensing Program. A candidate repository site at Yucca Mountain, Nevada, is currently under evaluation. A fundamental concern in evaluating its suitability as a geologic repository for HLWs is the possibility of radionuclide migration to the accessible environment as dissolved constituents in groundwater. An important mechanism for attenuating radionuclide migration is the sorption of radionuclides on minerals encountered along groundwater flow paths. In support of NRC's licensing program, the CNWRA has undertaken research in "Sorption Modeling for HLW Performance Assessment." The project comprises experimental and modeling activities designed to provide a better understanding of sorption processes and to develop practical, but scientifically defensible, approaches to sorption modeling that can be incorporated into performance assessment codes.

The CNWRA Sorption Project has been in progress for about four years and is scheduled to continue at least into 1996. We are organizing an independent review of this program to be held in San Antonio, Texas, during the June-July, 1995, time frame. The general goals of the review are to: (i) examine the objectives and approaches of the CNWRA sorption research, (ii) evaluate research progress and results, and (iii) improve the research scope and methodologies. Reviewers are expected to focus and lead discussions on issues that they deem important, rather than be restricted to a predetermined agenda. The reviewers will be contracted by the CNWRA as consultants and will be paid for their time and associated expenses. We anticipate a total time commitment of about 80 hours, of which about 24 hours will be for the meeting and travel.

The first step in this review is to select an independent panel of recognized experts in experimental and modeling aspects of sorption studies. Because of your expertise in sorption research, we need your assistance in identifying candidates for the three- to five-member review panel. We would greatly appreciate your recommendation of several individuals whom you would regard as experts in the above field. Your recommendation will be kept confidential and will only be used to compile a list of potential candidates for the panel. Selection of panel members will be based on the recommendations of experts such as yourself, on availability, and on freedom from conflicts-of-interest. The latter requirement will preclude us from having employees of the Department Of Energy and associated national laboratories and contractors (e.g., Los

Alamos, Sandia, Lawrence Livermore, SAIC) on the review panel. However, for the purpose of this elicitation, you can recommend individuals from any organization or any country.

We hope to finalize the panel membership by the end of January, 1995. Thus, we would appreciate receiving your recommendations by November 30, 1994. If you have any questions or comments, please contact me at (210) 522-5304 [FAX: (210) 522-5184; e-mail: rpabalan@swri.edu].

Sincerely yours,

Roberto T. Pabalan
Senior Research Scientist

APPENDIX B

FORMAL LETTER OF INVITATION FOR PEER REVIEW PANEL

Center for Nuclear Waste Regulatory Analyses

SOUTHWEST RESEARCH INSTITUTE • 6220 CULEBRA ROAD • SAN ANTONIO, TEXAS, U.S.A. 78238-5166
(210)-522-5160 • FAX (210) 522-5155

February 11, 1995
Contract No. NRC-02-93-005
Account No.

Address

Dear Dr.:

Recently Dr. Roberto Pabalan of the Center for Nuclear Waste Regulatory Analyses (CNWRA) contacted you about participating on a peer-review panel for the Sorption Modeling for High-Level Waste (HLW) Performance Assessment Research at the CNWRA. Having received your preliminary indication of interest, we are initiating formalities to acquire your services as a consultant to the CNWRA for this purpose. A brief introduction to the CNWRA and an outline of the review we desire is included in this letter, along with a request for information from you to permit us to initiate a contract.

The CNWRA is a Federally Funded Research and Development Center that has been established with a mission to provide quality research and technical assistance to the Nuclear Regulatory Commission (NRC) toward licensing the first national HLW repository. The CNWRA is situated at the Southwest Research Institute (SwRI) in San Antonio, Texas, and is operated by SwRI. The CNWRA currently has professional staff spanning all areas of geosciences and engineering relevant to HLW geologic repositories.

As the licensing authority, the NRC has a strong interest in the evaluation of Yucca Mountain, Nevada, as a potential HLW repository and sponsors several research projects at the CNWRA to help in this evaluation. One of these research projects relates to sorption behavior of radionuclides. Federal regulations (10 CFR 60) explicitly recognize as favorable conditions those geochemical processes that promote precipitation or sorption of radionuclides; conversely, geochemical processes that would reduce sorption of radionuclides are considered as unfavorable. The present performance standard for the HLW repository requires that no significant release of HLW to the accessible environment occurs during the next 10,000 years.

Both the NRC and CNWRA recognize that peer-review will improve ongoing research programs significantly. The intended goals of the current review are to (i) examine the overall objectives and approaches of CNWRA sorption research; (ii) improve and possibly expand the research scope and methodologies; and (iii) evaluate CNWRAs interpretations of the available data and hypotheses. The review panel will consist of five senior scientists such as yourself, with expertise in experimental and/or modeling studies of sorption processes. The CNWRA has developed and implemented a formal quality assurance program, which includes procedures for

the performance of peer reviews. A copy of this procedure, CNWRA Quality Assurance Procedure QAP-002, is enclosed for your information.

We anticipate holding the review at the CNWRA in San Antonio, Texas, on Monday and Tuesday, June 19-20, 1995. The principal investigators on the CNWRA sorption project, Roberto Pabalan and David Turner, will present a synopsis of CNWRA research activities. These presentations will supplement the study plans and reports which will be sent for you to review in mid-April. The review-panel members will elect a chairman, who will preside over the meeting. The chairman will then lead discussions on the research program in general, followed by specific topics from the panel member's areas of expertise.

We expect that the review of the background material and preparation for the panel meeting will require about 40 hours of your time. Participation in the meeting and associated travel will require an additional 20 hours. Following the meeting, panel members are expected to produce a written report of about 10 pages, which provides their evaluation of the CNWRA research program and recommendations for improvement. We expect that the preparation of this report will require about 40 hours of your time, and that the report will be completed by the end of August, 1995.

To meet CNWRA Conflict of Interest requirements, and to assist us in setting up a consulting agreement, we must receive from you the following items (if you have not provided them with your previous letter):

- Conflict of Interest Statement (form and a sample copy of a letter enclosed)
- A copy of your current curriculum vitae
- Your fee schedule

We would appreciate your attention and quick response in supplying these items. Please send them to the CNWRA, attention Anna Lopez. We greatly appreciate your interest in helping the NRC and the CNWRA in this matter of national importance. If you have any questions about the review, please contact Dr. Roberto T. Pabalan (210 522-5304) or Dr. Larry McKague (210 522-5183) at the CNWRA.

Sincerely,

Dr. Budhi Sagar
Technical Director

Enclosures

| | | |
|-----|------------------------|------------|
| cc: | W. Patrick | R. Pabalan |
| | CNWRA Directors | D. Turner |
| | CNWRA Element Managers | A. Lopez |

APPENDIX C

**OUTLINE FOR THE EXPERT PANEL REVIEW
OF THE CNWRA SORPTION RESEARCH PROJECT**

OUTLINE FOR THE PEER REVIEW OF THE CNWRA SORPTION MODELING FOR HIGH-LEVEL WASTE PERFORMANCE ASSESSMENT RESEARCH PROJECT

Main Goals

- Critical review of the objectives and approaches of the CNWRA Sorption Research Project and its application to licensing issues relevant to the proposed Yucca Mountain HLW repository site
- Recommendations to improve research scope and methodologies, and identify new issues that may not be part of the original research plans
- Evaluate interpretations of available data and the models used to represent sorption data; explore alternative interpretations and models
- Help prioritize future activities taking into consideration resource and time constraints imposed on the project and anticipated programmatic schedules

Synopsis of Regulatory Bases for Conducting Sorption Research

Title 10 Part 60 of the Code of Federal Regulations (10 CFR 60): Nuclear Waste Policy Act (1982) and amendments task the U.S. Department of Energy (DOE) to receive and to store high-level nuclear wastes (HLW) in a geologic repository. DOE is required to obtain a license to construct and operate the repository from the Nuclear Regulatory Commission (NRC). 10 CFR 60 requires the geologic setting of a HLW repository to exhibit an appropriate combination of geologic and geochemical conditions which are sufficient to provide reasonable assurance that releases of radioactive materials to the accessible environment following permanent closure of the repository conform to the generally applicable environmental standards for radioactivity established by the U.S. Environmental Protection Agency (EPA) and set forth in 40 CFR 191.

40 CFR 191 (currently remanded by the courts and will be amended): Provides cumulative release limits (cumulative releases to the accessible environment for 10,000 yr after disposal). These cumulative release standards are based on an approximate calculation of fatal cancers in the global population due to exposure to radioactivity through biological pathways resulting from release of radionuclides from a geologic repository. Each radionuclide is assigned a release limit in curies per metric ton of heavy metal (Ci/MTHM) in spent fuel (or the spent fuel equivalent for reprocessed waste).

10 CFR 60.122: Siting criteria: The DOE must evaluate the repository site to demonstrate that the geologic setting and engineered barrier systems exhibit sufficient favorable conditions (FACS) to provide reasonable assurance that the performance objectives related to waste isolation will be met. The following are explicitly considered as favorable conditions with respect to radionuclide retardation:

- Geochemical conditions that promote precipitation or sorption of radionuclides [10 CFR 60.122(b)(3)(i)]
- Geochemical conditions that inhibit the transport of radionuclides by particulates, colloids, and complexes [10 CFR 60.122(b)(3)(iii)]

- Mineral assemblages that, when subjected to anticipated thermal loading, will remain unaltered or alter to mineral assemblages having equal or increased capacity to inhibit radionuclide migration [10 CFR 60.122(b)(4)].

The following are explicitly recognized as potentially adverse conditions (PACs):

- Geochemical processes that would reduce sorption of radionuclides [10 CFR 60.122(c)(8)].

For PACs, DOE must demonstrate that the following specific criteria are met:

- 1) The PAC has been adequately investigated, including the extent the condition may be present but undetected;
- 2) The effect of the PAC on the site has been adequately evaluated using analyses which are sensitive to the PAC and assumptions which are not likely to underestimate its effect; and
- 3) The PAC is shown
 - a) to not affect significantly the ability of the repository to meet the performance objective related to waste isolation, or
 - b) to be compensated by the presence of favorable conditions, or
 - c) can be remedied

The NRC will have 3 years to evaluate the DOE license application, and determine whether or not the proposed site could result in significant health risks to the population. This evaluation process may be highly contentious and subject to intense scrutiny by groups with divergent views on nuclear waste in general and the proposed repository site at Yucca Mountain in particular.

Sorption Research Key Technical Uncertainties (KTUs): KTUs were developed by the NRC to guide the research needed to effectively evaluate the DOE license application. The main KTU associated with radionuclide sorption/retardation research is: Uncertainty in identifying geochemical processes and conditions that affect radionuclide retardation and determining and predicting the magnitude of the effects at Yucca Mountain. Resolution of this KTU is believed to be difficult because radionuclide retardation is a function of numerous geochemical conditions and interrelated processes that must be interpreted over large spatial and temporal scales. These conditions and processes, their couplings, and their spatial and temporal variations are not well understood.

CNWRA Sorption Research Project
(Approximate level of effort: 1.65 FTE)

Objectives:

- Obtain a mechanistic understanding of important radionuclide sorption processes and the physical and chemical parameters that affect sorption behavior in the Yucca Mountain environment

- Develop practical but theoretically sound and scientifically defensible approaches to modeling sorption for Yucca Mountain performance assessments and to generate the databases required to support such models
- Investigate the applicability of coupled hydrogeochemical models to Yucca Mountain performance assessments using simplified approaches to sorption modeling

Project Results and Products to Date:

1. Developed experimental and analytical laboratory for sorption research
 - a) acquired alpha-, beta-, and gamma-spectrometry and other equipment (e.g., controlled atmosphere glove boxes, etc.)
 - b) developed protocols and procedures necessary to acquire radioactive material license; acquired Np, Pu, U and other radioisotopes for use in sorption experiments
2. Major Milestones:
 - a) Work plan for hydrogeochemical modeling of radionuclide transport
 - b) Work plan for experimental studies on uranium sorption on geologic media
 - c) Literature review of sorption modeling for high-level waste performance assessment
 - d) Technical report on mechanistic approaches to radionuclide sorption modeling
 - e) Technical report on a uniform approach to surface complexation modeling of radionuclide sorption
 - f) Letter report on summary assessment of the radionuclides relevant to research on the geologic disposal of HLW
3. Other written material (publications/semiannual reports/abstracts)
 - a) Experimental study of U(6+) sorption on the zeolite mineral clinoptilolite
 - b) Uranium sorption on alpha-alumina: effects of pH and M/V
 - c) Experimental and modeling study of U(6+) sorption on quartz
 - d) Approaches to sorption modeling for HLW performance assessment
 - e) Uniform surface complexation approaches to radionuclide sorption modeling
 - f) Molecular dynamics simulation of uranyl sorption on mineral surfaces
 - g) Experimental and modeling study of U(6+) on montmorillonite

4. Ongoing and unreported research:
 - a) Neptunium sorption experiments on quartz, clinoptilolite, and montmorillonite
 - b) Plutonium sorption experiments on quartz, clinoptilolite, and montmorillonite
 - c) Competitive sorption experiments: uranium±neptunium±plutonium

Scope Of Work For Peer-Review Panel

The peer-review will be accomplished through the following tasks:

1.
 - a) Review the research project plans and workplans developed by CNWRA PIs. Although some effort has been made to update the project plan, adjustments to the technical approach which have been made in response to programmatic directions and DOE plan changes may not be accurately reflected in the project plan. The workplans have not been updated since their approval by NRC and are therefore out of date, although the general approach remains valid.
 - b) Review the literature produced under the CNWRA sorption research project. Semi-annual reports and other technical reports will be reviewed in general. Background material such as the report on assessment of important radionuclides, are provided for familiarization. Published papers and conference proceedings papers will be reviewed in general.
 - c) Become familiar with the regulatory and programmatic aspects of sorption research.
 - d) Review the small amount of DOE material provided in the review package. These are provided so that the peer reviewers can evaluate the CNWRA work in the context of what DOE's approach is with respect to radionuclide transport modeling. The review panel is not tasked to critically assess DOE's approach.

A total of 30-40 hours is estimated for this task.

2. Attend a 1-1/2 day meeting in San Antonio, Texas, beginning June 19, 1995, to discuss the principal objectives of the review with CNWRA and NRC staff and other review panel members. A total of 20 hours is estimated for this task.
3. Prepare a written report of comments and recommendations. Report is due by August 31, 1995. A total of 30-40 hours is estimated for this task.

APPENDIX D

**AGENDA FOR THE PEER REVIEW MEETING
ON THE CNWRA SORPTION RESEARCH PROJECT**

**AGENDA FOR THE SORPTION RESEARCH PROJECT
PEER REVIEW MEETING**

June 19, 1995 Monday. Meet at CNWRA (SwRI, Bldg. 189, 2nd floor Conference Rm. 237)

8:30-8:35 - Introductions for Panel, CNWRA, and NRC participants (R. Pabalan)

8:35-8:50 - Management overview of the CNWRA and relationship to SwRI and NRC
(W. Patrick)

8:50-9:05 - Introduction (R. Pabalan)

- Objectives and brief history of the CNWRA Sorption Project
- Objectives of peer-review

9:05-9:30 - Overview of regulatory issues at Yucca Mountain (YM) site (D. Turner)

- Regulatory basis for research
- Key Technical Uncertainties (KTUs)
- NRC Vertical Slice activities
- Sorption research in relation to YM performance assessments
- Summary of YM geochemistry

9:30-10:15 - Sorption Project experimental task (R. Pabalan)

- Technical approach
- Experimental results
- Current and future activities

10:15-10:30 - Coffee break

10:30-11:15 - Sorption Project modeling task (D. Turner)

- Technical approach
- Modeling results
- Current and future activities

11:15-11:50 - Expert panel caucus. Panel members will:

- Elect a Chair for the meeting. The Chair will recognize questions from the participants and limit discussions if necessary to remain on schedule. Panel members will send individual reports in August to the Chair, who will ensure that the reports are complete and add a summary statement if so desired.
- Decide on the agenda for the rest of the meeting. The review panel will lead the discussions. As a guide, the discussions could focus on the Sorption Project technical approaches and results in relation to its objectives, and comparisons with other sorption/transport investigations.

[Separate CNWRA-NRC caucus/teleconference; bring-up issues of concern, comments, suggestions]

- 11:50-1:00 - Lunch break (SwRI cafeteria)
- 1:00-1:45 - Tour of CNWRA laboratory facility
- 1:45-3:15 - General discussions based on agenda set by review-panel
- 3:15-3:30 - Coffee break
- 3:30-5:00 - Continue general discussions
- 5:30-7:00 - Further technical discussions; dinner

June 20, 1995 Tuesday. SwRI, Building 189, 2nd floor Conference Room 237.

- 8:00-8:15 - Expert panel caucus to determine scope of the morning session. As a guide, discussions could focus on individual reviewer's preliminary recommendations to improve the project and what they see as critical issues relevant to radionuclide transport at Yucca Mountain.

[Separate CNWRA-NRC caucus/teleconference; bring-up issues of concern, comments, suggestions]

- 8:30-9:45 - General discussions based on agenda set by review-panel.
- 9:45-10:00 - Coffee break.
- 10:00-11:00 - Continue general discussions.
- 11:00-11:30 - Expert panel caucus. Chair to solicit preliminary recommendations and determine individual reviewer's schedule for submission of peer-review report.
- 11:30-12:00 - Expert panel final comments. Close out discussions.

APPENDIX E

**REPORT OF THE CNWRA SORPTION RESEARCH PROJECT
PEER REVIEW PANEL**

August 25, 1995

Dr. Budhi Sagar
Technical Director
Center for Nuclear Waste Regulatory Analysis
Southwest Research Institute
6220 Culebra Road
San Antonio TX 78284

Dear Dr. Sagar:

Enclosed is the report summarizing our 1995 review of the CNWRA research project, "Sorption Modeling for High-Level Waste Performance Assessment," of which Roberto Pabalan and David R. Turner are principal investigators. All of the reviewers have indicated their approval of the report; a cover letter with original signatures of all reviewers is circulating and will be sent to you when completed. If you have any questions, you may contact any of the reviewers at the addresses given in the appendix of the report.

Sincerely,

LC / jcw
Laurent Charlet

DAD / jcw
David A. Dzombak

JAD / jcw
James A. Davis

John Westall 8/25/95
John C. Westall (Chairman)

JMZ / jcw
John M. Zachara

Review of Research Project on
Sorption Modeling for High-Level Waste Performance Assessment

Center for Nuclear Waste Regulatory Analysis
Southwest Research Institute
San Antonio, Texas

Roberto T. Pabalan and David R. Turner
Principal Investigators

Review Panel

Laurent Charlet

James A. Davis

David A. Dzombak

John C. Westall

John M. Zachara

August 25, 1995

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INTRODUCTION

This review document is divided into two major parts. In Part I, we address eight of the most significant issues that arose during the meeting of the review panel at CNWRA on June 19-20, 1995. For each of these issues, one to three of the reviewers volunteered to be the primary authors, and their names are listed with the reviews, in order that CNWRA can put the comments into perspective. All of the reviewers have read all of these sections and have had a chance to make input into the final version.

In Part II, we present the comments of each of the reviewers about the project. These comments are focused on the published reports, since they represent completed work, but the comments are not restricted to these materials. The comments in these sections reflect primarily the opinions of the authors, and were not subjected to extensive internal review by the panel. Initially we had intended to integrate these comments, but as it turned out, we have left them in their original form and feel that they are more valuable this way; the repetition of some issues among these reviews serves to emphasize the important points.

Overall the tone of this review is critical, focussing on the weaknesses, and skipping over the strengths without much comment. There are some exceptionally positive aspects of this program that are barely mentioned in the review. Thus, the review should be taken in the spirit of "many things have been done very well, and we'll recognize that without much comment, and focus our efforts on areas in which we recommend modifications."

We have not prepared a concise executive summary for this report because we felt that many of the recommendations and ideas expressed here are complex and should be seen in the proper context. However, recommendations listed in each of the Sections 1-8 in Part I do provide that sort of summary.

PART I - Major Issues

1. Goals, Objectives, and Scientific Approach of CNWRA Project - John M. Zachara and James A. Davis

Comment

On a broad and general level, the goals of the CNWRA "Sorpton Modeling for HLW Performance Assessment (PA) Research Project" were clear to the reviewers. This goal may be stated as follows as a quote from one of the reports: "The broad objectives are to develop sufficient understanding of radionuclide transport issues so that timely prelicensing guidance can be provided to the U.S. Department of Energy (DOE) and a sound basis be available for evaluating the DOE license application (LA). Specifically, the results will be used in addressing NRC needs in evaluating the use of empirical sorption coefficients (e.g., K_d 's) in modeling sorption."

What, however, was not clear to the reviewers was (i) what knowledge, capability, or data the CNWRA research team wanted to have in hand by what date, and (ii) how this knowledge, capability, or data would be put to use in evaluation of the LA. Without this understanding, the reviewers were inadequately prepared to judge whether the performed research was, in fact, relevant to the broadly stated goal. It was the reviewers consensus that the CNWRA team must develop a strategy, now, for how the LA may be evaluated and to use this strategy to identify critical data needs or activities that must be obtained or completed by the time of LA in three years. Without such forethought, the NRC team may not be positioned optimally to perform a credible, rigorous, scientific evaluation of DOE's PA calculations. The strategy must be flexible, allowing appropriate and needed change as new results are obtained by the NRC team and DOE's site characterization and sorption studies programs.

While the research team may have such a long term strategy, it was not clearly or explicitly relayed to the reviewers. For example, the modeling and research presented in CNWRA 93-019 and 95-001 was considered to be a credible effort by all of us, but it was not clear how the resulting surface complexation data base for single mineral phases would be applied to LA evaluation. There did not appear to be activities planned to test ways or approaches to utilize the data base for PA calculations, nor did the research team have a clear view as to how the information developed to date would be used in the LA evaluation. The review team felt that now is the time to think about and resolve this question, rather than after the LA is received.

Recommendations

The CNWRA researchers should develop a plan on how they are likely to evaluate the relevant sections of the LA and how the data base and models developed by the project would be utilized in this process. For example, does the team anticipate that they will try to estimate K_d 's for different tuff units or fracture filling mineral assemblages based on mineralogic properties information? If so, for what radionuclides, and how would the predictive approach be validated beforehand? Will the effects of different solution conditions on the K_d 's for composite mineral material be computed as well? How will geochemistry, generally, or K_d 's, specifically, be incorporated into transport/PA predictions?

The plan should not be general, but should be specific. It could also include multiple scenarios to assure that NRC is prepared for the evaluation regardless of DOE's final modeling or PA approach. The investigators should try to identify what they may wish to model in the evaluation and how, specifically, it would be done. Focused thought will clarify critical data and information needs, and identify needed model developments.

Once the plan is completed, the team must determine specific scientific objectives and a logical series of steps (scientific activities including experiments or modeling) to achieve this endpoint. Because financial resources are tight and the magnitude of the challenge is high, the review panel recommends that the scientific objectives and approach be developed with rigor and detail and formally articulated in report form. While seemingly restrictive, this approach will focus project resources on key activities needed for the eventual LA evaluation. While DOE's approach to the Yucca Mountain sorption studies may be criticized along various scientific grounds, the reviewers felt that they had an effectively communicated scientific approach that defined the scope of their activities. Such clarity of presentation was not evident for the CNWRA Sorption Modeling project.

2. Selection of Radioactive Elements for Study - David A. Dzombak and Laurent Charlet

Recommendations

- o Perform a critical review of the methods used by DOE to develop groupings of the radionuclides of concern.
- o Develop groupings of the radionuclides of concern based on quantities, chemical properties, reactivity, migration potential and/or any other relevant factors.
- o Document the rationale for selecting Np, Pu, and U for detailed study.

Comments

The rationale for focusing the experimental and theoretical studies in the CNWRA Sorption Project on neptunium, plutonium, and uranium needs to be documented and explained better. As DOE has identified 15-20 radioactive elements of concern, there is clearly a wide range of elements for which potential subsurface transport is an issue. It is not clear that the elements chosen for detailed study by the CNWRA team will yield information sufficient to draw conclusions about the sorption behavior of all

15-20 elements of interest. While the reasons for choosing uranium (chemistry is well known and similar to that for transuranic elements) are discussed carefully in CNWRA reports, the rationale for studying neptunium and plutonium is not evident. The chemistry of Np(V) is similar to that of Pu(V). Why should both of these elements be studied to the exclusion of others? Americium, nickel and other elements in the DOE list of elements of concern may have sorption behavior substantially different than Np, Pu, or U and perhaps should be examined.

An effective way to demonstrate that the elements chosen for study are sufficiently representative of the radioactive elements of concern would be to form groupings of the elements, as has been done by DOE. The panel recommends that the DOE groupings of radioactive elements with respect to their sorption properties be reviewed critically, and that CNWRA adopt or develop a set of groupings. For classification of elements by sorption capabilities, groupings based on chemical properties and reactivity are suggested. As demonstrated by Schindler et al., Dzombak and Morel, Smith and Jenne, Whitfield et al., and others, grouping of elements according to their solution complexation properties (e.g., hydrolysis constants, acidity constants, complexation constants) can be useful in interpreting trends in sorption of elements on minerals. Development of element groupings would help justify the choice of elements to be further investigated experimentally, and would allow the CNWRA Sorption Project results to be linked to the studies and data provided by DOE with their license application.

The panel recognizes that only limited experimental work can be conducted by CNWRA in the Sorption Project. This experimental work must be designed to obtain data that encompass the broadest possible range of radionuclides and anticipated subsurface conditions. Careful selection of representative elements via an element grouping scheme will ensure that the experimental design is appropriate.

References

Dzombak, D.A. and Morel, F.M.M. (1990), *Surface Complexation Modeling: Hydrous Ferric Oxide*, Wiley-Interscience, New York.

Schindler, P.W., Furst, B., Dick, R., and Wolf, P.U. (1976), "Ligand Properties of Surface Silanol Groups. I. Surface Complex Formation with Fe^{3+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} ," *J. Colloid Interface Sci.*, 55:469-475.

Smith, R.W. and Jenne, E.A. (1991), "Recalculation, Evaluation, and Prediction of Surface Complexation Constants for Metal Adsorption on Iron and Manganese Oxides," *Environ. Sci. Technol.*, 25:525-531.

Turner, D. R., Whitfield, M., Dickson, A. G. (1981), "The Equilibrium Speciation of Dissolved Components in Freshwater and Seawater at 25 C and 1 atm Pressure," *Geochim. Cosmochim. Acta*, 45:885-881.

3. Relation of CNWRA Work to DOE Work - John C. Westall

Recommendation

- o State clearly in the work plan the relation of the CNWRA work to the DOE work.

Comments

Initially in the review CNWRA did not transmit clearly to the reviewers the relation of their work to that of DOE: whether CNWRA should track the work of DOE and essentially check up on the work of DOE as it is completed (defined as "Level 4 Review"), or whether CNWRA should work more independently, arrive at their own end points, and then evaluate the work of DOE based on their own, independent experience (defined as "Level 5 Review").

The reviewers conclude that most activity really needs to be "Level 5 Review," since (i) there is still enough uncertainty to warrant an independent approach and (ii) the basic assumptions (e.g., high T, low T, fracture, matrix, etc.) are still subject to change, making it very difficult to track DOE activities directly. This status should be clearly stated and justified.

4. Analysis of Dominant Flow Paths and Surface Mineralogy - David A. Dzombak and Laurent Charlet

Recommendations

- o Collaborate with CNWRA hydrogeologists to decide upon the flow scenario (matrix or fracture flow) likely to be dominant for groundwater transport of solutes from the repository.
- o Assess the mineralogy of the pore surfaces along the dominant flow path.
- o Identify the most important surface mineral phases with respect to sorption.

Comments

While a wide range of mineral phases exists in the rocks beneath the proposed repository, only those at the solid/water interface in the pore spaces will affect radionuclide sorption/desorption reactions. It is critical that the most important sorbing phases be identified for evaluation of the possible effects of sorption on radionuclide transport.

Identification of the relevant sorbing phases requires that the groundwater flow path(s) be understood, both in the unsaturated and the saturated zones. At the repository site, groundwater flow occurs both in the porous matrix of intact rock, and in fractures that occur throughout much of the rock. From the summary of hydrogeological investigations and modeling provided to the panel, it seems that fracture flow is believed to dominate both the unsaturated and saturated flow systems beneath the repository. The degree of confidence that CNWRA has in their understanding of hydrogeological conditions is unclear to the panel, however.

The range of reference mineral phases that must be considered in evaluating potential radionuclide sorption could be narrowed if a dominant flow path for solute transport was identified, i.e., if the dominance of fracture flow was verified. The panel recommends that the Sorption Project team consult and collaborate with the CNWRA hydrogeology team to establish conclusions about the dominant flow paths for groundwater in the unsaturated and saturated zones. If available data enable a consensus that fracture flow is indeed dominant, then surface mineralogical characterization efforts of the Sorption Project team can focus on the fractures. Some techniques have been developed for study of sorption of radionuclides [e.g., U(VI) and Th(IV)] on intact mineral faces isolated from fractured rock samples (see *Radiochim. Acta*, 58/59:219-233, 1992).

5. Study of Reference Minerals vs Rocks from the Site - John M. Zachara and James A. Davis

Recommendations

- o Verify that fracture flow is most likely to be the dominant mode of subsurface solute transport at Yucca Mountain, and in that case:
- o Obtain fracture filling materials from Yucca Mountain rock samples or samples from a similar site;
- o Characterize the mineralogic composition of the fracture filling materials and determine selected surface properties that are relevant for surface chemistry calculations;
- o Perform sorption experiments with fracture filling materials for a wide range of conditions;
- o Apply surface-complexation based models to describe sorption on the fracture filling material;
- o If matrix flow is found to be dominant (rather than fracture flow), substitute a procedure similar to the one outlined above but based on matrix materials.

Comments

In Section 7 we discuss modeling approaches to describe sorption to geologic materials and to extrapolate adsorption equilibrium constants from reference minerals (RM) to rocks from the site (RFS). Here we would like to reinforce the need for experiments and modeling of radionuclide sorption to rocks and mineral assemblages from Yucca Mountain, as the sorption behavior of natural mineral composites may be far different than anticipated based on RM.

The panel believes that the ultimate challenge faced by the CNWRA team is to understand and qualitatively predict the sorption behavior of mineral surfaces in the tuff matrix (for unsaturated conditions) and the fractures (saturated conditions), and the changes in sorption that may occur with changes in solution composition and temperature. While significant insights may be obtained by experimentation and modeling with RM, these cannot and should not replace studies with materials from the site. For example, the site clay minerals may differ from the RM in crystallite size (that effect the exposed hydroxyl concentration of the sorbent), and in type, locations (i.e., octahedral vs. tetrahedral layer), and amount of isomorphous substitutions. Site iron oxides may contain substituent impurities such as Al or Si, or have surface precipitates or strongly attached sorbates, all affecting surface properties and charge. Likewise, compositional variations in the zeolite phases may cause variations in both charge density and internal structure. Site calcites may contain significant concentrations of co-precipitated Mg, Mn(II), or Fe(II) that influence surface defect density and reactivity. These departures from ideal RM properties may induce changes to ion retention and radionuclide adsorption that are large, not entirely expected by intuition, and difficult to model with "mechanistically based" models.

The mineral phases/surfaces responsible for radionuclide sorption in the site materials may also be co-associated in complex physicochemical ways that influence both the kinetics and magnitude of sorption. Factors such as aggregation and particle-particle interactions, change with ionic strength and solution chemistry, and are important in composite mineral materials containing surfaces with contrasting charge such as Fe/Al oxides and layer silicates/zeolites.

Reliance on studies with RM alone may position the CNWRA research team at disadvantage with respect to rationalizing K_d 's proposed by DOE for transport flowpaths from the repository. It may be found that solid phases presumed to be the most important sorbents based on RM studies, are not the most important sorbents in natural material for reasons noted above. Furthermore, natural materials can exhibit lessor or greater adsorption selectivity then expected from RM studies as a result of the presence of minor phases or surface modifiers that are challenging to characterize. The adsorption stoichiometry

with respect to H^+ may also be significantly different from RM (lower slope) as a result of multiple binding reactions to different surfaces. Consequently, studies with the natural materials are required to assess effective site concentrations for different sorbates, and binding selectivities or energies and their apparent heterogeneity.

Moreover, it is critical that the CNWRA team resolve, in consultation with others, the most likely transport scenario from the repository so that relevant materials can be selected for study. Is it one of fracture or matrix flow? The reviewers were concerned that not enough thought had been given to the distinctions between these scenarios and the resulting implications to data needs, modeling capabilities, and the eventual LA evaluation. If fracture flow is the presumed dominant transport vector, then work must be initiated now in order to (i) identify the mineral associations that line fractures in the different formations, (ii) determine the reactivity of the contained phases and different fracture filling mineral suites toward radionuclides, and (iii) establish effective modeling approaches to describe and possibly predict values and trends in K_d . It is recognized that some or much of this information may come from DOE as part of their characterization and sorption studies.

We recommend that CNWRA obtain Yucca Mountain fracture filling material from DOE, and, if that is not available, to obtain the most relevant material as is possible from the tunnels in Rainier mesa. These materials could be used for K_d measurements and to develop a experimental data base on the impacts of variation of key solution parameters such as hydrogen ion concentration, ionic strength, carbonate concentration or $P_{CO_2(g)}$, and sulfate. Application of the SCM reactions parameterized in CNWRA 93-019 and 95-001 and the modeling approaches described in Section 7 to this experimental data is encouraged to test whether SCM-based strategies can be established to describe trends in and predict K_d 's in Yucca Mountain fracture filling materials.

6. Effects of Water Composition on Adsorption Behavior - Laurent Charlet and James A. Davis

Recommendations

- o Consider effects of dissolved organic carbon (DOC).
- o Consider effects of silicic acid and high pH waters.
- o Consider effects of ionic strength and cation exchange.

Comments

The review panel recommends to take into consideration in future working plans the following three solution parameters and their possible consequence on reactivity of mineral surfaces.

A. DOC

Within the Sorption Project, more attention should be given to the presence of dissolved organic carbon in the Yucca Mountain Groundwaters. Some of the documents presented to the Review Panel mentioned a DOC concentration ranging from 0.14 (Turner, 1991) to 2.5 mg/l (Simmmons, 1994). Although these values may be an overestimate of the overall DOC groundwater concentration, the occurrence of DOC and its impact on actinide speciation should be carefully evaluated.

Attention should be given to previous work dealing with the solid-actinide-humic substances interactions (e.g. Moulin et al., 1989, 1992a, 1992b; Allard et al., 1989).

B. Silicic acid and high pH waters

1. Occurrence of dissolved silicate ions. The occurrence of H_3SiO_4^- as a possible complexing anion for actinides should be evaluated. If extensive use of concrete is made in the Yucca Mountains for tunnels and other civil engineering works (one speaks of 10 km³ of concrete to be used!), high pH values will occur in the near field, as a consequence of portlandite dissolution. Hydroxide ions will react with silica present in tuff, in military borosilicate glass waste products or in concrete (as $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$). At high pH the dissolution of silica occurs at high rate and leads to high concentrations of H_4SiO_4 and H_3SiO_4^- .
2. Possible formation of silica colloids. The possible occurrence of an "alkali reaction" between alkali-rich high pH waters and silica present in tuff should be evaluated. This reaction has been recognized to be responsible in concrete for secondary fracture formation and exudation of amorphous silica colloids or gels. The presence of such silica gels has been reported in the Yucca Mountain area (Levy, 1992). These colloids could enhance the transport of actinide ions in the Yucca Mountain. This has not been confirmed in the field but could be a significant issue in the License Application.
3. Actinide- H_3SiO_4^- complexation constants. These constants are expected to be rare. Some data are available, e.g. for Al(III), and these data could be used to estimate these unknown formation constants, e.g. with a correlation procedure similar to that used in the estimation of MeCO_3o formation constant. These constants can also be extracted from spent fuel dissolution experiments, underway at CNWRA by the same team but in another project. Once these complexation constants are estimated, one could compute whether at high pH values, silicic acid is, in the same way as carbonic acid, responsible for a "desorption isotherm" or "high pH adsorption edge".
4. Counter effect of Ca^{2+} . The above-mentioned silica effect could be counterbalanced by the presence of Ca^{2+} . In presence of concrete, calcium ions are produced together with OH^- ions by the dissolution of portlandite ($\text{Ca}(\text{OH})_2$). These ions react with dissolved silicic acid to form CSH (calcium silicate hydrates) which have such a low solubility that they may lead to conditions undersaturated with respect to quartz (Lichtner and Eikenberg, PSI Report 95-01). A mass balance exercise should be thus performed to estimate the risk associated with high dissolved concentrations of silicic acid.

C. Ionic strength and cation exchange

Results from the Sorption Project appear to indicate a very small effect of ionic strength on sorption. However the Review Panel has pointed out that these experiments were performed within a small range of ionic strength which did not include the ionic strength expected in the Yucca Mountain, and that the effect of ionic strength should be much more obvious on clay sorption than on oxides.

Cation exchange reactions at the surface of clays (zeolites, smectites) have been neglected, being suppressed by the high ionic strength used in the experiments. However at low ionic strength cation exchange reactions play an active role in the immobilization of cations, up to the pH value at which adsorption on the edges of the clay crystallite begins. This pH value is specific for each cation (see e.g. Charlet et al., 1993). In the pH conditions prevailing in Yucca Mountain, one can expect cation exchange to be the dominant mechanism for Ba, Sr.

However, implementation of cation exchange reactions in a general model to be used in performance assessment calculations is not straightforward (Fletcher and Sposito, 1989; Dzombak and Hudson, 1995), except in the case of clays nearly saturated with Na^+ (Charlet et al., 1993). Therefore we recommend that the Sorption Project modeling continue to be developed in the framework of surface complexation alone; however, if data indicate that ion-exchange reactions

are indeed significant for the natural materials, these reactions could be incorporated in the model with an approach based on half reactions and a distribution of exchange constants.

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7. Modeling Approach - John C. Westall, James A. Davis, David A. Dzombak

Recommendations

- o Continue diffuse layer model approach for pristine reference minerals.
- o Ensure that the data sets used in model development have surface coverages broad enough to ensure applicability to field conditions.
- o Initiate use of nonelectrostatic model for rocks from site; for continuity, use nonelectrostatic models for some reference minerals materials as well.
- o Discontinue use of triple layer and constant capacitance models.
- o Ensure that all species are chemically plausible.
- o Use an approach in 7.E listed below to bridge the gap between reference minerals and rocks from site.

Comments

A. Guidelines for introducing additional sites and additional surface species.

In principle, it is good to keep the number of distinct sites and number of surface species small, but additional sites and surface species may be necessary to represent the experimental data.

The number of distinct sites and species necessary will depend on many factors, among them: the modeling approach (to be discussed in detail in Section 7.E), whether electrostatic or nonelectrostatic models are used, whether the data are for "reference minerals" or heterogeneous "rocks from site," and the range of surface coverage in the experimental data set.

For the nonelectrostatic models, additional sites or species may be necessary to introduce the variability in binding energy that would otherwise be provided by the electrostatic term in electrostatic models.

Heterogeneous "rocks from the site" generally yield pH sorption edges that are broader and isotherms that are less Langmuir-like than those from the more homogeneous "reference minerals;" thus, sorption models may require more species or more sites.

For data sets with a wide range in free aqueous concentration of sorbate (and accompanying wide range in surface coverage), more site types may be necessary; generally 1-site type per factor 100 change in free aqueous concentration is sufficient.

B. General recommendations for interpreting and presenting data.

For all figures include ALL of the following information (on the figure or in the caption): identity of sorbent, identity of sorbate, total concentration of sorbate, ratio of mass of sorbent to volume of solution (M/V), specific surface area of sorbent (A_{sp}) if known and relevant, and electrolyte composition. The availability of all of that information (with the figure, not buried in the text) allows the reader to interpret the data more readily.

In the simple limiting case of $M + H_nX = MX + n H$ with $[H_nX] \gg [MX]$, the effect of M/V on pH adsorption edges is simply to shift the adsorption edge. This simple relation doesn't seem to have been recognized explicitly in most of the publications. Recognition of this simple relation aids in interpreting and explaining the data.

The statement was made several times that "we have confidence in the predictive powers of the SCM." That statement should be clarified with respect to the term "predictive powers;" the committee would agree that some confidence in the INTERPOLATIVE powers is warranted (over M/V, total U, pH), but the case has not been made for EXTRAPOLATIVE powers over solution composition and certainly not for EXTRAPOLATION from reference minerals to rocks from the site. When CNWRA wants to make a statement about "confidence" in the models, the committee feels strongly that they should (i) define exactly what function of the model it is (e.g., interpolation, extrapolation, over what range) in which they have confidence and (ii) provide adequate reference to the data that are the basis for their confidence.

C. Recommendations for interpreting and presenting adsorption-edge data from experiments in which a significant fraction of the U adsorbs on the container.

1. Determine experimentally (i) the total U in solution, (ii) the total U on the sorbent, and (iii) the total U on the container. Verify that the mass balance is acceptable, then forget the data for total U on the container.
2. For FITEQL, define a Type I component with $T_U = \text{total U in solution} + \text{total U on the sorbent}$, and a Type II component with $T_U = \text{total U on the adsorbent}$. Determine the values of the adjustable parameters.
3. Present the adsorption edge through three types of data. Plot: (i) experimental total U in solution / (experimental total U in solution + experimental total U on the sorbent); (ii) calculated total U in solution / (experimental total U in solution + experimental total U on the sorbent). These data come directly from FITEQL and the two sets of points illustrate the agreement between the model and the data, albeit at varying total U. Then plot an "idealized" adsorption edge. Use FITEQL and the constant total U concentration added to the system (i.e., in solution + on the sorbent + on the container) and the model to plot calculated total U on the sorbent / total U added to the system. This line involves an extrapolation in total U concentration, but presents the data in a form that people are used to seeing.
4. Isotherms. Knowledge of the characteristics of the isotherm at a few characteristic constant pH values helps us to think "mechanistically" about the adsorption reaction.

If the agreement of the model and the experimental data is good (as described in Section 7.C.3), all of the values for these plots can be calculated; if the agreement is not so good, the amount of U on the sorbent should be interpolated from the experimental data -- however, in this case, one must compare the error introduced from the imperfect model with the error introduced from the non-constant total U in the experimental data, and choose the best solution to the problem.

Bearing all of this in mind, calculate, for a few pH values (e.g., 4, 7, 9), total U adsorbed, and the corresponding values of (i) total U in solution, (ii) $[UO^{2+}]$ in solution, and (iii) $[UO_2(OH)_2]$ in solution, etc. Then plot log total U adsorbed vs each of these quantities to yield, at constant pH, (i) conventional Freundlich isotherms and (ii, iii) some hints about the "effective adsorbed species" at various pH values. For example, if the plot of total U adsorbed vs $[UO_2(OH)_2]$ is linear, then $UO_2(OH)_2$ is the "effective adsorbed species" and this knowledge helps one in thinking about the adsorption reaction. However, chances are that none of these plots will be particularly linear, and little insight may be gained.

5. Alternatively, and particularly useful for systems with varying M/V, are plots of log K_d vs pH to yield variation in K_d with pH, the slope of which is related to the total proton stoichiometry of the adsorption reaction. Also, plots of log "activity K_d " (which are

defined in MINTEQA2) vs $\log [\text{UO}_2(\text{OH})_2]$ or $\log K_d$ vs $\log [\text{UO}_2^{+2}]$ are useful for determining "effective adsorbed species."

6. The discussion above has been cast in terms of K_d ; the same sort of discussion applies for K_a (L/m^2), the surface area analog of K_d (L/kg).

D. The range of concentrations and surface coverages in the experimental data set.

The influence of surface coverage on the modeling efforts must be fully appreciated. The CNWRA experimental conditions have tended toward fairly high surface coverages (amount of sorbate per mass or area of sorbent) relative to that which one would expect to find under far-field conditions. However, it appears that CNWRA also plans to use some data from the literature collected at very low surface coverages to generate adsorption constants. Generally one observes lower K_d values at higher surface coverages. This fact must be borne in mind in (i) design of experiments and selection of data from the literature, (ii) selection of "conservative" values of K_d , and (iii) determination of the number of site types in the model.

E. Recommendations for modeling approaches (MA) to relate information from reference minerals (RM) to rocks from site (RFS).

As discussed at the review, the reviewers see basically three MAs that could be used to relate information from the RM to the RFS.

1. MA 1 (JAD). This method is more likely to lead in the long term to a better understanding of the sorption reactions and the factors to which K_d is sensitive. However, it does require additional surface chemical analysis. With this modeling approach, CNWRA would have to carry out at least steps a-f as the MINIMUM necessary to establish the applicability of RM to RFS.
 - a. Determine the surface mineralogy of the RFS. Information on surface mineralogy (obtained by XPS, SIMS, TEM, extractions, etc.) is in general preferred to information on bulk mineralogy (XRD), but work with whatever information is available.
 - b. Estimate the surface area or mass of each of the pure mineral components of the RFS.
 - c. Predict K_d of the RFS based on the identity of the minerals and "the best estimate" of the surface area (or mass) of each component of the mixture. Guidelines for applying models developed for RM to RFS are given in the postscript at the end of Section 7.E.1.
 - d. Measure the K_d or K_a of the RFS as a function of solution chemistry (pH, C_T , etc.). This step is quite similar to MA-3, which is discussed below, although the number of variations in experimental conditions might be less in MA-1 to allow time for the additional work with RM.
 - e. Compare measured to predicted. Adjust surface area or mass of each RM component of the RFS to improve agreement.

- f. Comment on the degree to which RM help to predict K_d vs pH at various C_T , etc:

functional dependence on pH

functional dependence on C_T

agreement in magnitudes of K_d

- g. Attempt to resolve differences by more extensive surface characterization of RFS and re-running adsorption experiments with RM under more complicated conditions that are more likely to represent RFS (e.g., in presence of H_4SiO_4 , Ca^{+2} , Al(III), DOC, etc.).

Postscript to MA-1: Application of models developed for RM to RFS.

Because the heterogeneity of RFS may be greater and different in character from the heterogeneity of RM, the pH dependence of adsorption observed on RFS can be quite different (generally less steep) than that of RM. Thus, the species and EDL model chosen to fit data for RM may not be useful for modeling adsorption on RFS unless the heterogeneity of RFS is well understood. Furthermore, the appropriate electrostatic term for the RFS is likely to be unknown. Thus, it is difficult to say exactly how to extend the EDL factor and the closely associated species stoichiometry from the RM to the RFS.

As an example of how models developed for RM can be extended to RFS, consider the approach taken by researchers at the USGS quite recently:

- h. Fit adsorption data on RFS with the smallest number of species possible, possibly one, to determine the relevant species type that gives the observed pH dependence for sorption on RFS.
- i. Derive the appropriate stability constants with FITEQL for reaction with RM using the same species and stoichiometry, even though it likely does not describe the pH dependence on RM well. The point is to get the chemical energy associated with the reaction as close as possible given that species.
- j. Determine the abundance of various site types representative of the RM on the surface of RFS.
- k. Predict adsorption on the RFS from the constants derived in b). Then attempt to resolve differences as described in 7.E.1.g.
2. MA 2 (DAD). This MA is an easier route to a conservative K_d , which might also meet the EPA/DOE/NRC requirements. Thus, in spite of the fact that it doesn't advance the understanding of adsorption processes, it might be all that is necessary to deliver the required answer. This MA is based on the presumption that it is possible to make CONSERVATIVE ESTIMATES of K_d for RFS based on K_d for RM, even though it may be impossible to transfer ACTUAL VALUES of K_d from RM to RFS. While MA 2 is conservative, it is rooted in surface complexation modeling, making it possible to transfer general reaction mechanisms (e.g., dependency on pH, C_T , etc.).

Effectively this MA boils down to the following inequalities to assure sufficient retardation (LSRM = least sorptive reference mineral):

$$K_d(\text{RFS}, \text{pH}, C_T) \geq K_d(\text{LSRM}, \text{pH}, C_T) \geq K_{d \text{ critical_for_safety}}$$

Note that the notion of LSRM is valid only when coupled with conditions of "least sorptive water chemistry, LSWC," that is, conservative values for water chemistry parameters.

- a. Determine the surface mineralogy of the RFS. Estimate the least sorptive phase that is reasonably abundant (a few percent by weight or greater) from this information.
 - b. Estimate the surface area or mass of the least sorptive RM component of the RFS.
 - c. Calculate the K_d of the least sorptive RM (LSRM), as a function of conservative pH, C_T , etc., based on the model developed from experimental data for the LSRM.
 - d. Use these calculated K_d in the transport model. These K_d values can be considered conservative for transport, and, if they are sufficiently large to ensure safety, no further work must be done.
 - e. Additionally, one might measure the K_d or K_a of selected RFS as a function of solution chemistry (pH, C_T , etc.), just to confirm that this MA works for selected RFS.
 - f. The calculation based on the LSRM would generally be very conservative, and may not yield a K_d that would predict an adequate level of safety. In this case, one may then consider the retardation afforded by the TWO least sorptive reference minerals as another conservative assumption. Obviously this step is somewhat in conflict with the initial presumption of MA 2 and might seem like back-pedaling, but it might be justifiable after careful analysis of the data.
3. MA 3 (JCW). MA 1 is indisputably an excellent approach for unravelling the mysteries of adsorption mechanisms. However, it is likely to require several iterations between RM and RFS, and some specialized surface analyses before agreement between the RFS and RM is achieved. Furthermore, one should note that this is still an area of current research, and it is still not absolutely certain that agreement between RM- and RFS-values of K_d can even be achieved. MA 2 is a fast track to a defensible conservative K_d , which might in fact turn out to be too conservative to be acceptable.

An alternative is MA 3, in which we say, good, we have learned something about pH and C_T dependence from the RM, and we have learned something about conducting experiments in well controlled media, but beyond these qualitative understandings, there is really nothing quantitative that we can transfer a priori from the RM to the RFS. This is the most conservative assumption with regard to the relation between RM and RFS. If it turns out that the RFS mimic quite closely RM, then we could certainly use that information, but we do not make any such assumptions a priori.

Thus, in MA 3, we focus on analyzing surface mineralogy from the site, trying to determine end members, and then run as many experiments with RFS as possible, using the pH and C_T experiments with selected reference minerals to help design the experiments to capture important sensitivities. Then we model the results from these experiments with generic nonelectrostatic sites, and then calculate the K_d distribution for

incorporation into the transport model. In keeping with the presumption that there is really nothing quantitative that we can transfer a priori from the RM to the RFS, the reactions that are used to model sorption to RFS do not necessarily have to reflect reactions used to model sorption to RM. The labor required for MA 3 is probably less than that required for MA 1. One learns less about mechanisms, but one has more data directly from the RFS.

Appendix to Section 7. Detailed comments on introduction of additional sites and species.

1. For pH adsorption-edge data with a gradual slope, either additional surface species or species with a low H^+ stoichiometry might become necessary. However, most typical adsorption edges should be represented with no more than 1 or 2 species (or types of sites). In the presence of carbonate or DOC, additional species may become necessary to describe experimental data.
2. For reasons discussed in Section 7.D, it is generally desirable to develop models with data over a wide range in surface coverages. However, this wide range of data may necessitate a second (strong) site type. If radionuclide competition for strong sites is to be considered in modeling, then it will be necessary to arrive at a common value for the strong site density for such calculations. This could be accomplished with a weighted-average value for the strong-site density for the radionuclides being considered. Binding constants used in the modeling, of course, must be consistent with the site density from which the constants were derived.

Although consideration of data sets with a wide range of surface coverages is desirable for the reasons discussed in Section 7.D, it does make it more difficult for sorption data base development, due to the difficulty in defining the density of strong binding sites that works well for many different ions. Thus, if the range of data is not too large anyway, it might be more convenient to maintain a single site type.

3. For some pH adsorption edge data sets, inclusion of multiple surface species may eliminate the need to consider two site types. The need for multiple surface species rather than two types of sites depends on how the solution speciation of the adsorbing ion changes with pH. For elements that exhibit significant changes in speciation with pH (e.g., some oxyanions, actinides), consideration of multiple surface species could be more effective in fitting data than introduction of a second type of site. Thus, the use of a single surface species, as was done in some of the work that was reviewed, may need to be re-evaluated for some cases.
4. As one might infer from the preceding paragraphs, the authors of this section have somewhat different perspectives on the merits of multiple site types vs multiple surface species as the preferred means of improving agreement between the model and the data. The fact that many factors influence speciation (e.g., sorbate to sorbent ratio, pH-dependence of solution speciation, competing cations and anions on the surface and in solution, electrostatic vs nonelectrostatic model, etc.) makes it difficult to reach a simple, generally valid conclusion on this issue.

However, the reviewers do agree that resolution of these modeling issues should not assume a life of its own in the CNWRA Sorption Project; the reviewers agree that it is far more important to collect experimental data over a wide range of experimental conditions -- or conditions relevant to the problem being studied -- and then take care of the modeling in the most logical way. The "wide range of conditions" includes both variations in surface coverages (which might be handled most easily with additional site types) and pH variations (which might be modeled most easily with additional surface species or site types). In the experimental work that has been completed to date, the pH values have covered the range foreseeable for the Yucca Mountain far field; in contrast,

the surface coverages are generally higher than those anticipated in the Yucca Mountain far field.

8. CNWRA Plans for Further Work - John C. Westall

Recommendations (based on plans presented by CNWRA):

- o Focus on experimental work on Pu, being mindful of the great experimental difficulties caused by the redox activity of this element.
- o Focus on the development of a comprehensive conceptual model of transport in the unsaturated zone, pending clarification of the relative importance of matrix flow vs fracture flow.
- o Incorporate rocks from the site in the experimental and modeling work.

Comment

This section of the report pertains only to the short presentation of "Further Work" given by Dr. Pabalan on Tuesday, June 20, 1995 at CNRWA. The points proposed by Dr. Pabalan were:

- Spectroscopy (EXAFS, Raman, etc.)
- Molecular dynamics simulation
- Sorption experiments [with] other actinides (e.g., Pu(IV, V, VI), others?)
- Competitive sorption experiments
 - radionuclide mixtures
 - mineral mixtures
- Transport (column) experiments
- Elevated temperature experiments
- Variable saturation transport experiments?

The reviewers felt that some of these topics could not be developed sufficiently in the time frame of the CNWRA Sorption Project to yield benefits to the practical problems of the project. The recommendations that are listed above reflect the discussion that followed Dr. Pabalan's brief presentation.

Part II. Comments of Each Reviewer

1. Comments of Laurent Charlet

1. Since the ultimate goal of the fitting exercise (CNWRA 95-001 and CNWRA 93-019) is to allow CNWRA to critically evaluate the DOE License Application data, it would be worthwhile to re-plot all data contained in the two above cited reports both as % adsorbed vs. pH (what has been done) and as K_d vs. pH (as done in Report CNWRA 94-02S). Otherwise it is often hard to judge results presented in a K_d format when one is accustomed to thinking in the % sorbed format. It would also point out the physico-chemical conditions in which K_d falls below 100, i.e., those conditions which have to be regarded with a special care, according to DOE's minimum K_d strategy.

2. Np adsorption on biotite (CNWRA 93-019, p. 4-23 and CNWRA 93-01S). Actinides are usually more mobile in their highest oxidation state. Therefore, the Sorption Project has considered sorbates only in their higher oxidation state. However, sorption of "Np(V)" on biotite should be handled with care. It has been shown recently by XPS (Ilton and Veblen, 1994) that Cr sorption onto phlogopite and biotite results in a reduction of Cr(VI), coupled with the oxidation of structural Fe(II). The same could probably occur with Np(V). You should report the equilibrium criteria used in the study you are using. The surface reduction could be a slow process.

3. Np(V) adsorption on magnetite (CNWRA 95-001, p. 4-7). Same comment. Furthermore, one would like to know the aqueous complexation of Np(V) which is responsible for the predicted adsorption decrease at high pH, and the reason why only 50% at the most of Np can be adsorbed. So please list all solution reactions and corresponding equilibrium constants used.

4. U(VI) adsorption onto magnetite (CNWRA 95-001, p. 4-18). Same comment. The data appear to me to indicate a precipitation process. It would be worth to compare with J. Bruno's results on coprecipitation of Fe^{3+} and UO_2^{2+} .

5. U(VI) adsorption on quartz (Bertetti et al., Draft Document). In order to fit the data, the authors have introduced two type of sites. Some spectroscopic data could (and should) be invoked to support such a choice (see e.g. Gallei and Parks, 1972; Sindorf and Maciel, 1983; and a paper using RBS spectroscopy for the study of uranyl adsorption on silica: *Radiochim. Acta*, 58/59, 219-233 (1992)). If not, the fit should be compared with the one produced by a single-site model with additional surface species.

6. U(VI) onto alumina (Prikryl et al., *Radiochim. Acta* 1994). In this paper you invoked hydroxy-carbonato uranyl surface complex, whereas you don't need this complex in the fitting of uranyl sorption data onto montmorillonite and kaolinite (CNWRA 95-001). Since the aluminol groups would be the most active clay edge sites, the two sets of data are incoherent. Please justify this difference.

7. U(VI) sorption on montmorillonite (CNWRA 94-01S). Montmorillonite pretreatment involves only a saturation at near neutral pH, whereas experiments are performed from pH 2.0 to 9.0. You should either (i) expose montmorillonite to low pH values during the pretreatment (see e.g. Sposito's recipe, 1981, and the AFM pictures published recently in *Clays and Clay Minerals* (Hartman et al., 1990) of the clean surface obtained; or (ii) follow the presence of aluminum and silica in solution. Your solution chemistry may be more complicated than that which you imagine.

8. Acid-base characteristics of montmorillonite (CNWRA 93-02S and 94-01S). You claim that potentiometric data are rarely available for clays. However, since Riese (1982) quite a few papers have been published on the subject (for montmorillonite see Charlet et al., 1993; Stadler and Schindler, 1993). It would be worth comparing these data with your "established" combined silanol-aluminol model.

9. Am(III) adsorption on silica (CNWRA 95-001, p. 4-4). Americium sorption data are very poorly fitted. The adsorption edge spans over 5 pH units, and clearly a single species single site model cannot (whatever the model) fit the data correctly. It would be worth trying a two-site model (see above point) in order to see whether the U and Am data can be fitted by a single model of silica surface chemistry. It could also be useful to look at the data of Moulin and Stammose (1989) and Degueudre and Wernli (1993) for Am sorption on silica.

10. Np adsorption on goethite (CNWRA 95-001, p. 4-6). A combination of Comments #1 and #5. Np sorption isotherm is not sharp enough to be fitted by a single-site, single-species model. Np could also be reduced at the surface of goethite. Bidoglio and co-workers (1993) have shown by XANES spectroscopy that traces of Fe(II) within an Atkinson-type goethite were enough to induce this reduction.

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2. Comments of James A. Davis

Report: Turner and Sassman (1994) Approaches to Sorption Modeling for High-Level Waste Performance Assessment, Migration-93 Conference Proceedings.

Many comments on this report also apply to Turner (1995) - A Uniform Approach to Surface Complexation Modeling of Radionuclide Sorption.

1. Pg. 746, Site Density: A single site density was assumed for the modeling. The authors state that model simplification for PA is a desired goal and one of two reasons for this assumption. However, the downside of this assumption is an inability of the model to describe the Freundlich isotherms that typically describe radionuclide adsorption data. Use of SCM's with PA has generally been proposed as a way of estimating K_d's for use in PA models. If so, the introduction of a second site type poses no computational problems. If PA models were rewritten to include SCM's, I still do not believe a second

site type would pose a problem. I see the EDL term itself posing a greater computational problem than the second site type, since solving the EDL equations cause additional iterations and sometimes leads to nonconvergence within the desired criteria. The second reason offered for not including a second site is that little data is available for site heterogeneities on mineral surfaces. I would argue that there is an abundance of data on site heterogeneities on various mineral faces, however, these observations have not been included in SCM's. However, a strong site can also be viewed as a necessary model construct rather than an accurate description of site heterogeneities, i.e. a second site is desirable in order to describe adsorption as a function of adsorbate concentration under otherwise constant conditions (the isotherm). Without this evaluation it is perhaps far too difficult to extend the experimental data at surface coverages (with associated K_a values) observed in laboratory experiments to real-world simulations.

2. Pg. 746, Chem. Equil. Model: The solubility of aluminum oxide phases should be considered in evaluating the titration data.

3. Pg. 748, Radionuclide sorption Goethite example. It is stated that the uranium equilibrium constants were selected from the NEA Thermodynamic Database. However, one species considered in the modeling was apparently $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, which is NOT in the NEA database, but was used by Tripathi. Have they used the Tripathi constant for this aqueous species?

4. Pg. 749, near eq. 8: The selection of species and reaction stoichiometry for modeling seems too arbitrary. While the principle of parsimony should be adopted, one can be TOO parsimonious by simply fitting a single adsorption edge. The experimental studies generally suggest that protons are released as U(VI) is adsorbed - why then are so many XOH and XOH₂ species considered? It is important to propose a chemically defensible surface species, and to recognize that the dominant surface species may not be identical to the predominant aqueous species under the same conditions. For the case of U(VI), the choice of appropriate surface species, in the absence of spectroscopic data or other structural arguments, must be judged on its ability to fit experimental adsorption data. While one can take the parsimonious approach in selecting species to fit a single adsorption edge, the choice of species cannot be considered convincing until it can be shown that it fits data for adsorption over a wide range of chemical conditions. For example, the choice of multinuclear species for adsorbed U(VI) made by Kohler et al. (1992), Hsi and Langmuir (1985) and Payne et al. (1992) was made without fitting any data as a function of total U. Waite et al. (1994) have shown that this was likely an error in experimental design and modeling strategy.

Modeling with the TLM for U(VI) adsorption should be done with β -layer ("inner-sphere") surface complexes because of the observed independence of adsorption as a function of ionic strength.

6. Pg. 751, Modeling sorption with CO₂: It is not made clear how the modeling in Fig. 3 is done. Are only the surface species containing U(VI)-carbonate complexes being considered, or does the modeling include the best hydrolyzed species from Fig. 2 as well? If not, why not? Wouldn't it be expected that such species should be included in an equilibrium model?

Report: Pabalan et al. (1993) Experimental study of U(VI) sorption on the zeolite mineral clinoptilolite

7. Pg. 779, Sorption methods: It would appear that sorption to the container walls would be maximized by the 10-day equilibration of U(VI) solutions at a variety of pH values before the addition of zeolite. The solutions can be equilibrated with CO₂ and NaHCO₃ to reach a stable pH before adding U(VI). The experimental method should also be evaluated to see if the results and container sorption are identical when the zeolite is added before the U(VI) instead of after.

8. Pg. 781: Ion exchange could be important at low ionic strengths. I could not find where the ionic strength or concentration of Na was given. Was it variable due to NaHCO₃ addition?

9. Pg. 296: Equil. Study: The concentration of dissolved Al should be monitored kinetically for those experiments conducted at low and high pH.

3. Comments of David A. Dzombak

1. Connect with research at other DOE labs on radionuclide sorption.

There is work going on at other DOE-related laboratories on radionuclide sorption and subsurface transport of radionuclides that is relevant to the CNWRA Sorption Project. Communication with these groups should be established. There are a number of research groups at Savannah River, for example, doing work relevant to the goals of the Sorption Project. Dr. Steve Serkiz of the Savannah River Technology Center and Dr. Sue Clark of the Savannah River Ecology Laboratory are working collaboratively on studies of uranium sorption on sand aquifer materials (Johnson et al., 1995), effects of chelating agents on nickel sorption on hydrous ferric oxide (Bryce et al., 1994), identification of dominant sorbing phases in aquifer materials, and other topics. Dr. Paul Bertsch and his group are working on measurement of in situ chemical speciation of uranium in soils (Bertsch et al., 1994) and on colloid generation and transport in the subsurface (Seaman et al., 1995).

2. Identify relevant range of groundwater chemical compositions.

The chemistry of the saturated and unsaturated zone groundwater at the Yucca Mountain site has been studied to some extent and is described in various reports, e.g., on pp. 5-8 to 5-11 of Turner (1991a). Saturated zone groundwater is reported to be essentially an oxidic, dilute solution of sodium bicarbonate, while unsaturated zone groundwater is similar but exhibits more variability. Available data seem to yield a reasonably clear picture of the current range of groundwater chemical composition, but I found no discussion of how groundwater chemistry is expected to evolve over the repository performance period of 10,000 years. It was mentioned during the panel review meeting that groundwater chemical evolution is being investigated in a separate project. To identify the range of chemical compositions appropriate for investigation in the Sorption Project, there needs to be some linkage with the groundwater chemical evolution research at CNWRA.

3. Identify major sorbing phases; investigate role of surface coatings.

While a wide range of mineral phases exists in the rocks beneath the proposed repository, only those at the solid/water interface in the pore spaces will affect radionuclide sorption/desorption reactions. It is critical that the most important sorbing phases be identified for evaluation of the possible effects of sorption on radionuclide transport. This will require evaluation of dominant groundwater flow paths and mineral assemblages along these flow paths. As these evaluations are conducted, it will be important to examine the role of surface coatings in determining the sorption properties of the target mineral assemblages. In some of the previous work performed in the sorption project with clinoptilolite (Pabalan et al., 1993) and quartz (Bertetti et al., 1995), pretreatments were employed to ensure that all surface coatings were removed from the solids. In the field, these surface coatings may control surface reactions.

4. Sorption kinetics depend on sorbate/sorbent ratio.

As demonstrated by Dzombak and Morel (1986) and others, the rate of sorption of ions onto oxide minerals depends on the sorbate/sorbent ratio, i.e., on the relative amounts of sorbate ions and surface sites. When surface sites are in great excess, sorption kinetics are rapid. The rate of sorption slows as the sorbate/sorbent ratio increases. The dependence of sorption rate on sorbate/sorbent ratio means that statements about whether sorption is fast or slow (e.g., in Pabalan et al., 1993) should be qualified with the special conditions under which the kinetics experiment is conducted. Thus, it is not true in general

that transition metal adsorption on iron oxides attains equilibrium in "a matter of hours" (Turner, 1991b, p.2-16); this occurs only at low sorbate/sorbent ratios.

5. Surface site density is a fundamental property of a mineral phase.

The approach of fixing surface site density at 2.3 sites/nm² for every mineral phase (Turner, 1993, 1995; Turner and Sassman, 1994) is expedient for modeling mineral assemblages but is crude. Oxide minerals exhibit a fairly significant range of surface site densities, and identification of the approximate value for a particular mineral is fairly straightforward if sorption data exist for the solid. By compiling and examining maximum observed sorption densities for different ions on the solid of interest, the surface site density for the mineral can be approximated if 1:1 binding is assumed. A database of surface complexation constants constructed with an assumed site density may have use for screening purposes but should not be regarded as definitive for the mineral. If sufficient sorption data exist to enable estimation of surface site density for a particular mineral, then N_s is not an adjustable parameter. Turner (1995, p.2-4) implies that N_s is always an adjustable parameter, but this is not the case. For example, Dzombak and Morel (1990) estimated N_s for hydrous ferric oxide from experimental sorption data, as did Ali (1994) and Mathur (1995) for goethite.

Also, while site concentration may vary in a nonlinear manner with solid concentration in some systems as noted by Turner (1991b, p.2-8), e.g., an aqueous suspension in which substantial coagulation of particles is occurring, a linear relationship between site concentration and solid concentration is usually assumed. The so-called "solid concentration effect" is not well understood, its effect on sorbed concentration is typically not more than a factor of 2 to 3 (see DiToro et al., 1986), and some of the data used to support its existence may be the result of experimental artifact (Gschwend and Wu, 1985). In the absence of new, clarifying information, it is reasonable to assume a linear relationship between site concentration and solid concentration.

6. Correct for container sorption without explicit modeling of container surface.

In experiments with weakly sorbing minerals such as quartz, sorbate sorption to the walls of the suspension container may become significant. This was the case in the work described in Bertetti et al. (1995), and was exacerbated by the fact that the sorbate was added to the solution before the quartz was added. To account for sorption on the container walls, Bertetti and coworkers incorporated surface sites for the container walls in a surface complexation model for the aqueous suspension. This approach unnecessarily complicates the correction needed. Sorption on the container walls can be ignored if the total sorbate in the aqueous and sorbed phases is known through measurement. The system can then be modeled using the total sorbate mass in solution and on the mineral to define the TOT sorbate concentration for the system.

7. Need to consider competition with major electrolyte ions.

For conservative simulation of radionuclide sorption under a particular groundwater chemical condition, effects of competitive sorption should be considered. While most radionuclides present will be at sufficiently low concentrations that competition among them should not be an issue, there may be some competition of radionuclides and major electrolyte ions that can sorb significantly. Calcium, magnesium, fluoride, and sulfate are all electrolytes of interest in this regard. Surface complexation constants for these and any other sorbing electrolyte ions should be developed for the reference minerals selected, and simulations should include competition of electrolyte ions and radionuclides for surface sites.

8. Difficult to incorporate ion exchange reactions in a surface complexation model.

At the panel review meeting there were some discussions about the extent to which weak sorption of some radionuclide ions on various minerals may be an ion exchange process rather than a site-specific chemisorption process. A proposal was made that ion exchange reactions could be incorporated in an enhanced surface complexation model. While ion exchange reactions can be incorporated in chemical equilibrium models in various ways, incorporating such reactions in a surface complexation model in a

rigorous manner is complicated and data intensive (Dzombak and Hudson, 1995). Whether simple exchange reactions or calculations of sorption in the diffuse layer are employed, proper formulation of mass balance and surface charge equations can be difficult. I recommend that the Sorption Project modeling continue to be developed in the framework of surface complexation alone. The mineral/water partitioning of abundant but weakly sorbing electrolyte ions is not a topic of great relevance to the CNWRA Sorption Project.

9. List all solution reactions and corresponding equilibrium constants used.

In CNWRA reports of surface complexation modeling efforts, it would be useful to list in a table all the solution complexation reactions employed, the corresponding equilibrium constants, and the source of the reactions and constants. In the various modeling reports provided, there were statements in the text about the sources of the solution reactions and constants, but the specific reactions and constants were not provided. It would also be useful to provide solution speciation diagrams for the radionuclides of interest, as Pabalan et al. (1993) did for uranium(VI).

10. Sorption of radionuclides on potential colloidal materials should be investigated.

There is growing evidence that mineral colloids exist and are mobile in groundwater systems (e.g., Ryan and Gschwend, 1994; Seaman et al., 1995). Simulations and some limited experimental data indicate that enhancement of transport by groundwater colloids could be very significant for strongly sorbing chemical species that exhibit slow desorption or that sorb irreversibly (Adeel et al., 1995; Roy and Dzombak, 1995). While colloid-enhanced transport has not yet been verified in the field, it is likely that such confirmation will be obtained within the next several years. Colloid-enhanced transport has the potential to be a very significant issue for Yucca Mountain, and it is recommended that CNWRA get ahead on this issue. In the DOE literature provided to the review panel, there is some indication that DOE is planning to sample groundwaters at the repository site for colloids. CNWRA should follow this work closely, and should consider experiments to investigate sorption of radionuclides on these sampled colloids.

11. Don't force a one-species fit in surface complexation modeling.

Much of the surface complexation modeling in the Sorption Project to date has been conducted under the self-imposed constraint of one surface species. This constraint was introduced early on in the application of surface complexation modeling by CNWRA, apparently to keep the model as simple as possible to facilitate eventual direct coupling with a transport model. One surface species has been sufficient for adequate fits in most cases, but in some cases (e.g., the discussion on p.4-14 of Turner, 1993) the one-species constraint has led to difficulty in obtaining good fits of data. While maintenance of model simplicity is certainly a useful goal, there seems to me to be little need to force a one-species fit in all cases, especially since direct coupling of the surface complexation model with a transport model is now only a remote possibility. Multiple species are usually required for a good fit of sorption data for ions that undergo significant changes in speciation over the pH range of their sorption edge.

12. Clarifications regarding discussions of DLM and CCM in Turner (1995).

On p. 2-3 of Turner (1995), it is stated that the DLM and CCM "assume a one-layer interface." The DLM and CCM are two layer models: one surface layer plus the diffuse layer of counterions. Also on p. 2-3 of Turner (1995), it is stated that "unlike the DLM and CCM, the TLM allows for adsorption of the background electrolyte." Consideration of electrolyte sorption is not precluded with the DLM and CCM, it is just that in the DLM and CCM the electrolytes must be considered to sorb in the same plane as all other specifically sorbing ions. This is not satisfactory to many people, but it can be done. In the TLM, electrolyte ions are placed in a second surface layer.

13. Be clear about the definition of intrinsic versus apparent surface complexation constants.

In the presentation of surface complexation reactions in several CNWRA reports (e.g., in Turner, 1993; Turner and Sassman, 1994; Turner, 1995), there is not a careful definition of the surface complexation equilibrium constants. With reactions written in terms of solution ions as the reacting entities, as is done in the CNWRA reports, the equilibrium constants are actually apparent constants: the coulombic effects are incorporated in them. However, it is intrinsic constants that are extracted with FITEQL and employed in the chemical equilibrium models. The distinction between apparent and intrinsic surface complexation constants should be clear in CNWRA reports. In most of the CNWRA publications cited, the authors should have referred to intrinsic constants in the text, for that is what was provided in the tables of FITEQL-extracted values. Careful definition of surface complexation constants will be needed even more if CNWRA undertakes some modeling with the no-electrostatic model (NEM) for which the equilibrium constants will be apparent constants.

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4. Comments of John C. Westall

General Comment.

1. The team has not had an exceptional amount of experience in surface complexation experimentation and modeling. However, the team is bright and has come up to speed rapidly. Nonetheless, I feel that there would have been significant benefit to the program if this panel had been assembled four years ago. From the periodic reports and publications, it is apparent that a lot of energy has been invested rediscovering the wheel (e.g., sorption to container walls).

J. D. Prikryl, R. T. Pabalan, D. R. Turner, B. W. Leslie. Uranium Sorption on α -Alumina: Effects of pH and Surface-Area/Solution-Volume Ratio. *Radiochimica Acta*, 66/67, 295-300 (1994).

2. The idea to use NIST materials with known surface areas is rather original. However, since the authors do not pretreat the samples, it is important to know how they were prepared. No information is given on this topic.

3. p. 296: The pH range was 2 - 9; over this range of pH, the possibility of dissolution of alumina should be considered, investigated, and reported.

4. p. 298, 1st paragraph: apparently the authors assume that the amount on the wall is not affected by the presence of alumina; I think that this is a poor assumption.

R. T. Pabalan, J. D. Prikryl, P. M. Muller, T. B. Dietrich. Experimental Study of Uranium(6+) Sorption on the Zeolite Mineral Clinoptilolite. *Mat. Res. Soc. Symp. Proc.* Vol. 294, 777-782 (1993).

5. p. 779, top: apparently no salt (other than counterions of acids and bases) was added to the solution in these experiments. The reason and possible effects of this atypical procedure should be discussed.

6. p. 780, bottom: the species and the constants from the NEA data should be listed explicitly, since two people going to the same book could come back with different sets of constants (e.g., Table V.7, log K for $\text{UO}_2(\text{OH})_2 \leq -10.3$...).

7. p. 781: Obviously the arguments for and against ion exchange would be stronger if some information on the salt concentration were given.

F. P. Bertetti, R. T. Pabalan, D. R. Turner, M. Almendarez. Experimental and Modeling Study of Uranium(6+) Sorption on Quartz. Manuscript in Preparation.

8. Two points about this paper are particularly good: (i) the effect of wall adsorption is handled appropriately and (ii) the effect of M/V on sorption edges is recognized and the advantage of plotting conditional K_d vs pH is seen. It is a bit unfortunate that these points were not incorporated earlier, but certainly better late than never.

9. I recommend that the model for wall adsorption be discontinued. In my experience the walls of different vessels exhibit different properties. I would simply determine U in solution, on solid, on wall; determine distribution from amount on wall and amount on solid; and verify mass balance from all three pieces of data.

10. The isotherms at constant pH (Figure 5) are valuable and should be continued in the groups work.

D. R. Turner. A Uniform Approach to Surface Complexation Modeling of Radionuclide Sorption. Report CNWRA 95-001, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, 1995.

11. p. 2-2, bottom: "the Stern-Grahame extension of the" should be deleted to correct this sentence.

12. p. 4-28, middle: I believe that the authors statements about M/V in the two sentences beginning "According to Pabalan et al. (1994)," are incorrect, although I can't say that I understand totally what the author is trying to say.

13. The data tables appear to be complete; this is commendable.

D. R. Turner. Mechanistic Approaches to Radionuclide Sorption Modeling. Report CNWRA 93-019, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, 1995.

14. The approach taken in this report is very thorough and systematic, and shows that the author has good background information. The progress that the author has made from his "non-surface-complexation" background is commendable.

15. The author shows a good appreciation of the "fact and fiction" of mechanistic models.

16. Critical analysis of this work and recommendations for further work are outlined in Section 7 of Part I.

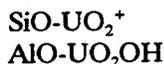
5. Comments of John M. Zachara

General issues identified from pre-review of reports and written material

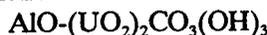
1. The scientific approach of the effort is not clear. What are the tangible products of both the experimental and modeling efforts, and how will these be used for license evaluation? What is the logic for activities and research progression? The two scientific plans provided in the review documents provide detail on long term directions and approach, yet they do not appear to have been followed by the researchers.
2. Extensive modeling has been performed on a variety of phases whose potential presence in the repository is not clear.
 - Detailed mineralogic data is needed from the repository site for both formation tuffs and fracture filling mineralogy.
 - A listing of key phases from Yucca mountain is needed including their potential abundances, compositions, surface areas, and other relevant properties.
 - What compositional and mineralogic variations are expected from zeolites at the site?
3. Solution chemistry and the issue of surface saturation has not been sufficiently addressed.
 - Al and Si concentrations should be measured in all pH edge sorption experiments with layer silicates, zeolites, and site materials.
 - Given that significant sorption of H_4SiO_4 occurs to Al and Fe oxides at intermediate to high pH and that high concentrations of dissolved Si exist in waters contacting tuff, won't Si saturate or strongly compete with radionuclides for sorption sites in the repository environment? Should this competition be explicitly considered in the sorption studies and modeling?
 - Experiments seem to be performed under unrealistic conditions of ionic strength and surface saturation. Note, Na and Ca concentrations range from 0.3 - 7 mM in Yucca mountain groundwaters, while the sorption experiments have been performed at 100-1000 mM.
4. The sorbents used for experiments and as a basis for modeling have, in general, not been sufficiently characterized.
5. A matrix must be established for relevant experimental parameters and their expected range in and surrounding the repository. Experiments and modeling must traverse this parameter space. Such parameters include, but are not limited to the following: $[Na]_{aq}$; $[Ca]_{aq}$; $[pH]$; $[SO_4^{2-}]$; $[H_4SiO_4]$; $[U]_T$, $[Np]_T$, ...; $[SOH]_T$, and $[X]_T$, where X is fixed charge on zeolites and clays. What levels of radionuclide surface saturation could ever be expected?
6. Are the few select groundwater analyses reported in the DOE documents really relevant to the repository. Are porewaters in the unsaturated zone at 80% volumetric water content likely to be significantly different in composition?

7. Modeling parameters are too arbitrarily chosen, especially surface species. For example, note that the pH adsorption edges for U(VI) on the cheto smectite, α -alumina, and clinoptilolite in presence of $P_{\text{CO}_2} = 10^{-3.5}$ occur at approximately the same pH. However, very different sets of surface species were used to model these data in spite of a common surface site (AlOH):

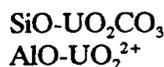
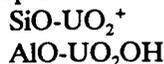
a.) smectite



b.) α -alumina



c.) clinoptilolite



After reading all the documents provided, this reviewer feels that significant improvements should be made in the selection of surface species. Surface species have been chosen both inconsistently and indiscriminately and this yields discomfort in the merits of the entire activity. A more credible approach would seem to be to identify those surface complexes that are realistic from a coordination chemistry perspective and constrain the fitting to those or simple/plausible combinations of them. Limiting the data fitting to one surface species seems overly restrictive, especially for many of the radionuclides that display complex aqueous speciation.

8. Too much emphasis has been placed on modeling sorbents that are not well characterized and data of questionable merit, and not enough placed on experiment.
9. The mM and sub-mM concentrations of electrolyte cations reported in Yucca mountain groundwaters suggest that ion exchange of various radionuclide cations may be a significant adsorption mechanism that can retard the transport of radionuclides from the waste repository. Ion exchange has been suppressed in most of the CNWRA experimental studies with layer silicates and zeolites through use of unrealistically high ionic strength electrolytes. Experiments with these sorbents and composite mineral materials from the site should be performed at lower, relevant ionic strengths to investigate potential contributions of ion exchange. Ideal exchange can be assumed as a first approximation of the exchange process (a valid assumption at the low radionuclide concentrations being studied) that can be described with a half reaction modeling approach (Fletcher P. and G. Sposito. 1989. The chemical modeling of clay/electrolyte interactions for montmorillonite. *Clay Miner.* 24:375-391). The half reaction approach can be linked with standard SCM calculations within FITEQL to describe surface complexation and ion exchange reactions on multiple site sorbents such as smectite, biotite, and zeolites (Zachara, J.M. and S.C. Smith. 1994. Edge complexation reactions of cadmium on specimen and soil derived smectite. *Soil Sc. Soc. Am. J.* 58:762-769).

10. The predictive capability of the SCM's is often overstated. While this reviewer feels that the research team has done an excellent job in developing a common set of parameters to drive SCM calculations, he feels that they should be used cautiously for extrapolative predictions. The fact is, that CNWRA research team has calibrated/fit SCM's to experimental data and, in so doing, has shown that the models and their associated parameters can reproduce the noted sorption behavior with its attendant range of experimental variables. Without further experimentation, the authors are unjustified in extending the SCM parameters beyond the experimental range of their measurement.

Reviews of Selected Documents

CNWRA 95-001

A more comprehensive review was given this document because it represents a culmination of several recent years of research, and defines the current status project.

11. General synopsis

Overall approach is good

- o fixing site density and K_+ based on that is a good point of departure.
- o the selection of surface complexes is a problem
 - model calculations will likely degenerate under certain conditions
 - many defied chemical intuition
 - others are inconsistent between like sites on different solids, e.g., AlOH on alumina, kaolinite, smectite
- o solids are modeled that are insufficiently characterized; e.g., biotite, kaolinite, smectite
- o use of the term "predicting" should be de-emphasized SCM were used to fit or were calibrated to/not predict experimental data
 - this reviewer still believes that extrapolation beyond the experimental conditions is not warranted.
- o thought and emphasis must be given toward the application of SCM to natural materials, that is a real challenge.

Comments referenced to page or section

12. Section 4, general comment

Further concerns on surface species - Many of the surface species evaluated are simply not plausible from a coordination chemistry standpoint. For example, on pages 4-18 to 4-22 it seems unlikely that only neutral SOH sites would be involved in UO_2^{2+} adsorption. It is also suspicious that the best fits to the data occur using hydrolysis species that are not stable in the aqueous phase over the pH range of the experiment. As another example, the complex suite $AlOH_2-NpO_2OH^+$ and $SiOH_2-NpO_2OH^+$ as used for biotite on page 4-25 seems highly unlikely. Furthermore, the value for K_+ for SiOH is not well known because of the extremely low pH at which proton adsorption occurs to the neutral site. This reviewer recalls that K_+ for SiOH was not used to model the titration data for silica in CNWRA Report #93-019. A more credible approach would seem to be to identify those surface complexes that are chemically realistic and constrain the fitting to those or simple/plausible combinations of them. The fact that unlikely

surface complexes can, at times, be fit to the experimental data is not a test of modeling but of curve fitting.

13. Page 4-24

Regarding extrapolation to pH values beyond the experimental range. Extrapolation should be performed cautiously if at all. The modeling exercises performed herein are only curve fitting. There is ample evidence in the report that a single surface species that fits the data at one pH or over a specific range, may become irrelevant at higher or lower pH values if the aqueous speciation changes.

14. Pages 4-2 to 4-30

Results of SCM modeling of radionuclide sorption to different reference minerals. The following represents a qualitative evaluation by this reviewer of the ability of the applied SCM to fit the experimental data.

| | <u>System</u> | <u>Modeling</u> |
|-----|----------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. | Am ³⁺ - Al ₂ O ₃ | good |
| 2. | Am ³⁺ - αAl ₂ O ₃ | poor |
| 3. | Am ³⁺ - αSiO ₂ | poor |
| 4. | Np(v) - Al ₂ O ₃ | good, don't understand how these give comparable fits to the data |
| | | $\text{AlOH} + \text{H}_2\text{O} + \text{NpO}_2^+ = \text{AlO} - \text{NpO}_2\text{OH} + 2\text{H}^+$ $\text{AlOH} + \text{H}_2\text{O} + \text{NpO}_2^+ = \text{AlOH}_2 - \text{NpO}_2\text{OH}$ |
| 5. | Np(V) - goethite | fair - poor |
| 6. | Np(V) - magnetite | fair - poor |
| 7. | Np(V) - boehmite | fair - poor |
| 8. | Np(V) - lepidocrocite | fair - poor |
| 9. | Np(V) - αAl ₂ O ₃ | data not sufficient |
| 10. | Np(V) - ferrihydrite | good |
| 11. | Np(V) - SiO ₂ (a) | fair - good |
| 12. | Pu(IV) - goethite | fair - requires multiple species |
| 13. | Pu(V) - goethite | fair - don't see how modeling runs represent convergence |
| 14. | Pu(V) - alumina | good/marginal data |
| 15. | Th(IV) - Al ₂ O ₃ | fair |
| 16. | Th(IV) - SiO ₂ (a) | poor |
| 17. | U(VI) - magnetite | fair - poor |
| 18. | U(VI) - ferrihydrite | good |
| 19. | U(VI) - goethite | good |
| 20. | U(VI) - alumina | fair |
| 21. | U(VI) - quartz | good |
| 22. | C - ferrihydrite | good |
| 23. | Np(V) - biotite | fair |
| 24. | Np(V) - kaolinite | fair |
| 25. | U(VI) - kaolinite | good |

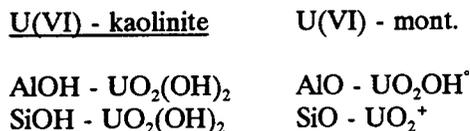
This subjective, yet simple review indicates that the one surface species SCM modeling approach can and should be improved because the model fits to the data are not outstanding.

15. Fig. 4-27

Figure has some good attributes, shows that the experimental data, as collected, conforms to the Langmuir equation. What about sorbent poor systems where site concentrations may be low and surface saturation approached?

Need to bring in more anticipated boundary conditions from the Yucca mountain site in terms of site concentrations and solution composition.

The inconsistency in surface complexes, however, is maddening. Note that the surface complexes used for U(VI) adsorption to montmorillonite and kaolinite are summarized below. A different surface speciation scheme is used for U surface complexes on the edges of the two minerals. However, both kaolinite and smectite have exposed aluminol (AlOH) and silanol (SiOH) groups on their edges that are likely to exhibit chemical properties that are similar to one another. Why then, would one expect or hypothesize that different surface complexes would form on the AlOH on smectite as compared to kaolinite, and vis-versa for SiOH? Such inconsistencies undermine the credibility of the approach and research in general.



16. Fig. 4-28

The model computation is based on the surface complex $>\text{FeO} - \text{UO}_2(\text{OH})_2$; yet this species was not even tested in Fig. 4-19 on page 4-20.

17. Section 4.4

Too much emphasis placed on the theoretical basis of the SCM without recognition of the fact that they have been calibrated to experimental data and are valid beyond that calibration range only if speciation does not change.

18. page 4-34

While K_d can be readily calculated for the U(VI) goethite system as shown in Fig. 4-29, performing such calculations for a natural material using this data and based on properties measurement is a different story. The conclusion that calibrated SCM can be used to compute K_d values for specimen sorbents over a broad range is not a surprise or new finding. The real challenge is to show how semi-quantitative estimates or predictions of K_d can be made for YM materials.

Note: Np(V) adsorption has been measured on Yucca mountain materials by the DOE team, why not try to model that and other comparable data?

19. Section 5

The phrase "principle of parsimony" is grossly over used; it has appeared in just about every report and is tiresome to say the least.

Uranium sorption on α -alumina: Effects of pH and surface-area/solution-volume ratio, by Prikryl, Pabalan, Turner, and Leslie

20. The paper presents some well performed experimental measurements of U(VI) on different surface area alumina's. The effects of vessel sorption are taken into account giving credibility to the experimental measurements. The results show that increasing the surface area of the mineral phase in suspension increases U(VI) sorption. This is not a new finding, but one that has been shown by others and is supported by intuition as well. The authors model the sorption data using a single surface complex: $XO-(UO_2)_2CO_3(OH)_3^\ominus$. This complex appears to describe the data well.

In actuality, the used surface complex should have been assigned a charge of -2 as both the reactive species, XO^- and $(UO_2)_2CO_3(OH)_3^-$, are negatively charged. This small mistake brings up a larger concern regarding the selection of surface complexes. The selected surface complex violates a general rule in surface complexation modeling, that anions do not bind to negatively charged surface sites and cations do not bind to positively charged sites. The selected surface complex therefore appears to be chemically unrealistic.

21. This reviewer was puzzled by several references to ion exchange within the structure of alumina; this seems like an implausible adsorption mechanism under any case.

Experimental and modeling study of uranium(6+) sorption on quartz, by Bertetti, Pabalan, Turner, and Almdarez

22. Like the preceding paper, this manuscript presents experimental results that appear of high quality. The consideration of the vessel sorption phenomena as a dynamic/competitive phase equilibria is excellent, and represents a clear progression in knowledge from the preceding study. It is clearly important for actinide sorption at low concentrations and has not been evaluated or considered sufficiently in past literature.
23. Before embarking on the surface complexation modeling, why not compare K_d to $[SiO^-]$. Surface charge development on silica shows a rather broad trend with pH as does the U(VI) sorption data.
24. Too much/unnecessary boilerplate on SCM.
25. The following comments are directed toward the sorption modeling.
- why was a different U(VI) surface speciation scheme selected for the single and two-site models? I would strive for consistency between them.
 - note that the reaction series employed for the two site model contradicts the generalized cation adsorption equation presented in equation 5. Any justification?
 - it is not clear how the uranyl sorption data were fitted (i.e., with or without the vessel sorption component). Figure cations seem to contradict the text. Clarification is needed.
 - explicit modeling of the vessel sorption process is good, a complex with $(UO_2)_3(OH)_5^-$ seems hard to justify, though, given its limited stability. A neutral complex with $UO_2(OH)_2$ seems the most plausible explanation for vessel sorption. It could be formulated in various ways using FITEQL.
26. I would rate this paper as a good one, and one of the better ones by the group. The experimental work seems to be of high caliber. Still, greater attention and care should be given to the selection and rationalization of the surface complexes.

Approaches to sorption modeling for high-level waste performance assessment, by Turner and Sassman

27. This paper represents a synthesis or condensed version of information presented in CNWRA 93-019 and 95-001. The authors should be commended for publishing this rather comprehensive piece. While technical criticisms can be leveled at portions of the work, its overall contribution is very positive and good. It is positive in that a simplified SCM approach is presented that is i.) shown to be workable for a broad range of mineral solids and ii.) is applicable to PA. The paper gives good visibility to the CNWRA research group. Their approach that begins first with evaluation of the potentiometric titration data and integration of this with the modeling of the sorption data is exactly what is needed to address this complex problem. The statistical manipulations of the constants and their weighing is good, and the authors comments on the effect of data set size and intercomparability of results between different labs provide insights on important but rarely discussed issues.
28. The paper does suffer from problems already discussed in relation to the other manuscripts, particularly in relation to surface species selection. Many of those tested and used are improbable or chemically unrealistic. It seems unlikely that an aqueous species that is not even present over the pH range (e.g., $\text{UO}_2(\text{OH})_4^{2-}$) could be the dominant sorbed species.

Appendix - Addresses of Reviewers

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