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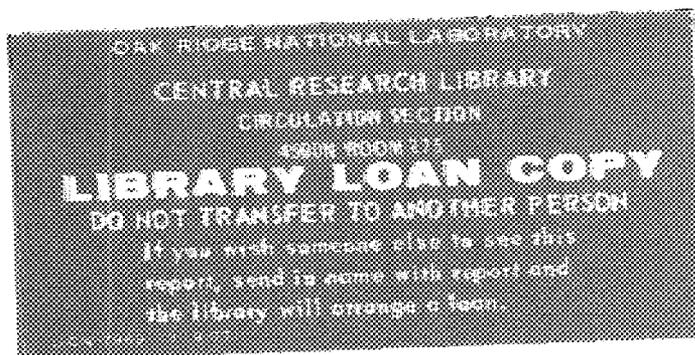
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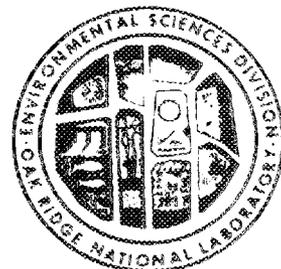
Proceedings of the First Geochemical Workshop on Shale

D. G. Brookins
S. H. Stow

(Environmental Sciences Division
Publication No. 2845)



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ORNL/TM-9865

ENVIRONMENTAL SCIENCES DIVISION

PROCEEDINGS OF THE FIRST GEOCHEMICAL
WORKSHOP ON SHALE

D. G. Brookins
S. H. Stow

Environmental Sciences Division
Publication No. 2845

NUCLEAR AND CHEMICAL WASTE PROGRAM
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ABSTRACT

D. G. BROOKINS and S. H. STOW. 1986. Proceedings of the First Geochemical Workshop on Shale. ORNL/TM-9865. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 55 pp.

This report represents the outcome of the first workshop dealing with geochemical research needs for a shale-hosted repository for disposal of high-level nuclear waste. The workshop was held at the University of New Mexico in 1985 and was attended by scientists representing academia, national laboratories, and the federal government. Research needs are grouped into three major categories: (1) characterization of baseline conditions, (2) radioelement behavior: ambient conditions, and (3) effect of waste emplacement. Within each category, specific needs are identified and discussed. For each, statements of justification, approach, and man-power requirements are presented. General levels of priorities are established for each research need.

1 INTRODUCTION

1.1 OBJECTIVE

The Oak Ridge National Laboratory (ORNL) is managing the Department of Energy's (DOE's) Sedimentary Rock Program (SERP), which is assessing shale as a possible host medium for construction of a high-level nuclear waste repository. For planning purposes, it is necessary to identify data and research needs that will be required in future years. Then, an information base for shale that allows site screening and repository design can be compiled. To this end, the SERP conducted a series of workshops in geochemistry, hydrology, and thermomechanical studies. The workshop, which is the subject of this report, had as its objective identification of the geochemical data and research needs that would aid in the site selection, construction, and licensing of a high-level nuclear waste repository in shale. As studies of shale continue under the SERP, additional workshops will be held. During future workshops, it is anticipated that more detailed research plans will be developed to investigate the needs identified in this report. These needs were identified within the context of federal legislation relevant to repositories (see Sect. 1.3).

1.2 BACKGROUND

The SERP has been directed toward evaluation and ranking five sedimentary rock types with regard to potential for a repository. The five rock types are anhydrock, carbonate (dolostone-limestone), chalk, sandstone, and shale. Based upon technical aspects relative to geology, geochemistry, hydrology, thermal performance, rock mechanics, natural resources, waste package material degradation, repository costs, and systems studies, shale was identified as having the greatest potential. The basis for this evaluation and the methods of ranking are contained in Croff et al. (1985).

Activities of the SERP have now been directed toward characterization of shale, which was initially to aid in a possible national survey that would identify regions of shale in the coterminous United States for more detailed study, and eventually to lead to regional, area, and site characterization. Plans for the national survey were cancelled in early 1986. In an effort parallel to the survey and site identification, a study is being made on

certain "generic" aspects of shale to more fully characterize and understand the broad spectrum of rocks called "shale" and to begin to evaluate possible impacts that waste emplacement might have on shales and their contained waters. One of these generic areas of study is the field of geochemistry.

1.3 REGULATORY REQUIREMENTS RELATIVE TO GEOCHEMISTRY

The context in which geochemical data and research needs are identified is defined by the Federal legislation that provides guidance on siting, licensing, and operation of a repository. There are three relevant pieces of legislation:

1. The U.S. DOE has established requirements for the site screening process for identification of a site for a repository (10 CFR 960).
2. The U.S. Nuclear Regulatory Commission (NRC) has developed regulations for the licensing procedures for siting, design, operation, and closure of a repository (10 CFR 60).
3. The U.S. Environmental Protection Agency (EPA) has issued a regulation that addresses the rate of release of radioelements from a repository (40 CFR 191).

Each of these regulations identifies preclosure and postclosure conditions for the repository.

The statements that address geochemical considerations from the DOE and NRC legislation are directed toward geochemical conditions that must be met (qualifying conditions), are favorable, or are potentially adverse in the siting and licensing process. These conditions are summarized and compared in Table 1. The EPA legislation, on the other hand, identifies release limits for radioelements of interest, specifically as cumulative releases to the accessible environment for 10,000 years after disposal (Table 2). The cumulative releases, of course, are largely controlled by the geochemistry and hydrology of the repository and its environs. Thus, the EPA legislation, through not specifically addressing geochemical aspects, must be considered in a discussion of geochemical studies on specific radioelements.

TABLE 1
GEOCHEMICAL CONDITIONS NOTES IN REGULATORY DOCUMENTS

<u>10 CFR 960</u>	<u>10 CFR 60</u>	<u>DISCUSSION</u>
<p>960.4-2-2 <u>Geochemistry.</u></p> <p>(a) <u>Qualifying Condition.</u></p> <p>The present and expected geochemical characteristics of a site shall be compatible with waste containment and isolation. Considering the likely chemical interactions among radionuclides, the host rock, and the ground water, the characteristics of and the processes operating within the geologic setting shall permit compliance with (1) the requirements specified in Section 960.4-1 for radionuclide releases to the accessible environment and (2) the requirements specified in 10 CFR 60.113 for radionuclide releases from the engineered barrier system using reasonably available technology.</p> <p>(b) <u>Favorable Conditions.</u></p> <p>(1) The nature and rates of the geochemical processes operating within the geologic setting during the Quaternary Period would, if continued into the future, not affect or would favorably affect the ability of the geologic repository to isolate the waste during the next 100,000 years.</p> <p>(2) Geochemical conditions that promote the precipitation, diffusion into the rock matrix, or sorption of radionuclides; inhibit the formation of particulates, colloids, inorganic complexes, or organic complexes that increase the mobility of radionuclides; or inhibit the transport of radionuclides by particulates, colloids, or complexes.</p> <p>(3) Mineral assemblages that, when subjected to expected repository conditions, would remain unaltered or would alter to mineral assemblages with equal or increased capability to retard radionuclide transport.</p>	<p>60.122(b)(1) The nature and rates of tectonic, hydrogeologic, geochemical, and geomorphic processes (or any of such processes) operating within the geologic setting during the Quaternary Period, when projected, would not affect or would favorably affect the ability of the geologic repository to isolate the waste.</p> <p>60.122(b)(3) Geochemical conditions that-- (i) Promote precipitation or sorption of radionuclides; (ii) Inhibit the formation of particulates, colloids, and inorganic and organic complexes that increase the mobility of radionuclides; or (iii) Inhibit the transport of radionuclides by particulates, colloids, and complexes.</p> <p>60.122(b)(4) 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.</p>	<p>Incorporates 10 CFR 60.113 by direct reference and 10 CFR 60.112 by reference to 960.4-1.</p> <p>Like 960.4-2-1(b)(2), this favorable condition applies to one of the factors covered by 10 CFR 60.122(b), in this case geochemical processes. The period of 100,000 years was again used to specify a conservative objective for the time period during which this favorable condition is to be operative.</p> <p>The phrase "diffusion into the rock matrix" was added to indicate another process of radionuclide retardation that would be appropriate for consideration under this guideline.</p> <p>The two conditions are identical in intent. The phrase "anticipated thermal loading" was replaced with "expected repository conditions" to include the full range of repository conditions being considered and therefore to be more conservative. "Inhibit radionuclide migration" was replaced with "retard radionuclide transport" for internal consistency and clarity.</p>

TABLE 1

GEOCHEMICAL CONDITIONS NOTES IN REGULATORY DOCUMENTS, CONT'D

<u>10 CFR 960</u>	<u>10 CFR 60</u>	<u>DISCUSSION</u>
<p>(4) A combination of expected geochemical conditions and a volumetric flow rate of water in the host rock that would allow less than 0.001 percent per year of the total radionuclide inventory in the repository at 1,000 years to be dissolved.</p>	<p>No comparable 10 CFR 60 condition, but guideline is based on requirements of 10 CFR 60.113(a)(1)(ii)(B).</p>	<p>Using 60.113(a)(1)(ii) as a quantitative performance measure, DOE has postulated that confidence in the engineered barrier system could be enhanced if natural constraints, such as solubility limits and low flow rates or volumes, make it unlikely that the engineered system limits could be exceeded, notwithstanding uncertainties in engineered system performance.</p>
<p>(5) Any combination of geochemical and physical retardation processes that would decrease the projected peak cumulative releases of radionuclides to the accessible environment by a factor of 10 as compared to those projected on the basis of ground-water travel time without such retardation.</p>	<p>No comparable 10 CFR 60 condition.</p>	<p>This condition was added to quantify an objective for geochemical retardation.</p>
<p>(c) <u>Potentially Adverse Conditions.</u></p>		
<p>(1) Ground-water conditions in the host rock that could affect the solubility or the chemical reactivity of the engineered barrier system to the extent that expected repository performance could be compromised.</p>	<p>60.122(c)(7) Ground water conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh-pH, that could increase the solubility or chemical reactivity of the engineered barrier system.</p>	<p>The intent of the two conditions is identical. The list of illustrative conditions was deleted because it is not all inclusive, and the conditions listed are not in and of themselves adverse. The relevant phrase is "that could increase the solubility;" e.g., all systems will have "geochemical composition" and "ranges of Eh-pH." The phrase "to the extent that expected repository performance could be compromised" was added to indicate the circumstances under which such ground-water conditions would be considered adverse.</p>
<p>(2) Geochemical processes or conditions that could reduce the sorption of radionuclides or degrade the rock strength.</p>	<p>60.122(c)(8) Geochemical processes that would reduce sorption of radionuclides, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.</p>	<p>The intent of the two conditions is identical. The phrase "or adversely affect the performance of the engineered barrier system" is considered to be implicit because of the wording of the qualifying condition that this potentially adverse condition accompanies.</p>
<p>(3) Pre-waste-enplacement ground-water conditions in the host rock that are chemically oxidizing.</p>	<p>60.122(c)(9) For disposal in the saturated zone, ground water conditions in the host rock that are not reducing.</p>	<p>The intent of the two conditions is identical. The phrase "chemically oxidizing" was used in place of "not reducing" for greater precision. "Not reducing" could include neutral conditions, which would not be adverse.</p>

TABLE 2

RELEASE LIMITS FOR CONTAINMENT REQUIREMENTS
 (Cumulative Releases to the Accessible Environment
 for 10,000 Years after Disposal)

Radionuclide	Release Limit (curies)
Americium-241.....	100
Americium-243.....	100
Carbon-14.....	100
Cesium-135.....	1000
Cesium-137.....	1000
Neptunium-237.....	100
Plutonium-238.....	100
Plutonium-239.....	100
Plutonium-240.....	100
Plutonium-242.....	100
Radium-226.....	100
Strontium-90.....	1000
Technetium-99.....	10000
Tin-126.....	1000
Any other alpha-emitting radionuclide.....	100
Any other radionuclide that does not emit alpha particles.....	1000

2 WORKSHOP DESCRIPTION

2.1 PARTICIPANTS

The workshop was held at the University of New Mexico on May 20 and 21, 1985. Participants were selected to represent academic and federal-institutional expertise in the area of the geochemistry of shale and high-level nuclear waste disposal. The following is a list of the participants.

David L. Bish, Los Alamos National Laboratory
Douglas G. Brookins, University of New Mexico*
Sambhudas Chaudhuri, Kansas State University
Ray E. Ferrell, Louisiana State University
C. Stephen Haase, Oak Ridge National Laboratory
Gary K. Jacobs, Oak Ridge National Laboratory
Sridhar Komarneni, Pennsylvania State University
James Krumhansl, Sandia National Laboratories
Steven J. Lambert, Sandia National Laboratories
S. Y. Lee, Oak Ridge National Laboratory
Robert Lowrie, Oak Ridge National Laboratory
J. Barry Maynard, University of Cincinnati
Paul Potter, University of Cincinnati
Ronald K. Stoessell, University of New Orleans
Stephen H. Stow, Oak Ridge National Laboratory**
Arthur White, Lawrence Berkeley Laboratory
Gene Whitney, U. S. Geological Survey, Denver

*Moderator for the meeting

**Convenor for the meeting

2.2 ORGANIZATION AND SCOPE

Three principal portions comprised the workshop: (1) presentations, (2) item-by-item discussion of data and research needs, and (3) overall ranking of tasks. The first half-day was devoted to presentations directed toward current research on shale geochemistry and historic studies on thermal reactivity of shale. Following is a list of the presentations:

Gene Whitney - "Some Compositional Controls on Smectite Reactivity"

Sridhar Komarneni - "Hydrothermal Alteration of Shales and Shale-waste Interactions under Hydrothermal Conditions"

James Krumhansl - "Near-field Effects on Argillaceous Materials: Field and Experimental Observations"

Sambhudas Chaudhuri - "Strontium Isotopic Data of an Aggregate of Clay Fraction from Shale Samples and Evaporite Samples from the Lower Permian Hutchinson Salt, Kansas"

Steven J. Lambert - "Sampling and Isotopic Studies of Evaporite Waters"

Abstracts for the presentations are found in Appendix A. The abstracts represent the views of the authors and do not reflect the discussions that took place during the workshop.

The major emphasis of the workshop was identification and discussion of geochemical data and research needs for site screening and repository design. Prior to the workshop, a broad-based list of needs was developed and distributed to the participants (Appendix B). Needs were put in four broad categories: (1) characterization of baseline conditions, (2) radioelement behavior-ambient conditions, (3) effects of waste emplacement, and (4) modeling. The list represented the focal point for discussion which centered on such questions as, What is presently known for various aspects of shale geochemistry, How are additional data obtained, and What is really relevant to a study of shale geochemistry for repository siting? This portion of the workshop represented the major activity.

Following the identification of research and data needs, participants reviewed the relative importance of each task and assigned a priority and schedule to each. This constituted the final phase of the workshop.

The following section of this report (Section 3) is devoted to an identification of the research and data needs (tasks) identified during the workshop. Each task is identified in a hierarchical fashion; Appendix C contains detailed statements of justification, approach, priority, and level of effort for each task. While the workshop was directed strictly toward identification of tasks and a discussion of approach and priorities, the hierarchical arrangement and levels of efforts were developed later from

workshop notes. During the workshop participants determined that modeling, the fourth category, was not pertinent as a major category. Rather, modeling was deemed an approach toward solution of tasks. Derivation of detailed schedules and equipment needs for a research program were developed by the workshop organizers after the workshop.

To help limit the scope of the discussions, two major geochemical aspects were not discussed: very near-field effects and shaft-seal problems. It was generally agreed that, although these represent extremely important considerations, both lie outside the scope of this initial two-day workshop. The reasons for not integrating the very near-field environment at that time were basically that reactions in the very near-field are quite complex and will require more detailed consideration at a later time. Despite the complexity of the very near-field and the possibility of increased solubility of radioelements in this environment, it is a local phenomenon compared with the entire repository and its environs. With regard to waste package degradations, the very near-field is of critical importance. It was, however, beyond the scope of the workshop to examine mechanisms and rates of waste package degradation; these topics may be examined during later workshops.

With regard to the shaft seals, current technology appears adequate to guarantee that the shaft seal proper will be relatively impervious to water. The interface between the shaft sealing material and the host rock is more difficult to assess and could be jeopardized by geochemical reactions that occur in the near-field of the repository. During discussion, participants agreed that study of this aspect was outside the scope of the workshop, but that it should be investigated at a future date. It was suggested that laboratory experiments, coupled with analog studies, be used to evaluate geochemical reactions and flow paths along interfaces.

Finally, it was recognized that because shales represent a diverse and highly variable type of rock, complete characterization of all types would be a formidable task that could take inordinate amounts of time. Workshop participants agreed that by selection and study of appropriate "end members" of shale compositions, efforts could be more efficiently directed. Accordingly, and as an outgrowth of other SERP activities, it was agreed

that four main shale types could be studied to gain information on the spectrum of shale variability. These four types are conceptually represented in Fig. 1. It was also noted that as the SERP completes a national survey and identifies regions of greatest priority for future study, it may not be necessary to continue complete characterization of all the various shale types. Detailed work will be directed toward shale types that dominate the regions of greatest priority.

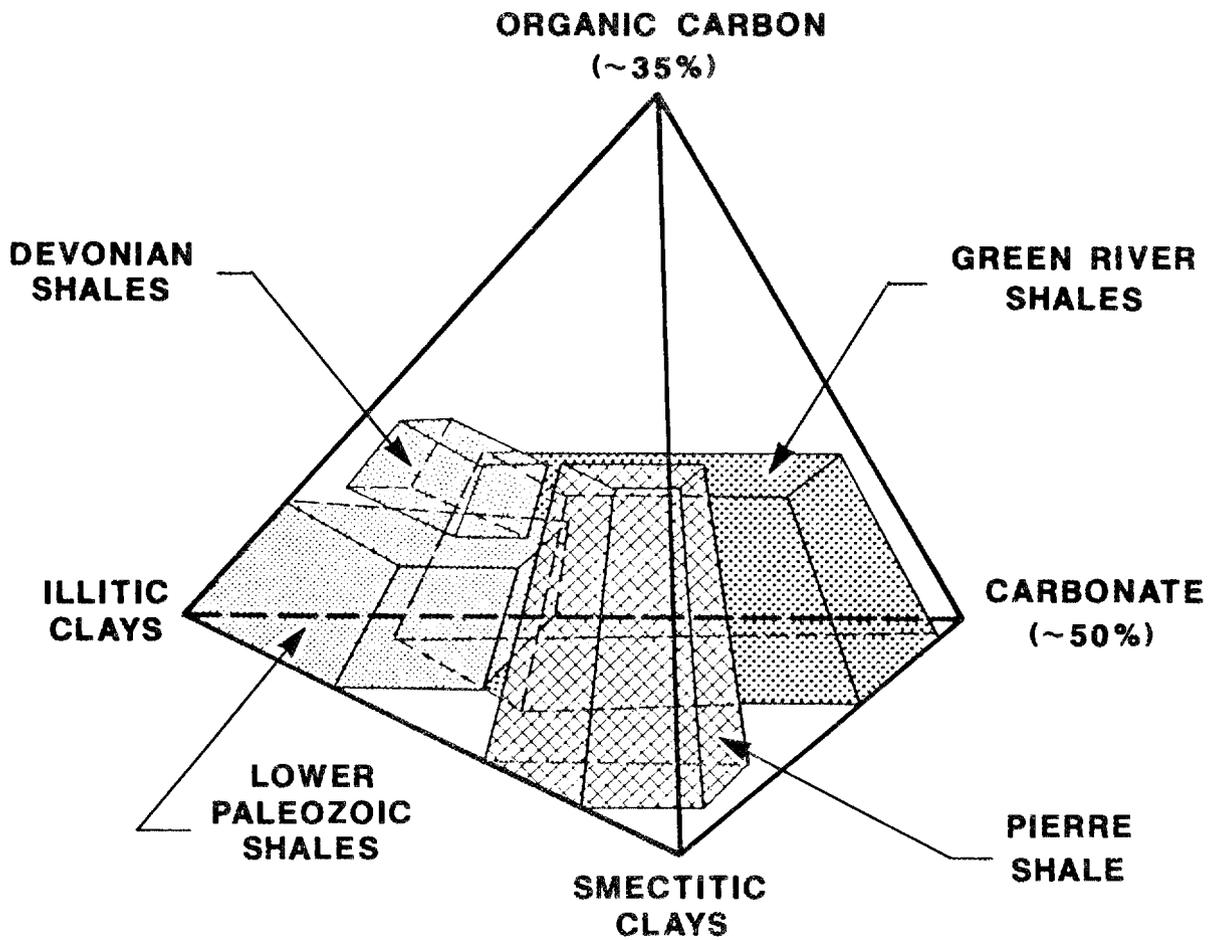


Figure 1. Generalized graphic representation of four shales in the illite-smectite-carbonate-organic carbon tetrahedron.

3 IDENTIFICATION OF RESEARCH AND DATA NEEDS

This section is directed toward an identification of the geochemical data and research needs required for development of a shale-hosted repository. Tasks are identified under three main headings: (1) characterization of baseline conditions, (2) radioelement behavior under ambient conditions, and (3) effects of waste emplacement. For each task, a justification, approach, relative priority, and man-year effort are described. Table 3 represents an outline of the tasks under the three major headings noted above. A hierarchical discussion of each task is found in Appendix C. The level of effort is intended to indicate an approximate number of man-years for completion of the task prior to site characterization. A level 1 effort represents less than two man-years; level 2 represents two to five man-years; level 3 represents five to ten man-years, and level 4 represents more than ten man-years. The following tasks represent a mixture of basic research and the acquisition and organization of existing data coupled with various approaches, including literature review, laboratory and field experiments, modeling, and analog studies. Section 4 of this report represents a schedule for implementation of these tasks, as well as an initial estimate of some equipment needs. As successively smaller geographical areas are identified for characterization, the geochemical research tasks are anticipated to become increasingly less generic.

TABLE 3

GEOCHEMISTRY TASK OUTLINE
(See Appendix C for discussion of each task.)

1. Characterization of Baseline Conditions
 - 1.1 Rocks
 - 1.1.1 Mineralogy
 - 1.1.2 Chemistry
 - 1.1.3 Organic Matter
 - 1.1.4 Fracture-Filling Minerals
 - 1.1.5 Occurrence of Elements
 - 1.2 Water
 - 1.2.1 Technique Development
 - 1.2.1.1 Sampling
 - 1.2.1.2 Age Determinations
 - 1.2.2 Geochemistry
 - 1.2.2.1 Inorganic
 - 1.2.2.2 Organic
 - 1.2.3 Colloidal Matter
 - 1.2.4 Redox Character
2. Radioelement Behavior: Ambient Conditions
 - 2.1 Critical Elements
 - 2.2 Solubility Effects
 - 2.3 Effects of Waters
 - 2.3.1 Speciation
 - 2.3.2 Mobility
 - 2.3.2.1 Complexation
 - 2.3.2.2 Diffusion
 - 2.3.2.3 Redox
 - 2.3.3 Retardation
 - 2.3.3.1 Sorption
 - 2.3.3.2 Ion Exchange
 - 2.3.3.3 Precipitation
 - 2.3.3.4 Redox
 - 2.4 Rock-Water Interaction
3. Effects of Waste Emplacement
 - 3.1 Description of the Environment
 - 3.2 Effects on Rock
 - 3.2.1 Mineralogy
 - 3.2.1.1 Phase Changes
 - 3.2.1.2 Chemical Changes
 - 3.2.1.3 Other Changes
 - 3.2.2 Organic Matter
 - 3.2.3 Porosity and Permeability
 - 3.3 Effects on Waters
 - 3.3.1 Overall Composition
 - 3.3.2 Redox and Complexing Potentials
 - 3.4 Effects on the Water-Rock-Waste System
 - 3.4.1 Chemistry
 - 3.4.2 Redox

- 3.4.3 Complexation Potential
- 3.4.4 Rock-Water-Waste Interaction
- 3.5 Effect on Radioelement Geochemistry
 - 3.5.1 Solubility
 - 3.5.2 Speciation
 - 3.5.3 Mobility
 - 3.5.4 Retardation
- 3.6 Other Effects
 - 3.6.1 Air Effect(s) on Near-Field Geochemistry
 - 3.6.2 Transition from Pre- to Post-closure

4 SCHEDULE AND LABORATORY EQUIPMENT NEEDS

4.1 SCHEDULE

Schedules for initiation and completion of each research task are shown in Table 4. The schedule of tasks is designed to yield basic geochemical data on shales during the first four to five years, with emphasis continually being narrowed to focus on shale types that occur in the regions and areas that remain under study. Specific schedules for years 6, 7, and 8 are not shown in Table 4. Geochemical tasks are anticipated to be similar to those identified in Section 3 and described in Appendix C and would be directed toward locations and site characterization.

4.2 MAJOR EQUIPMENT

Use is expected to be made of existing laboratories and equipment at major DOE facilities and at universities for some of the research tasks. It is doubtful, however, that complete facilities would be available for radionuclide and rock-water interaction studies. This is especially true in light of similar research that will be concurrently underway on other repository candidate host rocks. Capital expenditures on the order of several millions of dollars may be required for laboratory development.

In addition, certain single large-cost equipment items will be needed for the required research. The following items are some of the anticipated equipment.*

1. Plasma quod mass spectrometer, for analysis of very small (<2 to 4 mL) water samples, such as may be obtained from limited shale samples. This instrument allows determination of major and trace constituents (down to 10^{-6} m/L) on the small water samples, thus allowing very sensitive study of shale waters from restricted rocks at depth. This equipment costs about \$400,000.

*These items of equipment are tabulated here for the sake of completion. Should these measurements be needed, it may be more efficient and economic to use existing facilities on a contract basis for the measurements.

2. Plasma source emission spectrograph, for study of very small amounts of solids (e.g., surface phases and fracture fillings) with adequate precision. The estimated cost is \$300,000.
3. Mass spectrometer for stable isotopic work, in conjunction with items 1 and 2, where applicable. The estimated cost is \$200,000 each.
4. Gas chromatographs and related equipment, for the near-field experimental work. Use of laser pyrolysis GC, part of this system, can be used to characterize small amounts of organics in the rocks and waters. The estimated cost is \$200,000.

TABLE 4
 SCHEDULE FOR GEOCHEMICAL RESEARCH TASKS

<u>Task</u>	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8
Characterization of Baseline Conditions								
1.1 Rocks								
1.1.1 Mineralogy	█							
1.1.2 Chemistry	█	█	█					
1.1.3 Organic Matter	█	█	█	█				
1.1.4 Fracture-Filling Minerals	█	█	█					
1.1.5 Occurrence of Elements	█	█	█					
1.2 Water								
1.2.1 Technique Development								
1.2.1.1 Sampling	█	█						
1.2.1.2 Age Determinations		█	█	█	█	█		
1.2.2 Geochemistry								
1.2.2.1 Inorganic	█	█	█	█	█		
1.2.2.2 Organic	█	█	█	█	█		
1.2.3 Colloidal Matter			█	█				
1.2.4 Redox Character	█	█	█	█	█		

Years 6, 7, and 8 will have geochemical work directed toward location and site characterization

TABLE 4
 SCHEDULE FOR GEOCHEMICAL RESEARCH TASKS, CONT'D

Task	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8
2. Radioelement Behavior: Ambient Conditions								
2.1 Critical Elements	—							
2.2 Solubility Effects			—	—	—			
2.3 Effects of Waters								
2.3.1 Speciation		—	—	—				
2.3.2 Mobility								
2.3.2.1 Complexation		—	—	—	—			
2.3.2.2 Diffusion		—						
2.3.2.3 Redox	—	—	—					
2.3.3 Retardation								
2.3.3.1 Sorption	—	—	—	—	—			
2.3.3.2 Ion Exchange			—	—	—			
2.3.3.3 Precipitation		—	—	—	—			
2.3.3.4 Redox		—	—	—	—			
2.4 Rock-Water Interaction			—	—	—			

Years 6, 7, and 8 will have geochemical work directed toward location and site characterization

TABLE 4

SCHEDULE FOR GEOCHEMICAL RESEARCH TASKS, CONT'D

Task	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8
Effects of Waste Emplacement								
3.1 Description of the Environment	█							
3.2 Effects on Rock								
3.2.1 Mineralogy								
3.2.1.1 Phase Changes		█	█	█	█			
3.2.1.2 Chemical Changes		█	█	█	█			
3.2.1.3 Other Changes			█	█				
3.2.2 Organic Matter		█	█	█	█			
3.2.3 Porosity and Permeability		█	█	█				
3.3 Effects on Waters								
3.3.1 Overall Composition			█	█	█			
3.3.2 Redox and Complexing Potentials			█	█	█			
3.4 Effects on the Water-Rock-Waste System								
3.4.1 Chemistry			█	█	█			
3.4.2 Redox			█	█	█			
3.4.3 Complexation Potential			█	█	█			
3.4.4 Rock-Water-Waste Interaction			█	█	█			
3.5 Effect on Radioelement Geochemistry								
3.5.1 Solubility			█	█	█			
3.5.2 Speciation			█	█	█			
3.5.3 Mobility			█	█	█			
3.5.4 Retardation			█	█	█			
3.6 Other Effects								
3.6.1 Air Effect(s) on Near-Field Geochemistry				█	█			
3.6.2 Transition from Pre- to Post-Closure				█	█			

Years 6, 7, and 8 will have geochemical work directed toward location and site characterization

APPENDIX A

ABSTRACTS OF TALKS

Strontium Isotopic Data of an Aggregate of Clay Fraction
from a Shale Sample and of Evaporite Samples from the
Lower Permian Hutchinson Salt, Kansas

S. Chaudhuri

When a clay fraction, consisting of illite, illite-smectite mixed-layer, and chlorite minerals, separated from a sample of shale of Lower Permian Hutchinson Salt were treated in 1N, NaCl, KCl, and MgCl₂ solutions between 20°C and 100°C, both the Sr content and the ⁸⁷Sr/⁸⁶Sr ratio of the leachate increased with increasing temperature. Except for the very high temperature at 120°C, the amount of Sr released in the leachate was independent of the type of salt solution used. At the very high temperature, the KCl solution appeared to have released 20% more Sr from the clay fraction than the NaCl solution. The increase in the ⁸⁷Sr/⁸⁶Sr ratios of the released Sr is suggestive of isotopic heterogeneity in the intraparticle domain.

The Sr isotopic ratios of the halite samples from the Hutchinson Salt ranged between 0.70848 and 0.70897, and the ratios of the associated anhydrite samples were between 0.70815 and 0.70885. The Br contents of the halite samples were between 46 and 100 ppm. Although no relationship between the Br contents and the Sr isotopic compositions can be established, the sample with the highest Br content had the highest ⁸⁷Sr/⁸⁶Sr value. The Sr isotopic compositions of all the samples analyzed were marked by enrichment in ⁸⁷Sr relative to contemporaneous sea water. Post-depositional modification of the primary isotopic characteristics is one explanation for the observed isotopic dispersion among the evaporite samples. A model of evaporite deposition with syndepositional introduction of continental brine can equally explain the trace element and isotopic characteristics of the evaporite deposits of the Hutchinson salt.

Hydrothermal Alteration of Shales and Shale-Waste Interactions under Hydrothermal Conditions

S. Komarneni

High-level nuclear wastes in a sealed repository may generate hydrothermal conditions because of the heat generated by the decay of the radioactive species. Two types of hydrothermal effects can be envisioned in a radioactive waste repository: (1) an initial heating of the surrounding repository rock followed by a breaching of the waste package and thus leading to the release of radioactive ions; and (2) a breaching of the waste package during the hydrothermal period leading to the hydrothermal interactions of waste and repository rock. The objective of this investigation was to assess these effects on the immobilization of radioactive ions in a shale repository.

X-ray diffraction analyses of the hydrothermally altered Eleana shale show little or no change in mineralogy compared to the untreated shale. However, the poorly crystallized illite in Conasauga Group shale became well crystallized upon hydrothermal treatment of 150–250°C (30 MPa pressure) i.e., displayed a sharpened x-ray diffraction peak. No other changes in mineralogy could be discerned by the hydrothermal treatment of Conasauga Group shale. The sharpened illite XRD peak in Conasauga Group shale may have been a result of K incorporation in this phase, the K being supplied by the dissolution of feldspar in the shale.

Another method of detecting alteration in hydrothermally treated shales is by measuring the specific Cs exchange. Specific Cs exchange measurements on the hydrothermally altered shales show that the shales lose their exchange capacity for Cs and similar ions upon hydrothermal alteration. Earlier studies showed that the total cation exchange capacity decreased by the hydrothermal treatment of shales. Therefore, the ability of shales to exchange various nuclides in the immediate vicinity of the canister will be reduced as a result of mineralogical alterations due to hydrothermal conditions.

Results of the kinetics of shale dissolution show that the most soluble elements from shales are Na and Ca. These are the most common elements in shale waters and hence they are present in soluble form to begin with. In general, the percentage of Si increased with time and temperature. However,

the Si concentration is below the quartz solubility limit indicating that no equilibrium had been attained at all temperatures. Of particular interest is the solubility behavior of K because of its effect on the conversion of montmorillonite to illite. The percentage of K in solution appears to decrease with time as well as temperature indicating the immobilization of K. Based on the solubility behavior of individual minerals, K-feldspar appears to be controlling the K solubility. Since hydroxylated and hydrated phases are the most stable under hydrothermal conditions in the range of 100-250°C, feldspars in shales are expected to alter to hydroxylated or hydrated phases.

The scanning electron microscopy (SEM) and single crystal XRD results of simulated borosilicate glass (PNL76-68) interactions with shales at 200-300°C show that elements such as Cs and Sr from glass were immobilized in analcime-pollucite solid solution and/or feldspar. Pollucite has been determined to be the best host for Cs immobilization in earlier studies and thus the waste-shale interactions are positive. Hexavalent uranium solubilized from glass was incorporated in a crystalline alkali uranyl silicate phase, i.e., weavite, $(\text{Na, K, Cs})_2(\text{UO}_2)_2\text{Si}_6\text{O}_{15}\cdot 4\text{H}_2\text{O}$ at 100 to 300°C. These results, however, show that U was not reduced by shale. This is probably due to slow kinetics. Under equilibrium conditions, these shales are capable of reducing U to the tetravalent state as UO_2 by the oxidation of iron or organic matter. These hydrothermal interactions of shale and waste are positive because they led to the immobilization of waste elements in crystalline phases. The complete results of this waste-shale interaction study have been reported by Freeborn et al. [(Hydrothermal Interactions between Calcine, Glass, Spent Fuel and Ceramic Waste Forms with Representative Shale Repository Rocks' Topical Report No. 3. Battelle/ONWI Subcontract No. E512-00500, pp. 76 (1979)].

Near-Field Effects on Argillaceous Materials:
Field and Experimental Observations*

J. L. Krumhansl

A variety of argillaceous rock types have been considered for the containment of high level nuclear waste. These rocks range in age from Paleozoic shales rich in illite, kaolinite, and chlorite, to Mesozoic shales rich in bentonite. The information presented here regarding the behavior of older shales is based on the results of two waste-canister sized heater experiments fielded in the Conasauga Group, at Oak Ridge, Tennessee, and in the Eleana Argillite at the Nevada Test Site. In both cases it was found that, in spite of exposure to temperatures in excess of 300°C for many months, the silicate minerals were not demonstrably changed. Formation permeabilities were much reduced after the Conasauga test, but increased in the Eleana test due to the dehydration of a small amount of swelling clay in that formation. The near-field geochemistry of the Conasauga test was dominated by pyrite oxidation, neutralization of the sulfuric acid by carbonate minerals in the shale, and the subsequent precipitation and dissolution of the calcium and magnesium sulfates formed. The relatively greater solubility of magnesium sulfate resulted in its enrichment in the ground water to the extent of 1,700 ppm magnesium and 7,300 ppm sulfate. A substantial amount of anhydrite was precipitated on the heater surface and in cracks in the surrounding rock. Although little happened to the shale during these tests, it is less clear that the shales would remain unchanged if magnesium-rich brines were present for very long times. Studies at the WIPP site show that significant alteration to "trioctahedral illite" and mixed layer saponite-chlorite would be the likely end products of such reactions.

In younger shales, rich in montmorillonite, there is a wider range of concerns related to the stability of this clay at elevated temperatures. Dehydration is the first effect expected adjacent to a waste canister, and whether the clay will reexpand when the temperature falls is of concern in predicting near-field radionuclide migration. Studies showed that the loss

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of swelling is much greater at 320°C than at 150°C, and that magnesium-rich brines caused less swelling than sodium-rich fluids, which in turn were less effective at expanding the clay than deionized water. If one supposes early presence of high pressure brine in sufficient quantity then the question of the hydrothermal reactivity of the clay is also an issue. With potassium as the principal cation, it was found that mixed lattice illite-montmorillonite can form in the space of a few months at 250°C. If, however, a repository remained dry and cooled for roughly a century, the kinetics of the reaction are such that it is unlikely much of the clay would react in the 10^5 year lifetime of the repository. Another effective factor in slowing mixed layer illite-montmorillonite development is inclusion of magnesium in the brine. In this case, it was found that a saponitic clay develops in short order and the solution pH falls to around 3. With sodium as the principal cation, no reaction was detected at modest Na/H ratios, but at higher values analcime formed. In low ionic strength solutions kaolinite was produced. Thus, the stability of montmorillonite is a relative matter dependent on the nature and amount of fluid available to react with the clay. It is also suggested that a recirculating convection cell involving boiling and condensation could cause both high and low ionic strength solutions to act on different parts of a waste package. Finally, radiation studies carried out on bentonite and bentonite-brine mixtures under hydrothermal conditions indicated that gamma radiation induced no unusual mineralogic reactions to doses of 10^{10} rads. The principal effect was to produce radiolytic hydrogen and oxygen, the latter of which reacted more rapidly. Thus, the near-filed environment will be effectively oxidizing unless a specific mechanism can be found to promote the kinetics of hydrogen reduction reactions.

Field Geochemical Studies of Groundwaters in
Nash Draw, Southeastern New Mexico

Steven J. Lambert and Karen L. Robinson

Physiochemical properties of effluents from 15 pump tests in the water-producing horizons intercepted by six holes in Nash Draw east of the WIPP site in southeastern New Mexico were field-measured at intervals of a few hours. These properties were Eh, pH, specific conductance, specific gravity, bicarbonate/carbonate, chloride, divalent cations, calcium, hydrogen sulfide, and total iron. Observations were made over periods of 17 to 184 hr, during which the measurements reached varying degrees of steady state, but not necessarily equilibrium. The most useful indicators of steady state were divalent cations, chloride, and, in some cases, Eh. Typically, bicarbonate changed significantly during a pump test, seldom reaching steady state. This observation and the drilling history have shown that, given the nongeological sources of carbon, radiocarbon results will be difficult to interpret. Heavy-metal contamination from iron pipe in a well was not purged simply by displacing a well-bore volume, but is some complex function of "armor-coating" of iron by corrosion. This process of armor-coating is, in turn, influenced by pump rate, instantaneous solid-to-liquid ratio, dissolved gases, and aqueous thermodynamic properties. Thus, further determinations of trace constituents associated with heavy metals must be interpreted with care in view of the iron content. Reliable sampling of pumped wells requires a long observation time, detailed documentation of procedures, apparatus, and hole history, and a commitment of human and financial resources that may be much greater than those required for conventional laboratory analyses.

Some Compositional Controls on Smectite Reactivity

Gene Whitney

The reactivity of smectite may be related to the structural cation composition of the clay or to the interlayer cation composition. Although the question of reactivity of a particular smectite species in a specific set of conditions is complicated by a large number of variables, the following generalizations can be made:

1. The aluminous smectites are more susceptible to hydrothermal reaction than are the magnesian smectites.
2. The illitization of smectite is retarded by a deficiency of potassium, but...
3. Illitization proceeds at low potassium levels due to the selectivity of clay for potassium.
4. When potassium is absent, smectites with interlayer cations with intermediate hydration energies (Na, Li, Ba) are most likely to remain expanded.
5. Conversely, smectites having interlayer cations with very low or very high hydration energies most readily form collapsed layers and are, therefore, most likely to experience physical and chemical changes which alter the characteristics of the original smectite.

Despite a wide variety and abundance of experimental work on smectites, we do not currently have a thorough understanding of the principles of reactivity which would allow us to predict quantitatively the degree of reaction for a specific system at a given temperature. Much more systematic and thorough experimental work will be required.

In the meantime, detailed studies of natural smectite systems, such as bentonite alteration and the alteration of shales and basalts in burial or hydrothermal environments, will help tremendously in our understanding of the reactivity of smectite.

APPENDIX B

INITIAL LIST OF GEOCHEMICAL ISSUES DISTRIBUTED PRIOR TO THE WORKSHOP

GEOCHEMICAL ISSUES
SHALE-HOSTED REPOSITORY

Characterization of Baseline Conditions

- **Mineralogic Characteristics of Shales**

The mineralogy of shales is complex and diverse. It is necessary to compile information that summarizes the mineralogic compositions of shales as basic data for further geochemical studies. Data should be acquired relative to weathering and hydrothermally-produced phases as well as for unaltered shale.

- **Mode of Occurrence of Metals in Shales**

Very little is known of the actual mode of occurrence of metals in shales; they may occur as sorbed species, as minerals, etc. Knowledge of this aspect is important and as it provides a data base upon which rock-water interaction studies can be interpreted. This information also provides a natural analog that may allow for identification of various mechanisms of retardation for radioelements.

- **Character of Fracture-Filling Minerals**

In low permeability rocks, fluid movement is predominantly along fractures. It is important to understand the nature of fluids that have moved through the fractures and interactions that have occurred between the fluids and the adjacent rock. Determination of the origin and temperature of the fluids is important.

- **General Characterization of Waters**

The geochemistry of shale waters is of prime importance in understanding radioelement geochemistry. Little is known of the water chemistries, especially those for deep groundwaters. This data base should include information on critical variables (redox character, pH, complexing species, etc.) that greatly influence radioelement geochemistry.

- **Characterization of Colloids and Particulate Matter in Shale Waters**

Because radioelements may be transported in colloidal or particulate form, it is necessary to characterize the basic colloidal and particulate nature of shale waters and to establish the variables that control this nature.

- **The Redox Conditions of Shale Waters: How to Measure? What Controls?**

The oxidation state of waters is a prime factor that may control the geochemical behavior of some radionuclides. It is necessary to develop accurate methods of determining the redox character of shale waters and the relationship between radioelements and redox-sensitive components in waters. The relationship between the waters and redox-controlling constituents (sulfides, organics) in the rocks is not understood.

- **Age Determination of Waters**

There is need for multiple methods of groundwater age dating to verify hydrologic isolation at repository depths. Development and application of methods to shale water is needed.

- **Characterize Organic Components in Rocks and Waters**

The organic geochemistry of shale systems is of importance as it will help control the redox conditions of the environment and will influence radioelement retardation and mobility. Before these effects can be understood it is necessary to characterize the basic nature of the organic constituents in the rocks and groundwaters.

- **Accurate Sampling Systems for Waters**

Obtaining truly representative samples of groundwaters is critical, as many trace constituents may be important in understanding rock-water interactions and aqueous radioelement chemistry. Accurate and precise measurements of Eh are important. Sampling problems are magnified in low permeability rocks.

Radioelement Behavior/Ambient Conditions

- Identification of Critical Elements

Because it is impossible to characterize the behavior of all radioelements, it is necessary to identify a small number that characterize the total spectrum of radioelements. Thus, extrapolations can be made.

- Effects of Shale Water Characteristics on Radioelement Mobility and Retardation

The effects of saline composition of shale waters and the redox character of the waters on the geochemistry of radioelements is not well known. For instance, complexation and/or precipitation of nuclides must be studied. It is not realistic to extrapolate data from "fresh-water" systems to saline (100,000 TDS) systems.

- Effect of Rock Characteristics on Radioelement Mobility and Retardation

While the aqueous chemistry of a shale system may immediately control many aspects of radioelement geochemistry, the aqueous chemistry itself may be largely controlled by rock composition. In addition, there may be direct reactions between nuclides in solution and rock components, thus resulting in retardation through sorption, precipitation, etc. It is necessary to characterize mechanisms of nuclide retardation for shale constituents.

- Speciation of Radioelements

The basic speciation geochemistry of many important radioelements (Tc, Am, Np) is poorly known. Information is needed on the effects of pH, redox, complexation, etc. on the behavior of such elements.

- Mechanisms of Diffusion

The influence of the geochemical environment on the diffusion of radioelements is largely unknown. It is necessary to establish rates of diffusion of different species and in different states (dissolved, colloidal, etc.) in shale-water systems.

- Solubilities of Radioelements

Little is known of the solubility of radioelements in natural waters. In order to evaluate mobility of the elements, solubilities must be quantified.

- Long-Term Nonequilibrium Conditions

It is unclear if equilibrium conditions are achieved for radioelement migration even under long-term conditions. It is important to establish if equilibrium, or static, conditions occur, and what the kinetics of equilibrium-directed reactions are.

Effects of Waste Emplacement

- Effects on the Rocks

Shales are complex rocks consisting of a variety of silicate, sulfide, oxide, and carbonate minerals and organic matter. The stability of these components under elevated temperature and in a radiation field is unknown. Mineral (and organic component) changes may be detrimental for radioelement isolation through loss of sorptive character, etc. Alternatively, changes could be beneficial. Establishment of these effects is needed.

- Effects on Waters

Emplacement of wastes may drastically alter the chemistry of shale water through production of peroxides and elemental gases, and an increase in the ability for complexation of radioelements. Evaluation of these effects is necessary.

- Effects on Rock-Water Interactions

The interaction of rock and water in a elevated thermal environment and in a radiation field is unknown for shale systems. It is necessary to understand such phenomena as formation of secondary phases, reactions of fracture-filling materials, changes in porosity and permeability, etc. may occur.

- Effects on Radioelement Mobility and Retardation

The effects of emplaced waste on the basic geochemistry of the radioelements and the mechanisms by which the elements are mobilized or retarded are unknown. Changes in temperature, pH, redox conditions, mineral phases, etc. must be evaluated.

- Mass Transfer of Chemical Constituents

Under a thermal load, mass transport of dissolved material may occur. Removal and/or precipitation of mineral constituents will affect porosity and permeability, thereby affecting retardation of radioelements. It is important to evaluate and to model possible mass transfer processes.

- Temporal Affect of Waste Emplacement

Some recent work suggests that clays may degrade at low temperatures over long time periods; most data are for short time periods and indicate that significant degradation does not occur at low temperatures. Long-term thermal effects should be more fully studied.

Modeling

- Improve Mass Transport Models

Existing models do not include all variables or handle adequately, processes that may be important to the study of radioelement behavior. Models should be developed that include algorithms for sorption, diffusivity, colloidal and particulate transport, disequilibrium, etc.

- Fracture Flow Models

Flow through low permeability rocks is chiefly through fractures; thus, transport of elements is along fractures. Development of fracture flow models for shale systems is necessary.

- Coupling of Models

To effectively understand the behavior of radioelements in a shale system, may be necessary to couple geochemical and transport models.

Efforts should be directed toward this end, especially toward methods of computer time saving.

- Sensitivity Analysis

It is unrealistic to assume that all variables for all radioelements can be modeled. Thus, it is necessary to identify those variables that are most critical in the models and to concentrate efforts on modeling these variables for a group of select elements.

- Field and Laboratory Validation of Models

Validation of chemical transport models is justified though laboratory testing using column studies and relevant natural analog studies.

APPENDIX C

DESCRIPTIONS OF GEOCHEMICAL TASKS

1 CHARACTERIZATION OF BASELINE CONDITIONS

1.1 ROCKS

1.1.1 Mineralogy

Justification. The minerals contained in shales are important for many reasons. Not only do they influence radioelement migration, but they also influence water composition and may be altered under repository conditions. Information that summarizes the mineralogic compositions of shales needs to be compiled as a basis for further geochemical studies. Data should be acquired relative to secondary and hydrothermally produced phases as well as for unaltered shale.

Approach. A large data base of published information exists on shale mineralogy. This should serve as the basis for this task with emphasis placed on assessment of data on the four "shales" that represent the spectrum of compositions. The task should be augmented by other geochemical studies described below for specific shales (tasks 1.1.2, 1.1.3, 1.1.5).

Priority. This is a task with a medium- to medium-high-priority.

Effort. This is a level 1 effort.

1.1.2 Chemistry

Justification. Shales may vary widely in chemical composition, depending upon their mineralogy. The rock composition will help control the groundwater composition and certain rock-water interactions. Data are generally available for bulk composition of shales, but are less available for minor and trace elements. In addition, chemical compositional data need to be related to mineralogic and petrographic data. Some emphasis should be placed on assessment of the composition of hydrothermally altered shales under open system conditions as well.

Approach. An assessment of available data in the published literature should be made with emphasis on the four basic shale types. The relationship between mineralogic and chemical compositions should be established. It may be necessary to obtain additional data, especially for

minor and trace elements. This task should benefit from tasks 1.1.3, 1.1.4, and 1.1.5.

Priority. This is a moderate- to low-priority task.

Effort. This is a level 2 effort.

1.1.3 Organic Matter

Justification. Almost all shales contain organic matter; the amount may vary considerably and be as great as 35% or more. The organic components of the rock are of significant importance because they may help control the redox conditions in a repository, degrade under waste-loading conditions, release metals into waters, sorb radioelements, or yield complexing ligands. The abundance and nature of the organic matter may be a critical factor in selection of a shale host for a repository.

Relatively little is known of the chemical and physical character of the organic matter and its relationship to the other components of the rock. Certain questions need to be answered. For example, what are the different types of organic matter in shales? Is it a host for certain metals? What are the textural and physical properties of the organic matter? Does the nature of the material vary in shales that have undergone different levels of diagenesis or alteration?

Approach. The published data base for characterization of organic matter in shales is small. The bulk of this activity should involve new work using sophisticated analytical and microscopic techniques. Emphasis should be directed toward highly carbonaceous shales.

Priority. This is a high-priority task.

Effort. The assessment of available data is a level 1 effort; development of new data represents a level 3 effort.

1.1.4 Fracture-filling Minerals

Justification. It is presumed that fractures represent the primary pathway along which fluids have moved in shale. Fluids from a repository will likely move through shale along existing unfilled fractures, along newly created fractures, or by dissolution along existing filled fractures. It is important to characterize fracture-filling minerals to understand the nature of fluids that have moved through the fractures and the interactions

that have occurred between the fluids and adjacent rock. Equally important is characterizing the minerals to determine if their presence will aid or prevent future fluid flow and the resultant radioelement migration. In the case where fracture fillings are absent or only partially present, it is important to determine why this is the case. Determination of the relative abundance of open and closed fractures is important.

Approach. Few data are available on fracture-filling minerals in shale, especially for trace elements. This task should involve sophisticated laboratory work on selected samples using techniques such as microprobe and isotopic analysis. Modeling of fracture-flow and elemental-isotopic exchange reactions is needed.

Priority. This task is rated as a moderate- to high-priority activity.

Effort. This is a level 2 effort.

1.1.5 Occurrence of Elements

Justification. Shales, especially the more highly carbonaceous, may be enriched in many elements, including transition and lanthanide elements. The mode of occurrence of these elements is important because they may be considered as analogs for radioelements that will be released from waste packages and that may be retained by the host rock. Understanding the natural mode of occurrence, in either inorganic or organic form, will help in predicting retardation mechanisms for radionuclides. It is also important to understand the mode of occurrence of elements in shales because many elements may be released in a repository environment and influence radionuclide migration.

Approach. Little information is available on this subject. Activities for this task should be predominantly directed toward laboratory studies using state-of-the-art analytical and microscopic studies.

Priority. This activity is a moderate- to high-priority task.

Effort. This is a level 3 effort.

1.2 WATER

1.2.1 Technique Development

1.2.1.1 Sampling

Justification. Acquisition of groundwater samples with minimal alteration of their natural compositions is difficult. Changes in pH, redox character, and dissolved gas content occur rapidly. Many of these parameters are of utmost importance in understanding and predicting the geochemical reactions that will occur in the vicinity of a repository. Most (all) existing data on deep groundwaters have been acquired from samples whose chemical parameters changed upon sampling. Sampling protocols and techniques that will produce pristine groundwater samples from shales may need to be developed.

Approach. Protocols can be developed based largely on existing sampling programs, such as those of the EPA. It may be necessary to develop or to modify sampling systems so that water chemistry and dissolved gas content can be preserved.

Priority. This is a medium-priority task.

Effort. This is a level 2 effort.

1.2.1.2 Age Determinations

Justification. Methods for accurate and precise age determinations in groundwaters are not nearly as well developed as are those for rocks. Groundwaters are easily mixed and may readily exchange ions with rocks or sampling equipment, thereby yielding incorrect ages. Work is needed that is directed not only at proper sampling (task 1.2.1.1), but also at development of dating techniques that can be used for very old waters. The ^{81}Kr method represents one such technique that is partially developed and that has significant advantages over other methods.

Approach. Work should be directed toward refinement of the existing techniques and of the interpretation of the acquired data. Techniques should be assessed in light of the saline nature of shale waters, and continued development of promising techniques should be undertaken.

Priority. This is a medium- to low-priority item.

Effort. This is a level 2 effort.

1.2.2 Geochemistry

1.2.2.1 Inorganic

Justification. The inorganic composition of water in shale will be a critical parameter in evaluation of repository suitability. The water composition must be known for waste package performance assessment and for modeling elemental migration. It is important that compositional information be acquired for deep groundwaters representative of repository depths, rather than for shallow groundwaters, which almost certainly represent recent mixing with surface systems. Groundwater composition may vary for different types of shale and the compositional variations should be determined. It is also important to assess, where possible, if the groundwaters are in equilibrium with the host rock.

Approach. Water quality data bases are available; an example is the WATSTORE data base of the U.S. Geological Survey. The initial approach will involve acquisition of data from such sources; data should include major, minor, and trace constituents, pH, Eh, dissolved gas, etc. Solubility/speciation and reaction path geochemical models should be used to assess equilibrium, where possible. If water samples can be obtained from appropriate depths, analyses should be performed.

Priority. This is a high-priority task.

Effort. A level 1 effort is needed for assessment of available data; effort for analysis of new data will be variable.

1.2.2.2 Organic

Justification. The organic constituents of shale waters are important in assessment of radionuclide mobility through complexation and in determination of the redox character of the water. Organic components of the host shale are expected to determine the organic constituents of the associated water. As with task 1.2.2.1, such information must be acquired for deep groundwaters from shale.

Approach. The use of available data bases, as described in Task 1.2.2.1, is recommended as the initial approach. Efforts should also be directed at acquisition of samples for analysis and possibly at rock-water

studies to determine the influence of rock composition (organic) on water composition (organic).

Priority. This is high-priority task.

Effort. A level 1 effort is needed for assessment of available data; effort for analysis of new samples is variable.

1.2.3 Colloidal Matter

Justification. Recent observations have shown that radionuclides can be transported in groundwaters in association with colloidal matter. Thus it is important to understand the nature of colloidal matter in shale waters and to determine if it varies for different types of shales.

Approach. There is unlikely to be much information available on this subject. The approach will be to acquire samples of shale water and to characterize the associated colloidal matter. Methodology to allow taking colloid samples will need to be developed.

Priority. This is a low-priority task.

Effort. This represents a level 2 effort.

1.2.4 Redox Character

Justification. The redox character of groundwater is an extremely important parameter in determining waste package stability and radioelement mobility. In general, most multivalent elements are less soluble in their reduced form (i.e., U, Mo, Sb, Tc, and Ru). Because pH in deep shale waters is expected to vary from about 6 to 9, the redox nature may be a controlling factor in multivalent radioelement mobility in such waters. The redox nature of the groundwater may be largely controlled by the mineralogic and organic character of the host rocks, but this has not yet been determined for shale. Recent work has shown that in shallow waters from different rock types redox pairs do not yield consistent results on the redox state of the waters; no such work has been conducted on deep shale waters.

Approach. Maximum use should be made of available data bases, such as WATSTORE, to acquire data. Acquisition and analysis of deep groundwater and identification and development of methods for accurately measuring redox state are recommended.

Priority. This is a medium- to medium-high priority task.

Effort. A level 1 effort is needed for assessment of available data; analysis of new samples and development of measurement methods will be at least a level 2, and possibly a level 3 effort.

2 RADIOELEMENT BEHAVIOR: AMBIENT CONDITIONS

2.1 CRITICAL ELEMENTS

Statement. The most critical elements are those already identified by NRC and DOE; U, Pu, Np, Tc, and ^{14}C . Other radioelements should also be considered.

2.2 SOLUBILITY EFFECTS

Justification. The solubility of the radioelements of concern may be intimately linked to the solubility of the constituent minerals in shales that might contain these elements. The radioelements Pu, Np, Am, and Tc are not found in shales, but U can serve as an analog for the transuranics; Re and possibly Mn can serve as analogs for Tc. Although individual radioelement solubility is of great concern, it is usually strongly dependent on mineral solubility; hence, both must be considered. Parameters such as pH and Eh may have a pronounced effect both on individual radioelement and on radioelement-bearing minerals in the rocks. This is especially true when more complex shale-water-waste systems are considered (see task 3.4.4).

Approach. Establishment of mineralogic and chemical characteristics of shale and chemical characterization of shale waters (see tasks 1.1 and 1.2) must be supplemented by laboratory studies under varying Eh-pH conditions to predict the solubility of radioelements in shale. Many of the critical elements are polyvalent and, in general, more insoluble under low Eh conditions than under oxidizing conditions. Coupled reactions are important for some elements (Tc). The laboratory work on natural shales should focus on U for actinide behavior and on Re for assessing the geochemical behavior of Tc (i.e., Re and Tc show nearly identical chemical parameters in Eh-pH space). Although Re is an extremely rare element in the earth's crust, Re salts can nevertheless be used to approximate Tc behavior accurately under crustal conditions. Manganese occurrences can be used, with caution, for further assessment of Tc behavior. The behavior of radioactive Cs, Sr, and Ra can be investigated by close examination of the Rb-Sr systematics of natural shales. Laboratory studies of Rb-Sr mobilities can be directly applied to radioactive Cs, Sr, and Ra behavior in rocks. Radioactive Sn

will be less soluble than Tc, and the Re (or Mn) studies for Tc behavior will also be adequate to assess Sn behavior. These laboratory studies must take kinetics into account as well. In the case of ^{14}C , stable isotopic carbon studies of both laboratory and natural systems should be investigated to predict the behavior of ^{14}C in rocks. Finally, study of natural analogs (i.e., igneous dike contact zones in shales) can be used to study U, Mn(Re), C occurrences, which in turn can be used to assess indirectly the sought radioelement solubility.

Priority. This is a medium- to high-priority item.

Effort. This is a level 2, and possibly a level 3, effort.

2.3 EFFECTS OF WATERS

2.3.1 Speciation

Justification. Speciation of radioelements present in deep shale groundwaters is not known. Total dissolved solids may be higher in deep shale groundwaters than under more shallow conditions and may thus increase the number of species present. Laboratory studies to determine the chemical species present under a wide variety of conditions must be undertaken and followed by geochemical modeling using the newly determined data.

Approach. Where possible, deep shale water should be obtained for species identification. Search of the available petroleum geology literature may yield useful abundance data, which in turn can be used to calculate which species should be present. Data for bedded and domal salt brines and other waters may be used, with caution, as an upper limit on salinity for deep shale waters.

Priority. This is a medium- to high-priority task.

Effort. This is a level 2, and possibly a level 3, effort.

2.3.2 Mobility

2.3.2.1 Complexation

Justification. Complex ions are common for polyvalent ions such as U, Np, Pu, Tc, and, often, CO_3 . Complexes of high valence ions of U, Np, Pu, and Tc are especially soluble (see task 2.3.1), and only the stability fields of U-complexes are known with any degree of certainty. Complexes of

Np, Pu, and Tc are not as well known, and it is important to determine the type, number, and stability of their complexes.

Approach. As is the case for task 2.3.1, deep shale waters should be studied for U complexes. Laboratory work will allow Np, Pu, and Tc complexes to be studied.

Priority. This is a medium-priority task.

Effort. This is a level 3, and possibly a level 4, effort.

2.3.2.2 Diffusion

Justification. Diffusion may be an important factor in radioelement mobility. Few data are readily available on diffusion in shales or in deep waters in shales. Without such data, it is impossible to quantitatively assess the role of diffusion.

Approach. A thorough search of geochemical and sedimentary geological literature sources should be undertaken to identify key works on diffusion. Laboratory studies may be helpful as well.

Priority. This is a low-priority task.

Effort. A level 1 effort is required for assessment of available information. Laboratory work would require additional time, possibly as a level 3 effort.

2.3.2.3 Redox

Justification. Redox is an extremely important factor for assessing radioelement mobility. Under high redox potential, species of U, Np, Pu, and Tc may be readily soluble; under lower redox potential reduced species of these elements may be immobile.

Approach. Laboratory studies to assess redox characteristics of U, Np, Pu, Am, Tc, and Sn under widely varying conditions must be carried out. In addition, determination of thermodynamic properties for these elements must be studied further to prepare Eh-pH diagrams for use in qualitatively predicting redox behavior; these predictions should be tested by laboratory studies. Assessment of kinetics, metastability, and other factors should be made.

Priority. This is a medium- to high-priority task.

Effort. This is a level 3 effort.

2.3.3 Retardation

2.3.3.1 Sorption

Justification. Sorption (here used to mean surface fixation of elements other than by ion exchange or precipitation) is an important factor in radioelement retardation. Many experimental data vary widely for sorption-desorption measurements, even for replicate experiments. More-carefully-designed laboratory experiments to assess sorption of the radioelements of interest onto shales must be carried out.

Approach. Where possible, literature values for sorption-desorption (not including ion exchange, precipitation, etc.) should be compiled and evaluated. This compilation is expected to be inadequate to assess the role of sorption in shales, but the available data should prove useful in guiding subsequent experimental work. The laboratory work should be carefully designed to assess the role of sorption in shales under a wide range of expected natural conditions. Maximum use must be made of the state-of-the-art high technology equipment applicable to the study of surface phenomena.

Priority. This is a medium- to high-priority task.

Effort. A level 1 effort is required for assessment of available data; a level 3, possibly a level 4, is required for new research.

2.3.3.2 Ion Exchange

Justification. Ion exchange is an important process to retard many elements, especially mono- and divalent cations such as Cs, Sr, Ra, and I. It may be less important for high valence species of U, Np, Pu, Am, Sn, and Tc, but nevertheless, it should be investigated. Ion exchange may be more important for ^{14}C .

Approach. Studies of high cation (or anion) exchange capacity (CEC or AEC) clay minerals should be undertaken with solutions bearing U, Np, Pu, Am, Cs, Sr, Ra, Sn, I, and Tc. Maximum use should be made of instrumentation for surface analysis.

Priority. This is a high-priority task.

Effort. A level 3 effort is required.

2.3.3.3 Precipitation

Justification. Precipitation of radioelements may occur in response to redox conditions (see task 2.3.3.4) or to supersaturation under local conditions. In either case, retardation is enhanced by precipitation of radioelement-bearing phases. It is not known how efficient precipitation is versus other retardation mechanisms. For example, carbonate phases in particular may be efficient in removing not only ^{14}C , but also U (and other actinides?).

Approach. Laboratory studies to determine the amount of precipitation under simulated deep shale conditions should be undertaken. Coupled with redox studies (see task 2.3.3.4), this will allow assessment of U, Np, Pu, Am, Sn, and Tc behavior and ^{14}C if carbonate phases are involved. Study of fracture filling and similar sites in shales as natural analogs should be useful as well. Maximum use should be made of instrumental techniques for surface analysis.

Priority. This is a medium- to high-priority task.

Effort. A level 3 effort is required.

2.3.3.4 Redox

Justification. The mobile species of U, Np, Pu, Am, Sn, and Tc are the high-valence ones. Upon encountering low redox conditions, these species may be reduced to low-valence, highly insoluble species. U, Np, Am, and Pu will probably precipitate as insoluble oxyhydroxides, and Tc and Sn may precipitate as either an oxyhydroxide or a sulfide. In theory, C as CO_3 may be reduced to elemental C under some low redox conditions, but CO_3 is known to exist metastably under very low redox potential. Again (task 2.3.2.3), characterizing the redox character of deep shale waters and relating this to radioelement behavior is important.

Approach. Laboratory studies in conjunction with sorption, ion exchange, and precipitation experiments under different redox conditions (and different control media for redox) should be undertaken to assess the importance to redox on radioelement retardation. Theoretical Eh-pH diagrams may be useful to test and interpret the laboratory data qualitatively.

Priority. This is a medium- to high-priority task.

Effort. A level 3 effort is required.

2.4 ROCK AND WATER INTERACTION

Justification. The following factors are poorly known: factors that affect speciation, complexation, diffusion, and redox in waters; and factors that affect sorption, ion exchange, precipitation, and redox in the rocks; and the effects of these parameters on rock-water interaction. It is imperative to obtain data for these factors.

Approach. A thorough literature study should be of use here, as should some natural analog studies for rock-water interaction. Much of the necessary information, however, can only be obtained by extensive laboratory experimentation (see task 2.3).

Priority. This is a high-priority task.

Effort. A level 2 effort is required for the literature review; a level 3 (possibly 4) is needed for laboratory work.

3 EFFECT OF WASTE EMPLACEMENT

3.1 DESCRIPTION OF THE ENVIRONMENT

Justification. Emplacement of wastes in a shale-hosted repository will produce thermal and radiation fields in the very near and near fields, with a decreasing intensity in the far field. To competently study and understand the specific impacts of the emplaced waste on the geochemical characteristics of the repository, the magnitude and extent of the thermal and radiation fields must be described.

Approach. Based upon work done for the repository programs and knowledge of the thermal conductivity of shale, a description of the repository environment should be undertaken.

Priority. This is a high-priority task.

Effort. A level 1 effort is required.

3.2 EFFECTS ON ROCK

3.2.1 Mineralogy

3.2.1.1 Phase Changes

Justification. Thermal and radiation fields imposed by emplaced waste have varying effects on the stability of minerals. It is important to understand how mineral phases change due to the emplacement of waste. The associated thermal and radiation fields may alter existing minerals, yielding new phases and altering the predicted chemical environment in the repository. Changes that occur at relatively low temperatures (<100°C) over long time periods should also be addressed.

Approach. This task can be undertaken in three steps: (1) review of available data, (2) use of natural analogs, and (3) use of experimental work. Considerable information is available on the thermal effects on minerals, but not at low temperatures over long periods of time; data on radiation effects are very limited. Natural analogs may be of use, especially in areas where rocks have been subjected to slightly elevated temperatures over extended periods of time (e.g., buried Gulf Coast sediments, etc.). The analog work, however, is intended only to supplement the laboratory work.

Priority. This is a medium- to low-priority task.

Effort. Review of available data and study of analogs will require a level 2 effort; experimental studies will require a level 3, possibly a level 4, effort.

3.2.1.2 Chemical Changes

Justification. This task is closely linked to task 3.2.1.1 because many phase changes result in chemical changes. However, in some cases, chemical changes take place without an apparent phase change. For example, ion exchange may alter the chemistry of certain clay minerals, but not the structure of the clay mineral itself. Such changes, triggered by waste emplacement, should be characterized for shales.

Approach. Laboratory studies designed to test chemical changes with and without phase changes due to waste emplacement in a shale environment must be undertaken. Some literature search and natural analogs may be of use here but only in a role secondary to the laboratory work.

Priority. This is a low-priority task.

Effort. Effort is the same as for task 3.2.1.1 and may largely be coupled with that task.

3.2.1.3 Other Changes

Justification. Emplacement of wastes may have other impacts on the mineralogy through creation of surface films, such as oxyhydroxide layers, that will alter the chemical and physical character of the rock. Such surface alterations vary for different minerals and may be important in a geochemical assessment of a rock for a repository.

Approach. An analog and experimental approach is recommended.

Priority. This is a low-priority task.

Effort. A level 1 effort is required.

3.2.2 Organic Matter

Justification. The stability of organic matter under waste emplacement conditions represents a major unanswered question. Types of matter degrade at different rates; the products of the degradation reactions may produce significant changes in pH, redox conditions, gas pressures, radioelement complexation potential, etc.

Approach. With the exception of thermal effects, there is a sparse data base for this task. Analog studies of igneous intrusives into organic-bearing sediments and laboratory experimental studies must be undertaken. It is important to have characterization information of the organic matter prior to experimentation.

Priority. This is a medium-high-priority task.

Effort. Analog studies will require a level 1 effort; experimental studies will require a level 3, possibly a level 4, effort.

3.2.3 Porosity and Permeability

Justification. The porosity and permeability of the rock in the near field may be changed by mineral alteration, dissolution, or precipitation; such changes will affect the mass transfer of constituents in water. The relationship between rock changes and lithology should be identified.

Approach. As with other tasks (tasks 3.2.1, 3.2.2), this task should be approached chiefly through analog studies (igneous intrusives, diagenesis) and experimental means. A fairly large-scale drilling program may be needed to ensure adequate sampling.

Priority. This is a medium-priority task.

Effort. A level 1 effort is required for analog studies; the drilling program represents an added effort; a level 3 effort is required for laboratory research.

3.3 EFFECTS ON WATERS

3.3.1 Overall Composition

Justification. The overall composition of the water will be affected by waste emplacement (task 3.2), because minerals and organic matter in the rock will be dissolved and will change the water chemistry. In addition, gases may be produced in the radiation field, thus altering the water composition. These changes in composition may result in increased degradation of the waste package and increased radioelement mobility.

Approach. Initial calculations can be made for changes in water chemistry due to thermal dissolution and alteration of rocks based on experimental work and geochemical modeling. Because little information exists on radiation effects, an experimental approach must be used.

Priority. This is a medium-high-priority task.

Effort. This task will require a level 4 effort.

3.3.2 Redox and Complexing Potentials

Justification. This task is directly related to the task on the changes in overall composition of waters (task 3.3.1). The redox and complexing potentials are sufficiently important, however, to be addressed as a separate task. The near-field repository waters presumably will be oxic (although this is not entirely certain); thus some elements that are normally immobile may be mobilized by oxidation and formation of more soluble species. The extent of these near-field effects into the far field must be addressed.

Approach. An experimental approach coupled with geochemical modeling is recommended.

Priority. This is a medium-priority task.

Effort. This will require a level 4 effort.

3.4 EFFECTS ON THE WATER-ROCK-WASTE SYSTEM

3.4.1 Chemistry

Justification. Water chemistry in deep shales may be changed abruptly by addition of soluble material and particulate matter from the radwaste package. The amounts of these additives can possibly be estimated from near-field budget calculations, but how the interactions will occur is unknown.

Approach. Laboratory experiments, backed by calculations and modeling, should be used to address this task.

Priority. This is a medium-priority item.

Effort. This will require a level 4 effort.

3.4.2 Redox

Justification. The redox nature of shale water in the near-field water presumably will be more oxidizing than ambient shale water. This will result in greater mobility of some species in this mixed zone. However, as the ratio of shale water to contaminated water increases, the redox potential will again decrease.

Approach. Laboratory experimentation should be carried out to attempt to predict mobilities. Analog information may also be useful here.

Priority. This is a medium-high-priority task.

Effort. This will require a level 4 effort.

3.4.3 Complexation Potential

Justification. A potentially serious effect of the waste-water interaction will be the potential to form new, and possibly quite soluble, complexes of radioelements. The nature and reactivity of such complexes are not known.

Approach. Laboratory study must be undertaken to address this problem. The results should be interpreted in terms of theoretical considerations, coupled with studies of older hydrothermal shale-water-waste systems.

Priority. This is a medium-high-priority task.

Effort. This will require a level 4 effort.

3.4.4 Rock-Water-Waste Interaction

Justification. The interaction of waste-derived constituents with the shale water system will be complex. An understanding of these interactions is critical to be able to predict the degree of mobility or retention of the key radioelements. A combination of items (tasks 2.4, 3.2, 3.3, 3.4, 3.4.2, 3.4.3) presented above will be required.

Approach. A series of detailed experiments should be required, which will involve reactions in the waste-shale-water system under simulated natural conditions (i.e., varying pH, redox, T). Experiments will be designed to address many factors, including:

1. for waters: speciation, complexes, redox, composition, colloids, and mobility, and
2. for solids: sorption, surface phases, retardation, ion exchange, precipitation, redox, and other factors

Some natural analog studies may be of importance here as well.

Priority. This is a high-priority task.

Effort. This will require a level 4 effort.

3.5 EFFECT ON RADIOELEMENT GEOCHEMISTRY

3.5.1 Solubility

Justification. The effect of waste emplacement on the solubility of shale and solubility of waste materials may be significant. Due to the complex, locally (presumably) oxidizing reactions of the near-field environment, it is expected that the solubility of many solid phases in both rock and waste may increase. Both Eh and pH will be affected, and lower (but widely variable) pH and locally high Eh will increase solubility for many phases.

Approach. Careful mineralogic characterization of the shales (see tasks 1.1.1 and 2.2), coupled with detailed characterization of the phases present and predicted to form as a function of Eh, pH, and kinetic considerations, must be established. Natural analogs and selected hydrothermal experiments on shale-waste interactions should be carried out.

Priority. This is a medium- to high-priority task.

Effort. This task will require a level 3 effort.

3.5.2 Speciation

Justification. The effect of waste emplacement will cause many complex reactions in the near field, including formation of complex species due to combined redox, pH, and concentration effects. Because many of the complex species may, in some cases, affect solubility or removal of species from solution, prediction of the number of species, their individual characteristics, and their stability must be attempted. This will be a large and important project.

Approach. The existing literature on hydrothermal experiments on waste form-shale-water should be summarized for the various radioelement species. An attempt to summarize the extensive geothermal systems waters for the same purpose may be helpful.

Priority. This is a medium-high-priority task.

Effort. This effort will require a level 3 effort.

3.5.3 Mobility

Justification. The mobility of key radioelements is dependent on solubility of the various phases of each element, aqueous species, redox-pH conditions, the ability of the species to be sorbed or exchanged onto the available solids, as well as other factors. These numerous factors must be identified.

Approach. A summary of existing laboratory data from hydrothermal experiments dealing with waste form-water-shale should be made, as well as data from related experimentation that may be applicable. Natural analogs may be useful here as well, although only gross mobility may be obtained. More refined laboratory studies should be considered to test mobility under simulated shale-waste-water conditions.

Priority. This is a medium-priority task.

Effort. Review of data and analog studies will require a level 1 effort; laboratory studies will require a level 4 effort.

3.5.4 Retardation

Justification. Retardation of radioelements may be different in the near field than in the far field. Although several factors may promote mobility (see task 3.5.3), numerous factors may promote retardation. Films of surface oxyhydroxides, for example, may serve as excellent getters for actinides and some other elements. Further, some high-valence actinides may be fixed in insoluble phases in the near field and in nearby zones. (e.g., boltwoodite), and ion exchange and sorption may remove some as well. It is important to characterize these processes systematically.

Approach. More refined experimentation on radioelement retardation in the waste-shale-water environment must be undertaken (i.e., scanning and transmission electron microscopy, and autoradiography) as well as a summation of the existing literature in this area. Natural analogs may be useful here, especially for cases where actinides are retained in veins, on oxyhydroxide coatings, and on mineral surfaces. A summary of ways in which retardation factors can affect mobility should be made.

Priority. This is a medium-high- to high-priority task.

Effort. This task will require a level 4 effort.

3.6 OTHER EFFECTS

3.6.1 Air Effect(s) on Near-Field Geochemistry

Justification. Air will be present in the repository until well after closure. This air will be in contact with the shale, shale water, and the waste package. In waters, the effect will be to raise the redox potential, and the same effect will occur in the shale exposed to air. Some parts of the waste package will be oxidized by the air. The overall effect is for more (locally) oxidizing conditions, which in turn will complement radiolytic and other waste-water reaction effects. The combined effect of these processes is not known.

Approach. A series of experiments dealing with different fO_2 -pH-T to investigate the effect of air should be designed. Further, these experiments should be aimed at determining the effect of rapidly decreasing fO_2 away from the near field. Stable oxygen isotopes should be used for control, coupled with sensitive geochemical tracers. Some natural analogs, such as uranium-vein occurrences, may be important as well.

Priority. This is a medium-priority task.

Effort. This task will require a level 2 effort.

3.6.2 Transition from Pre- to Postclosure

Justification. With time, the air in the repository will become oxygen deficient. As this occurs, the redox conditions will become more reducing, and the reactions promoted by a higher fO_2 will change. A series of reactions reflecting these new conditions may result, and it is important to characterize them.

Approach. Laboratory studies to supplement those recommended above (task 3.6.1) with decreasing fO_2 should be carried out. Furthermore, a series of theoretical partial fugacity-concentration diagrams for the radioelements (and other elements of interest) should be calculated and cross checked with the experimental and field data.

Priority. This is a medium-priority task.

Effort. This task will require a level 2 effort.

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