THE TECHNOLOGY OF HIGH-LEVEL NUCLEAR WASTE DISPOSAL

**Advances in the Science and Engineering
of the Management of
High-Level Nuclear Wastes**

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Foreword

The work described in this collection of papers was performed as part of the National Waste Terminal Storage (NWTS) Program of the U. S. Department of Energy.

The objectives of this program are to develop the technology and to provide the facilities for the permanent isolation of high-level and transuranic nuclear wastes resulting from the commercial production of electric power. Major emphasis is on disposal of these wastes in deep geologic formations. This program is unique in its concern for the health and safety of present and future generations.

A satisfactory resolution of the nation's nuclear waste problem can be achieved only when a societal and institutional consensus regarding the validity of the concepts for disposal of such waste is obtained. To this end, the Department of Energy is making extensive efforts to inform regulatory agencies, state and local officials, the technical community, and the public about the conduct of its national program. Such efforts include continual consultation with state governors and state, tribal, and local officials to secure their participation in the resolution of repository siting and other issues. Local and national public information meetings are held and significant programmatic documents are made readily available. Independent reviews of the NWTS Program with respect to both its technical quality and its responsiveness to public concerns are solicited.

The first volume of papers of the proposed series of annual volumes is presented with the hope that it will contribute to a greater understanding of the National Waste Terminal Storage Program.

W. Wade Ballard, Jr.
Director
Office of Waste Isolation
U. S. Department of Energy

Preface

The National Waste Terminal Storage Information Meeting held Oct. 30 through Nov. 1, 1979, in Columbus, OH, was the first of a continuing series of annual conferences intended to serve as a forum for the exchange of technical information among participants in the NWTs Program and those with a technical or regulatory interest in the effort and to support the DOE public information program on nuclear waste management. The Office of Nuclear Waste Isolation (ONWI), operated for DOE by Battelle, was the host organization for the meeting.

The first meeting offered a detailed review of the FY 1979 ONWI technical program for siting a repository on non-DOE land. In addition, an overview was possible for the two NWTs projects focused on siting a repository on DOE land, i.e., the Basalt Waste Isolation Project (BWIP), operated for DOE by Rockwell Hanford Operations, and the Nevada Nuclear Waste Storage Investigations (NNWSI), operated by Sandia National Laboratories. In the subsequent conferences, detailed technical papers were presented on the activities under way in all three NWTs mined geologic repository projects, as well as on work being carried out by Sandia on the Subseabed Disposal Concept.

The NWTs program was organized by DOE in 1976 with the objective of bringing together the work already under way in the component projects into a coherent, integrated national effort. Subsequent volumes in this series will reflect this integration in that the papers included will become increasingly programmatic in orientation. In contrast, much of the work discussed in the 1979 meeting dealt with the resolution of basic generic issues associated with mined geologic isolation, and some of this work is reported in the papers included in this first volume. These papers cover some very good and interesting research and are worthy of the permanent preservation offered by a publication such as this.

Neal E. Carter
General Manager
Battelle Project Management Division

Editors' Preface

This is the first of a series of annual volumes dealing with advances in the technology for the disposal of high-level and transuranic nuclear wastes (HLW and TRU) in the United States. The papers included in this initial volume were selected from those presented at the National Waste Terminal Storage (NWTS) Program Information Meeting organized by Battelle Memorial Institute and held late in 1979 in Columbus, OH, under the sponsorship of the Department of Energy.

As most of our readers already know, the NWTS program constitutes a complex but highly structured and closely scheduled national effort to develop the technology and provide the facilities for safe, environmentally acceptable, permanent disposal of HLW (including spent fuel) and TRU waste generated by commercial nuclear power reactors. Although alternative disposal concepts (e.g., subseabed burial) have been or are being investigated as potential waste isolation options, the principal NWTS effort is focused on the disposal of HLW and TRU wastes by emplacement in mined repositories. Volcanic tuff, basalt, and two domal and two bedded salt formations are currently under detailed study as potential sites for such repositories.

The papers included in this volume were selected in the spring of 1981. We wanted papers addressing topics of current programmatic interest in the NWTS effort, but we also sought papers on subjects of generic or historical significance (and, perhaps, controversy) in the development of waste isolation technology. We were reasonably successful in both endeavors, but, unfortunately, because a number of promised papers did not materialize in time, the collection offered here does not represent the technical scope of the NWTS Program in 1979 as completely as we had originally hoped it would. We expect to remedy this kind of shortcoming in future volumes.

The papers in this initial compilation understandably involve a number of relatively narrow scientific disciplines and technical specialties, in many of which the editors cannot claim any particular competence. Hence, every contribution was subjected to the scrutiny of at least one appropriate member of the Editorial Review Board formed for the series. In addition to possessing excellent credentials, this Board is very much a working body and, as a group, carried out with commendable conscientiousness what is, at best, an often thankless and sometimes dreary task. We believe that the overall quality of the book has been demonstrably enhanced by the Board's dedicated work.

We should note that, in the interest of obtaining a modicum of currency in this volume, we prevailed upon the authors to update, where

appropriate, the information they originally presented at the 1979 meeting. Accordingly, the papers are of 1981 "vintage," even though the topics of many reflect the heavy R&D orientation of the NWTS program in the late 1970s. Papers in subsequent volumes in this series will reflect the increasingly programmatic orientation of the more recent activities. Ultimately, the series as a whole is intended to be both a compact historical record of the U. S. nuclear waste program and a useful and continually current information resource on the program's technical focus.

A routine problem confronting the editors of any collection of technical papers treating a variety of somewhat loosely related scientific and engineering topics is to devise a reasonably logical framework for their orderly presentation. In this volume, we settled on a relatively simple organizational approach based largely on the chronological sequence in which the kind of information and technology developed in the reported studies might be applied in siting, designing, and constructing a repository. Viewed from such a perspective, the papers in this volume, although they concern work differing widely in objective, scope, and discipline, can be divided into four general categories:

- I. Waste Isolation and the Natural Geohydrologic System
- II. Repository Perturbations of the Natural System
- III. Radionuclide Migration Through the Natural System
- IV. Repository Design Technology

Briefly, Part I contains four papers reporting studies on the characterization of geohydrological systems, with special reference to repository siting and performance considerations. Included is a report of how the novel application of relatively recently developed radiochemical analytical techniques can extend our general understanding of such systems. The lead paper in Part I, by J. O. Duguid, will be especially interesting to anyone unfamiliar with the general rationale and iterative methodology used to define and systematically resolve the geohydrological issues that must be addressed in identifying and, ultimately, qualifying a particular site for a repository. This paper was actually presented at the 1980 NWTS Information Meeting. It is included in this volume because its broad scope makes it appropriate as an introduction to the many facets of waste isolation technology that will be treated in this series of volumes.

The four papers in Part II discuss investigations of the effects of the heat and radiation generated by a repository on the natural geohydrological system. Two papers discuss the thermomechanical behavior of the host rock—a basic repository design consideration—and the other two deal with special issues associated with salt host rocks, brine migration, and radiation damage.

A key issue in the performance assessment of a nuclear repository is analyzing and modeling radionuclide migration through the natural system. A basic assumption of mined geologic disposal is that sites and waste forms can be chosen to minimize radionuclide release and to retard further migration of these nuclides. These issues are treated in the three papers that make up Part III.

The first four papers of Part IV, the last section of the volume, discuss phenomenological insights and data described earlier, as well as aspects of practical engineering as it is applied to the design and construction of a geologic repository. The work reported includes efforts to develop refined blasting techniques to minimize mechanical damage to

crystalline rock during repository excavation and to develop borehole and repository shaft sealing materials with the unique longevity required for waste isolation.

We had some difficulty in placing the remaining paper. We eventually decided that "An Overview of Nuclear Waste Disposal in Space," by E. E. Rice and C. C. Priest, fits best in Part IV. Although the present emphasis of the NWTS Program is on deep geologic disposal of nuclear wastes, several other possible disposal schemes have been under investigation for several years. The space option is viewed, not as a replacement for terrestrial disposal, but rather as a complement to it, particularly for certain radionuclides that are long-lived or relatively difficult to confine.

In summary, the 16 papers of this first volume span the gamut of high-level nuclear waste disposal science and technology, presenting an overview of the entire field and examining in some depth the special topics of current interest. We hope that this series will become a useful reference for tracking the progress of this special technology.

P. L. Hofmann, Editor
J. J. Breslin, Associate Editor

Acknowledgments

The annual publication of a series of books of the kind being inaugurated by this volume is an ambitious undertaking and involves the cooperative and mostly anonymous efforts of a great many people. Most of these people are, of course, simply doing their jobs. In the present instance, however, several otherwise busy individuals have gone out of their way to help launch this project. Special thanks is due to Robert C. Wunderlich, Director of Engineering and Technology, NWTS Program Office, Columbus, OH, whose personal enthusiasm for the publication of the books was instrumental in securing early approval of the project by the Department of Energy; to Beverly A. Rawles, Manager, Administrative and Information Services Department, Battelle Project Management Division, who coordinated the publication arrangements with DOE's Technical Information Center; to Maggie Jared, Technical Information Center, who served as the Publication Editor; and to Jean McLean, Office of NWTS Integration, who coordinated the solicitation, assembly, and review of the individual papers and carried out the extensive correspondence inevitably associated with this laborious task. The assistance of these people is sincerely appreciated.

Contents

Part I Waste Isolation and the Natural Geohydrologic System

Earth Science Developments in Support of Waste Isolation <i>J. O. Duguid</i>	3
Preliminary Assessment of Shales and Other Argillaceous Rocks in the United States <i>S. Gonzales and K. S. Johnson</i>	16
The Use of Radiogenic Noble Gases for Dating Groundwater <i>I. W. Marine</i>	42
Theoretical and Laboratory Investigations of Flow Through Frac- tures in Crystalline Rock <i>P. A. Witherspoon, D. J. Watkins, and</i> <i>Y. W. Tsang</i>	65

Part II Repository Perturbations of the Natural System

Thermomechanical Studies in Granite at Stripa, Sweden <i>N. G. W. Cook and L. R. Myer</i>	87
Dome-Salt Thermomechanical Experiments at Avery Island, Louisiana <i>L. L. Van Sambeek</i>	100
Domal Salt Brine Migration Experiments at Avery Island, Louisiana <i>W. B. Krause and P. F. Gnirk</i>	110
Radiation Damage Studies on Synthetic NaCl Crystals and Natural Rock Salt for Radioactive Waste Disposal Applications <i>P. W. Levy, J. M. Loman, K. J. Swyler, and</i> <i>R. W. Klaffky</i>	136

Part III Radionuclide Migration Through the Natural System

Elemental Release from Glass and Spent Fuel <i>G. L. McVay,</i> <i>D. J. Bradley, and J. F. Kircher</i>	171
The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program <i>R. J. Serne and J. F. Relyea</i>	203
The Oklo Reactors: Natural Analogs to Nuclear Waste Repositories <i>D. B. Curtis, T. M. Benjamin, and A. J. Gancarz</i>	255

Part IV Repository Design Technology

National Waste Terminal Storage Conceptual Reference Repository Description <i>I. L. Odgers and J. L. Collings</i>	287
Mining Technology Development in Crystalline Rock <i>W. A. Hustrulid, G. P. Chitombo, A. W. El Rabaa, R. H. King,</i> <i>P. M. Montazer, and P. V. Rosasco</i>	310

Geochemical Factors in Borehole-Shaft Plug Longevity <i>D. M. Roy</i>	338
Field-Test Programs of Borehole Plugs in Southeastern New Mexico <i>C. L. Christensen and E. W. Peterson</i>	354
An Overview of Nuclear Waste Disposal in Space <i>E. E. Rice and C. C. Priest</i>	370
Index	387

Part I Waste Isolation and the Natural Geohydrologic System

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Earth Science Developments in Support of Waste Isolation

J. O. Duguid

Battelle, Office of National Waste Terminal Storage Integration,
Washington, DC

Earth science issues in geologic waste isolation can be subdivided into smaller questions that are resolvable. This approach provides a mechanism for focusing research on topics of definable priority and monitoring progress through the status of issue resolution. The status of resolution of major issues in borehole sealing, interpretation of groundwater hydrology, geochemistry, and repository performance assessment is presented. The conclusion is drawn that the National Waste Terminal Storage Program has reached a point where the selection of sites, underground testing, and emplacement of waste can proceed on a well-defined schedule.

Introduction

Developing a geologic repository for disposal of high-level radioactive waste requires careful definition of scientific and engineering questions to subdivide a large multidisciplinary problem into components that are resolvable. The difficulties in defining technical questions arise because many phenomena that contribute to overall repository behavior (e.g., hydrologic, thermal, mechanical, and chemical responses) are closely coupled. Thus, to understand repository behavior, we must divide a complex system of interacting phenomena into individual components. This can be done by defining technical questions that involve a single phenomenon, conducting the research and development required to address that phenomenon, developing an under-

standing of the relationships among various phenomena, and combining our understanding of individual phenomena to yield an appropriate level of understanding of repository behavior. The predicted behavior of a repository can then be verified, to some extent, by comparing predictions to data obtained from tests conducted during the construction and operation phases of the repository.

The objectives of this paper are to present a specific set of earth science technical questions (as defined in the preceding paragraph), discuss their status of resolution, describe the research effort being applied to their resolution, and provide insight into the priority of resolution from both a waste management policy and a technical point of view.

Earth science technical questions (issues) have developed through an evolutionary process that began with waste isolation activities in the 1950s (National Academy of Sciences, 1957). Research and development, combined with results from field tests, led to identification of more detailed questions about repository performance. Questions have been reported and discussed by the Environmental Protection Agency (1978), Bredehoeft et al., (1978), the National Academy of Sciences (1978), and the Interagency Review Group (1978, 1979). Earth science technical questions were refined and organized by the Department of Energy and the U. S. Geological Survey (1980) in the Earth Science Technical Plan (ESTP). The ESTP also

indicates the status of resolution and remaining work needed to resolve each question. More recent discussions of technical problems are presented by the Department of Energy in the Confidence Rulemaking document (1980) and the Status of Technology document (Klingsberg and Duguid, 1980). This paper draws heavily on the Status of Technology document because it represents a combined version of the thinking that had preceded it (e.g., that of the Interagency Review Group, the Confidence Rulemaking document, and the ESTP).

The refinement of technical questions is important in developing a geologic repository for the following reasons: (1) to divide a large, seemingly insoluble problem into specific questions that are resolvable; (2) to provide a mechanism for focusing research and development activities on discrete questions for definable priority; and (3) to provide specific questions on which progress can be monitored by tracking their status of resolution.

This paper treats a specific set of earth science technical questions, as defined by the ESTP, and further limits that set of questions to those related to expected repository response in both the near and far field. In the discussion of the near field, the topics addressed are the relation of geochemistry to design of the waste package, thermomechanical response of the repository, and the effects of repository construction on the host rock. The geologic, hydrologic, and geochemical aspects of repository performance in the far field are discussed. Also included are discussions of sealing and of the calculation capability for both near- and far-field performance assessment.

The Near-Field Environment

The near field for a repository is defined as the volume of host rock in

which internal (waste- and repository-caused) driving forces are dominant over natural forces. Thus near-field phenomena include the chemical interactions of the waste, the components of the waste package, and the host rock; the response of the host rock and its fluid to the thermal loading supplied by the waste; and the effects of repository construction on the host rock.

The chemical interactions among the waste, the components of the waste package, and the host rock, including the water it contains, are controlled to a large extent by the temperature of the near-field environment. The rates of chemical reactions generally are faster at higher temperatures, and temperature can be controlled by aging the waste, widening the spacing between waste packages, or by a combination of these two steps. At any temperature, however, investigators are still faced with the problem of designing a waste package that provides reasonable assurance of containing the waste for 1000 yr and of controlling the waste release for 10,000 yr.

The two primary concerns about the behavior of the host rock at increased temperature are (1) the increased increment of stress caused by thermal expansion of the rock during heating, which can cause failure in the repository's isolation potential, and (2) the changes in the local groundwater system caused by the buoyancy of heated water. Both of these effects can be controlled to a large extent by reducing the temperature of the repository.

The effects on the host rock of constructing repository openings range from instability of the openings themselves to damage (e.g., cracking) caused by the excavation methods used. Stability of the opening can be controlled by its shape, its orientation, and the extraction ratio (i.e., the ratio of volume removed to total volume).

Excavation methods determine the amount of damage done to the host rock during excavation; these methods include, in order of decreasing damage, conventional blasting, smooth-wall blasting, and drilling.

To a large extent, near-field effects, which are caused by stress release during construction, by the thermal pulse that increases the rate of chemical reactions, and by the amount of local stress in the host rock, can be controlled through engineering design. This does not mean that these effects can be disregarded; rather it means that there is some flexibility in repository design, depending on the level of understanding achieved (e.g., conservatism can be applied in the design to compensate for uncertainties, as in the multiple-barrier and the systems approaches).

Research in the near field is centered on determining the expected repository environment (e.g., temperature, pressure, chemical interactions, and the amount of fluid present) and relating this environment to the behavior of the engineered components placed in it (the engineered components are the waste, the waste package, and the mined openings of the repository).

Waste Package. Research emphasis in the past has been on glass and spent fuel waste forms. More recently, research on spent fuel has diminished, and repositories are being designed with options to accept reprocessed commercial waste, spent fuel, or defense waste. Small-scale facilities have demonstrated the practicability of the vitrification process, and pilot glass plants have been developed in the United States and Europe. At the present time more attention is being devoted to other waste forms, and studies are being conducted to evaluate their properties, e.g., inertness, thermal properties, resistance to mechanical shock, phase

stability, compatibility with other components of the waste package, and economics.

The waste package functions to reduce the rate at which radionuclides enter the natural system. By definition, it includes everything that is placed in the repository emplacement hole, i.e., from inside out, the waste form, canister, overpack, buffer, sleeve, and backfill. If water enters the package, dissolved or entrained radionuclides must travel out through all these package components. Both a chemical and a physical delay would result, and the shorter-lived radionuclides would decay substantially during this time period.

Package backfill and filler materials are selected to impede the movement of groundwater, modify groundwater chemistry, and enhance the corrosion resistance of the metal components of the package. In addition to providing containment and corrosion resistance, the sleeve is designed to maintain an open emplacement hole. The overpack provides uniformity among different canisters, and the canisters give protection during handling.

Current research emphasis is on selecting materials and testing to obtain data for screening the large numbers of potential materials for various components of the waste package. At this stage there is little doubt that an appropriate package can be designed to meet all criteria; however, considerable effort is still needed to demonstrate this with reasonable assurance.

Repository Design. From an engineering viewpoint, a geologic repository for radioactive waste is not different from other mined cavities that have been built for centuries and have operated over long periods of time. Some have remained open for over 1000 yr, despite the fact that they were not constructed for long-

term stability. Within a waste repository, however, a substantial thermal pulse will be generated by the radioactive decay of the emplaced wastes. The design of a waste repository constitutes a major challenge for rock mechanics, principally because the thermal pulse has the potential to alter the stress state of the surrounding rock.

The thermomechanical response of host rock is relevant to problems of long-term waste isolation to the extent that it affects the hydrologic and geochemical characteristics of the host rock. Important features of this response are rock strength (ability to sustain differential stress) and ductility (ability to flow without fracture). Both strength and ductility are influenced by the presence of solutions and by increased temperature (in general, strength is decreased, and ductility is increased).

Heating is expected to increase the compressive stress in the immediate vicinity of the repository but to reduce the in situ compressive stress beyond this zone. The magnitude and distribution of stress changes, which are influenced by the waste package layout and the rate of heat generation, will change with time. The specific effects of stress on rocks depend on the relative magnitudes of the existing tectonic and overburden stresses and the physical characteristics of the host rock and surrounding geologic environment. It is possible, for example, that stress changes could produce slippage of existing fractures in the rock mass, and it is likely that changes in stress would cause changes in permeability. Therefore the existing state of stress in the region must be determined so that such events and their possible consequences can be evaluated. The extent of these and other related effects must be evaluated by the principles of rock mechanics, and data from both laboratory and in situ testing will be

required to develop analytical models of the repository site.

Rock mechanics aspects of repository design have been studied more extensively for salt than for other rocks. Analytic models that predict the near-field response of a mass of rock salt have been developed and checked against data obtained from experiments and from field tests of spent fuel and electric heaters in Project Salt Vault in Kansas. The applicability of these models, which were developed for bedded salt, to dome salt is being determined in heater experiments conducted at Avery Island, Louisiana.

An important design consideration for brittle rocks is an allowance for fracture rather than flow, and a major concern is that the properties of individual rock samples will differ from those of the rock mass.

Appropriate ways of correlating data from relatively small specimens with data from rock masses are still under review. Most data currently available are derived from laboratory measurements on individual rock samples, but a rock mass typically contains fractures and heterogeneities that weaken it and could significantly alter its response to excavation and construction. The approximation of continuum mechanics, which has been used successfully for salt, might not be applicable to a jointed and fractured rock mass.

Mechanical rock properties in rocks other than salt are being quantitatively analyzed. The principal uncertainty that must be resolved for hard rocks is that of failure modes. Field experiments under way in granitic rocks in Sweden and at the Nevada Test Site and experiments planned for basalt at the Hanford Site in Washington state are intended to establish the deformational response of these rocks, including mechanical properties and time- and temperature-dependent relationships.

In addition, a major experiment with spent fuel has been initiated at the Nevada Test Site to provide data that can be used collectively to evaluate mathematical models describing the near-field response of fractured rock masses to both heat and radiation.

The program of the Department of Energy in rock mechanics currently emphasizes aspects related to site-specific design and to instrumentation that will be reliable over the time required to conduct in situ tests. The objective is to provide a conceptual basis for defining acceptable stresses, pillar stability, and deformation and failure modes in the near field.

Inasmuch as there is considerable experience in developing large underground cavities in a variety of rock types, the existing rock mechanics technology appears to be fully capable of developing a stable cavity suitable for a waste repository.

Near-field questions can be resolved, or at least compensated for, by conservative engineering design. Near-field questions are not resolved by relying heavily on understanding the natural host rock environment but instead by relying on engineering and predicting the behavior of engineering materials in a controlled environment placed in the natural system (the repository environment).

More effort has to be devoted to identifying and analyzing far-field effects. Improved understanding of stress-strain relationships and of the mechanical response of layered media is needed for a refined analysis, but bounding limits probably can be established with existing information. The results would indicate the likely locations and magnitudes of displacements in the rock structures and locations in which the rock strength might be exceeded. To estimate accurately the fracture density and other fracture characteristics important to assessing changes in groundwater flow

in the rocks would be far more difficult—probably beyond the capability of today's models. Such information would have to be obtained from a combined analysis of data from experimental and theoretical studies and from modeling.

Because this paper deals primarily with earth science aspects of repository development, the remainder of our discussion concentrates on long-term far-field technical questions. The brief discussion of the near-field environment was presented to set the stage for long-term technical questions—to ensure that no aspect of far-field questions was overlooked.

The Far-Field Environment

The far field is defined as the volume of rock, outside the near field, in which external (natural) forces dominate. After a repository is filled and sealed, the most likely mechanism for the escape of radionuclides to the biosphere is dissolution and transport in groundwater. Repositories located below the water table, except those in salt, can be expected to become saturated with groundwater. The rate at which saturation occurs depends on the permeability of the host rock, the depth of the repository beneath the water table, the effectiveness of shaft and borehole sealing techniques, and, for salt, the rate of repository self-sealing as a result of plastic flow. After repository excavations are saturated, groundwater flow through and in the immediate vicinity of the repository will be influenced by a complex coupling of (1) the mechanical response of the host rock to repository construction, (2) the thermal pulse, and (3) the hydraulic gradients, permeabilities, and related factors that existed before the repository was constructed.

Dissolution of the wastes and transport of radionuclides by groundwater are influenced by the following factors:

(1) Solubility of the waste form and corrosion of its container in the repository conditions (temperatures and pressures); (2) rate and volume of groundwater flow; (3) sorptive properties of the host rock at repository temperatures and of all mineral surfaces along the groundwater flow path; (4) chemical properties of the groundwater, including its pH, oxidation potential, and ionic strength; complexing agents present; and chemical changes associated with the emplaced wastes. Each of these factors is a function of still other variables; e.g., the flow rate is a function of permeability, porosity, and hydraulic gradient. The sorptive properties of rocks, in turn, are a complex function of (1) the type of minerals lining the pores and fractures through which groundwater moves, (2) the available surface area of the sorptive minerals, (3) water velocity, (4) temperature, (5) pH and other chemical properties of the groundwater, and (6) the changing chemical composition of the groundwater as it moves along the flow path.

Once radionuclides are transferred to the groundwater as dissolved, complexed, or colloidal material, other factors in addition to water-rock chemistry also operate to determine the concentrations of radionuclides as they are transported. These factors include radioactive decay, dispersion, and mixing with water from adjacent geologic formations. Thus accurate prediction of the migration of radionuclides from a repository requires detailed knowledge of the chemistry of the waste-rock interactions; transient repository temperatures; the distribution of porosity, permeability, dispersivity, and hydraulic gradient; water sources and sinks and aquifer boundary conditions; sorptive characteristics along the transport pathways; and water chemistry and radiochemistry. This type of geohydrologic and geochemical information

is not fully available even for the best understood aquifers and would require considerable effort to obtain at a repository site because of the need to minimize disruption of the area by drilling. Some of this information for fractured media or porous media of very low permeability cannot be obtained until appropriate methods are developed. All types of data do not have to be known to an equal degree at specific repository sites, however, and it may not be necessary to have a high degree of precision in certain environments if the transport problem can be bounded through modeling.

The number of cited variables affecting radionuclide transport by groundwater, the complexity of their relationships, the long periods of time involved, and the need to evaluate their relative importance by sensitivity analysis necessitates the use of computer models to forecast the subsurface movement of radionuclides from a waste repository and radionuclide concentration under a variety of possible conditions. Such forecasts comprise basic input for performance assessment, which is discussed in the next section. Several mass transport computer models are operational. By varying boundary conditions and such generic input data as rock permeability, porosity, and sorption properties for specific radionuclides, we can use these models to measure the relative importance of flow path length, flow velocity, and aquifer sorption characteristics as barriers to radionuclide transport. Results indicate that, if a repository is located where flow paths are on the order of tens of kilometers (such as those in regional aquifer systems), where flow rates are low, or where the rock sorptive properties are high, then retention of radionuclides in the earth's crust for many thousands of years is possible if the natural flow is not short-circuited.

Current mass transport models of radionuclide migration in groundwater

include three widely recognized limitations: (1) Flow of fluids through fractured rock or through rocks of very low permeability cannot be modeled until a method for characterizing such formations is developed and tested. (2) Experimental data on the sorptive properties of common rocks for the actinide elements are insufficient. The experiments do not completely simulate the temperature, pressure, or chemical conditions expected, either in a repository or in a deep aquifer, and the experiments assume that equilibrium rather than kinetic conditions will always control partitioning of the actinides between solid and liquid phases. (3) It will not be possible to validate mass transport model predictions for long time periods before sealing a repository. Monitoring wells could be drilled, but such a procedure might compromise the integrity of a repository site. In any event, wells would not yield useful data for perhaps decades after the repository was sealed.

Confidence in the models might be obtained, however, by comparing their predictions with natural systems for which data exist or can be obtained. Other major difficulties pertinent to transport modeling involve the number of chemical reactions that can be modeled, the effect of mathematical approximations on the results, and the quantification of uncertainties. Some of these limitations (e.g., those pertaining to sorptive properties) will be reduced by research; others, such as model validation, will remain to some extent.

"Natural experiments," such as the Oklo natural reactor, uranium ore bodies, and underground nuclear bomb tests at the Nevada Test Site (NTS) are being examined for information on radionuclide transport by groundwater. With regard to the NTS, there is little evidence (except for tritium) of radionuclide migration in groundwater. This absence of migration is

thought to reflect a combination of the following factors: (1) Radionuclides are retained in glass phases formed by the nuclear detonations; (2) the detonations have occurred within rocks of high sorptive capacity for radionuclides (e.g., zeolitized tuff or tuffaceous alluvium); and (3) most detonations have taken place above the water table. However, it may simply be that sufficient time has not yet elapsed at the NTS to detect migration of radionuclides other than tritium. The Hanford Site appears to offer considerably more promise as a field experiment for radionuclide migration by virtue of its long history of disposal of low-level liquid wastes into unsaturated alluvium and the retardation of radionuclides by the unsaturated material above the water table.

The applicability of information from the Oklo reactor to the migration of radionuclides from a repository has been confirmed, but considerable additional research is needed to decipher the paleohydrologic and paleo-geochemical setting at Oklo. Its value as an analog to radionuclide migration from a proposed repository cannot be appraised until this research is done. Geochemical and geohydrologic studies of groundwater transport of uranium, thorium, and radium from uranium ore deposits or mill tailings may be another fertile research area for testing existing radionuclide mass transport models in a variety of underground environments.

These analyses of radionuclide migration generally assume that groundwater flow will be controlled only by hydraulic gradients and permeability. However, as stated in the opening paragraph of this section, groundwater flow in the immediate vicinity of a repository will also be influenced by the mechanical response of the host rock to repository construction and by the subsequent thermal pulse. Detailed studies of such

flow are important; for example, in areas with strong upward components of groundwater flow, shafts and drill holes constitute potential highly permeable short circuits to the natural flow.

The research emphasis in the far field centers around borehole sealing, interpretation of the groundwater hydrology, and geochemical measurements as they relate to understanding the hydrology and development of retardation factors used in transport modeling.

Borehole Sealing. Research and development on sealing boreholes and shafts must address the following questions: (1) Can the permeability of a seal be tested in the field? (2) Can the long-term stability of sealing material be evaluated?

The problem of testing the in situ permeability of a borehole seal arises not only because a pressure differential must be placed across a section of the seal at depth but also because the interface between the rock and the seal and any zone of rock surrounding the hole which was damaged by drilling must also be tested. The first tests of this nature were conducted by Sandia National Laboratories in a borehole in a stratified sequence of sedimentary rocks in New Mexico. Sealing materials (cements) were tailored to be geochemically compatible with the formation to be sealed. After emplacement of the seal material, pressure gradients were produced across vertical sections of the seal, and water flow through the seal material, seal-rock interface, and annulus around the borehole was evaluated. This experiment indicated that methods of in situ testing of borehole seals can be developed and implemented.

The question of long-term stability of sealing materials is being addressed in several ways. There is a considerable amount of geologic evidence

showing the chemical stability of natural materials, such as clays or clay-sand mixtures, over very long periods of time. For man-made materials, such as cements, there is some geologic evidence the specific minerals are stable, and cements from archaeological sites can be evaluated for changes in physical and chemical character over periods in excess of 1000 yr. Also, accelerated testing under increased pressure and temperature can be used to evaluate the long-term stability of sealing materials. However, the results of accelerated testing alone may not be sufficient to assure stability of sealing materials, and a combination of these methods may have to be applied.

Groundwater Hydrology. The primary question in groundwater flow is, Can the hydrologic system be adequately understood and interpreted? The resolution of this question is relatively straightforward in simple geologic settings where models based on flow through porous media apply. Continuum models and the techniques for obtaining their parameters have been effectively applied to water resource problems for several decades. The models produce good results for pressure heads over regional aquifer systems, along with estimates of the quantities of water recharged to and discharged from the system. However, values of velocity and consequently groundwater travel time are somewhat less reliable; this fact, in combination with the uncertainty in dispersion and retardation parameters, produces estimates of mass transport of radionuclides that are even less reliable. For this reason, calculations of radionuclide transport must be supported by an understanding of the geochemistry of the hydrologic system.

On the other hand, the understanding of water flow through fractured rock masses requires considerably

more development and verification of techniques. Models currently exist which can be used for interpreting field data, but the results from these models are still under development. In view of the progress that has been made over the past few years toward understanding groundwater flow in fractured systems, however, it is believed that appropriate models of groundwater flow and coupled thermal-mechanical-hydrologic properties will be available in the next 5 yr. These models will yield better answers to questions that currently can be bounded only by using simple, conservative modeling methods.

Geochemistry. The questions involved with understanding the geochemical system are related primarily to verifying groundwater flow and radionuclide transport models in the vicinity of the repository site. A detailed analysis of areal geochemistry allows us to (1) identify past and present geochemical processes, (2) determine the rates of these processes, and (3) predict the future geochemical environment. The techniques for making these determinations are largely available and for the most part await the collection of enough site-specific data so that they can be applied. Application of geochemical models to site-specific data will either confirm or disprove the interpretation of flow in the groundwater system.

Specific geochemical tools being developed are models of aqueous geochemistry based on either thermodynamic equilibrium or kinetic reactions between rock and water and methods of analysis for specific isotopes contained in both rock and water. The major reason for isotopic analyses of the rock-water system is to obtain an estimate of the age of the water and, thus, to calculate groundwater travel times from the point of recharge to the point of sample collection. Isotopic analyses can also aid in

understanding chemical processes in the system, including their rates. Currently groundwater dating techniques use ^{14}C , ^{36}Cl , the accumulation of helium from radioactive decay, and the disequilibrium between isotopes of uranium.

Understanding the geochemistry of the aquifer system also provides assurance that the retardation coefficients based on laboratory analysis and used in modeling of radionuclide transport are conservative. If we know the behavior of natural ions that are chemically similar to radionuclides in the groundwater system, we can be reasonably sure that results of short-term laboratory and field experiments applied to long-term transport problems are correct.

Another facet of geochemical research is the investigation of natural analogs for long-term transport of radionuclides. Currently, thorium and uranium ore bodies are being analyzed in an attempt to obtain data that can be used in verifying models of the transport of radionuclides. Also, the feasibility of applying geochemical models to the vast amount of geochemical data that have been collected from the Oklo natural reactor is being assessed.

Performance Assessment

Actual tests and demonstrations of the behavior of a repository system cannot be performed over the lifetime of the repository. Therefore mathematical models, with data collected during comparatively short periods of time, must be relied on to predict the long-term performance of a repository system. This is the only way to analyze the cumulative effects of changes in the properties of the repository, the effects of various design features of the repository, and the effects of the repository on the environment. Performance assessment provides not only this type of analysis

but also information that is useful in guiding research and development activities in site selection, repository design, and waste package design. Performance assessment treats concepts that can be quantified, i.e., failure analysis and consequence assessment.

Failure analysis identifies potential events and processes that cause changes in the site (i.e., scenarios) which may lead to release of radioactive material from a repository. It is based largely on a combination of scientific reasoning and engineering experience. There is no method to ensure that such analyses have identified all potential events of significance. After the failure analysis is completed, the next step is to estimate the probabilities that the postulated scenarios will take place. Given certain basic data, statistical methods (e.g., event trees and fault trees) are available for estimating probabilities of sequences of events and processes. The final step is the determination of the consequences of the release of radionuclides as postulated in the failure analysis. These consequences are typically quantified statistically in terms of radiation doses to persons or human health effects.

Because of the uncertainties associated with the predictive capability of earth sciences, especially in estimating probabilities of major geologic events, assessments to date have dealt primarily with failure analysis and consequence assessment. Since we are unable to estimate probabilities accurately, a satisfactory complete risk assessment cannot yet be accomplished. Work is proceeding in the area of probability estimation, but it is not known if the uncertainty in these estimations can be reduced to a level where repository risk assessment would be as reliable as other, better understood risks.

An assessment of the long-term performance of a repository analyzes

the events and processes that could release radionuclides from the waste and the phenomena that might transport radionuclides to the biosphere. These phenomena may be roughly classified as those occurring in the near field (where waste and repository forces dominate) and those occurring in the far field (at a greater distance from the repository, where natural forces dominate). Although these two regions are not separated by a precisely defined boundary, the distinction is useful because the physical and chemical effects of heat and radiation from the waste are limited to the near field. Different methods of analysis are, therefore, appropriate for the two regions. Near-field analysis deals with the combined effects of heat, radiation, repository design and construction, and the waste package. Far-field analysis considers the effects of phenomena that arise from the heat produced by the waste, from natural phenomena, and from human actions after the repository has been sealed. These phenomena usually appear in the geosphere and the biosphere outside the repository. Both near-field and far-field performance must be considered in determining how well the natural and man-made components of the disposal system meet the criteria for the repository.

As summarized in Fig. 1, four components of the complete waste disposal system—the waste package, the repository structure, the geosphere, and the biosphere—are assessed for long-term performance. The analysis begins by defining the state of the system for each component at the time the repository is sealed. The effects of phenomena that might breach the repository and cause the escape of radionuclides are then described. The failure mode (scenario) is used to predict the future state of the system's components, the manner in which groundwater could move to the waste, and the manner in which

Figure 1 General approach to performance assessment.

nuclides could then move through the host rock to reach the biosphere. Finally, the analysis predicts the effects of the radionuclides on the persons they are assumed to reach. As shown by the horizontal arrows in Fig. 1, all these analyses are strongly interrelated and must be considered together in predicting the performance of any or all of the components of the waste disposal system.

Before models can be used with confidence, they must be verified. The development and verification of individual performance-assessment models follow this procedure: (1) The phenomena to be modeled must be identified. (2) Available information about these phenomena and the disposal system from laboratory experiments and field tests is organized. (3) Models based on this information are developed. They can be empirical (based on direct observations) or theoretical (based on interpretation of the observations according to known physical laws). (4) Predictions of the models are compared with additional

observations of the disposal system under conditions different from those used for developing the models. (5) If the comparison shows significant differences between predictions and observations, the models are modified and tested again. This iterative process of model modification and verification continues until a satisfactory agreement between prediction and observation is obtained.

Peer review of both development and verification of a model is important in determining its acceptability. Finally, individual models are combined to form an "executive model," which manages the interactions among individual models.

The major effort in performance assessment is in integrating existing models into a system that can be used for both near- and far-field assessment. The far-field portion of this system has been integrated and applied to specific sites over the past several years (e.g., a salt dome, bedded salt in Utah, and the basalt sequence of the Columbia Plateau). The near-field

models (e.g., thermal, thermomechanical, geochemical, and groundwater flow and transport) are currently being integrated. In the near field, some models, such as the waste package model, waste form leaching models, coupled thermomechanical-hydrologic models, and fracture flow models, are in various stages of development. Even without these completed models, however, performance assessments can be made if conservative assumptions and simpler models are used to bound near-field repository behavior.

Conclusions

When a broad set of earth science technical questions are viewed from their status of resolution, their anticipated date of resolution or bounding, and their priority of resolution, the status of technology can be measured. From documents using this approach, e.g., the Interagency Review Group reports (1978, 1979), the Earth Science Technical Plan (Department of Energy and U. S. Geological Survey, 1980), the Department of Energy Confidence Rulemaking (1980), and the Status of Technology (Klingsberg and Duguid, 1980), we can conclude that:

- Because no single property, characteristic, or human action alone will determine the fate of radionuclides, the waste form, repository, geologic environment, and repository performance must be analyzed as a system.
- Successful isolation of radioactive waste appears feasible for periods of thousands of years if the systems approach is used and the influence of future human activities is minimized through adequate precautions.
- The feasibility of disposing of wastes safely in mined repositories can be assessed only on the basis of specific tests at particular sites to determine their suitability.
- Not all types of data have to be known to an equal degree at specific repository sites, and it might be unnecessary to have a high degree of precision in certain environments if the transport problem can be bounded through modeling.
- Some uncertainties can be bounded or compensated for and, therefore, need not be resolved in detail before selecting a site or constructing a repository. Other uncertainties can be resolved during repository construction and operation. Although reliance on appropriate engineering practices and multiple barriers can compensate for a lack of complete knowledge and predictive capability, some uncertainty will always remain.
- Studies of engineered barriers indicate that the components of the waste package can prevent or minimize release of radionuclides to the natural system by functioning as effective chemical and physical barriers.
- The use of continually improved models, along with the improved body of experimental data, will permit performance assessments to be done more completely and with more confidence in the future.
- Scientific and technological knowledge is adequate to identify potential repository sites for further investigation and development. No scientific or technical reason is known that would prevent selecting and characterizing a site that would be suitable for a repository if the systems approach is used to evaluate the suitability of sites and repository designs.
- The program leading to site selection in the mid-1980s is currently considering salt (both bedded and dome), basalt, granite, and tuff as potential host rocks. Of these potential hosts, the level of understanding is highest for salt, followed by

granite, basalt, and tuff, respectively.

These generally accepted conclusions indicate that the National Waste Terminal Storage program has reached a point where the careful stepwise selection of repository sites, development and testing in the underground facilities, and emplacement of waste in a geologic repository can proceed on a well-defined schedule.

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Preliminary Assessment of Shales and Other Argillaceous Rocks in the United States

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Shales and related clay-rich rock types throughout the conterminous United States are geologically characterized and evaluated on a regional basis relative to their promise as possible candidate rock sequences for the repository disposal of high-level radioactive wastes. Only stratigraphic intervals or parts of them that are laterally persistent, consist of 75 m or more of shale, mudstone, or argillite, and lie at depths of 305 to 915 m below the land surface are included.

The general properties of clay-rich rocks, as well as the several desirable characteristics that make them potentially attractive as disposal host candidates, are reviewed. Also discussed are the geologic factors that dictate the potential acceptability of any shale sequence relative to the regional subsurface distribution of units that meet the basic criteria of extent, thickness, and depth. Included in this context are the tectonic setting, geologic structure, seismicity, groundwater hydrology, mineralogy and content of organic matter, mineral resource potential of both the shales and the enclosing geologic basins, and any construction experience on underground openings, such as hydrocarbon-storage facilities.

The clay-rich strata that appear to be promising on the basis of this evaluation are inventoried according to their occurrence and distribution within nine geologic-

geomorphic regions throughout the country. Also considered are several, more localized occurrences of Precambrian argillites whose mineralogies make them a related yet separate group in comparison with the sedimentary strata already summarized. Topics for which data are insufficient or on which inadequate study has been conducted to date are also identified.

Background

Although for some time rock salt has been regarded as the favored host rock for the geologic disposal of high-level radioactive waste (Johnson and Gonzales, 1978), interest in other lithologies for this purpose has increased in recent years. The different rock types proposed from time to time as potential hosts include basalt, granite, volcanic tuff, serpentinite, certain "dry" limestones, and shales and clays. The greatest level of initial interest in argillaceous or clay-rich strata has been shown by several European nations (Italy, Belgium, and the United Kingdom), which either lack salt deposits or have nuclear facilities sited above thick deposits of clay. Examples of this latter circumstance are at Mol, Belgium, and Trisaia, Italy.

Even though various investigations were carried out on argillaceous rock units in the United States before the late 1970s, developments in both the foreign and domestic areas have

helped to stimulate greater interest in clay-rich rock media. When the multi-barrier concept from the Swedish KBS repository program was proposed, an essential component was a buffering material to be used as an overpack around the waste canisters. Bentonite, a clay mineral having high ion-exchange capacity, is a leading candidate material for this additional precaution against radionuclide migration.

On the domestic scene, the Interagency Review Group (1979) strongly recommended that the United States pursue the concept of regional repositories and more vigorously investigate non-salt lithologies. This paper is a preliminary and condensed version of a nationwide assessment of shales and other argillaceous strata in various geologic regions (Gonzales and Johnson, in

press) carried out under the geologic program of the Battelle Office of Nuclear Waste Isolation.

Several earlier studies have been of special value in assessing the general suitability of shales for radioactive waste disposal; these include literature and field investigations and in situ thermal experiments (Fig. 1). In an early effort by Merewether et al. (1973) several shales from throughout the nation were investigated. Regional studies were directed at the New Albany and Maquoketa Shales in Indiana (Droste and Vitaliano, 1976), the Porter's Creek and Yazoo Clays and certain other shales and clays in the Eastern Gulf Coast-Black Warrior Basin area (Mellen, 1976), and several Triassic shale-bearing basins along the Atlantic Coastal Plain-Piedmont trend (Weaver, 1976). Work on these

Figure 1 Map of the United States showing the location of previous field and subsurface studies and in situ thermal experiments conducted on shales and other argillaceous strata.

regional-level projects was supported and directed by the now defunct Office of Waste Isolation of the Union Carbide Corporation. A more recent followup study on the Triassic Basins of the eastern United States has been completed (Dames and Moore, 1980) and issued through the Savannah River Laboratory.

For many years the U. S. Geological Survey (USGS) has conducted a wide spectrum of studies of the basic geology, geochemistry, and mineralogy of the Upper Cretaceous Pierre Shale in the northern Great Plains. Shurr (1977) interpreted much of these data in relation to nuclear waste disposal.

Because of their great importance as a potential source of unconventional natural gas, the Devonian-Mississippian shales in the Appalachian, Illinois, and Michigan Basins have been studied in great detail since the late 1970s. A massive amount of geologic data, acquired under the Eastern Gas Shales Project, has been of considerable value in studying the applicability of these shales, especially zones with low hydrocarbon potential, to the waste disposal program. A recent report by Lomenick et al. (1982) summarized these interpretative studies.

Both the Conasauga Shale in eastern Tennessee and the Eleana Argillite at the Nevada Test Site have been examined by means of in situ thermal experiments conducted by researchers at Sandia National Laboratories. Results on the test methods and the analytical results are presented by Krumhansl and Sundberg (1980) and Lappin and Olsson (1980).

Interest in shales for radioactive waste containment has been further stimulated by the results of numerous studies conducted on the Oklo Phenomenon, which has been shown to be a fossil nuclear reactor that developed within a high-grade uranium deposit in the Republic of

Gabon in Africa (Brookins, 1976). Of particular relevance is the retention for some 1.8 billion yr of many radionuclide species produced by this natural fission event within a quartz- and carbonate-rich shale. Brookins emphasized that, if an impure shale can be this effective in containing radionuclides under natural conditions, a carefully selected shale with better physical-chemical properties definitely is promising as a host rock.

General Properties of Shale

Shale is the common name given to a large group of sediments or sedimentary rocks characterized by a predominance of clay minerals or clay-sized mineral grains less than 4 μm (0.004 mm) in diameter, although Weaver (1977) found that many so-called shales contain a predominance of silt-sized grains. Alternatively, the adjective argillaceous is commonly used (as in "argillaceous strata") to describe rock units containing abundant clay-sized particles or clay minerals. Other, more specific terms, such as mudstone, claystone, marlstone, siltstone, and argillite, have also been used to describe certain fine-grained sedimentary rocks on the basis of variations in textures and/or sedimentary structures.

Shales and other argillaceous strata have been proposed as potential host rocks for radioactive waste disposal because they have a number of geologic properties favorable for containing the waste. Such rocks generally display moderate to high plasticity; very low permeability; good ion-exchange characteristics, especially with regard to alkali and alkaline-earth elements; and very low solubility. In addition, thick, fairly homogeneous shale and clay strata are present in many structurally undeformed regions of the United States at depths considered favorable for the geologic isolation of radioactive waste.

Geologic properties that represent potential disadvantages to disposal of waste in shale include possible dewatering of hydrous clay minerals as a result of thermal loading, possible presence of organic matter and/or petroleum hydrocarbons in the shale itself or in associated strata, and possible difficulty in mining low-strength to plastic shales and retaining the structural integrity of underground excavations.

Grim (1968), Pettijohn (1975), Weaver (1977), Blatt, Middleton, and Murray (1980), and Potter, Maynard, and Pryor (1980) have summarized the general properties of shales and similar rocks. Studies focusing on the potential use of shales and other argillaceous strata for radioactive waste disposal include those by Merewether et al. (1973), Johnson (1975), Walsh and Bathke (1976), Weaver (1976, 1979), Witherspoon (1977), Dames and Moore (1978), Apps, Cook, and Witherspoon (1978), Connolly and Woodward (1980), and Isherwood (1981).

Regional Geologic Characteristics Important for Waste Disposal

The sole technical criterion that must be met in the disposal of high-level radioactive wastes is that the repository must contain the radionuclides. Stated another way, the wastes must be isolated from the biosphere until radioactive decay has sufficiently reduced the activity of the radionuclides so that they no longer pose a hazard to humans and the environment. The length of time during which radioactive waste materials must be isolated varies with the type of waste and its initial level of radioactivity. The isolation period for high-level wastes ranges from several thousand years to several hundred thousand years. The most likely natural mechanism by which radionuclides

might migrate from a subsurface repository into the biosphere is groundwater transport. Thus special attention must be given to the geologic and hydrologic characteristics of any rock medium on a site-specific basis (International Atomic Energy Agency, 1977).

Thick deposits of shale and other argillaceous strata have existed below the land surface for hundreds of millions of years, and many of them have persisted for these long periods without undergoing apparent significant changes. Substantial parts of these deposits have remained free of circulating groundwater since their initial compaction and partial expulsion of pore fluids. By studying individual shales and the hydrology, structural geology, and general geologic framework of nearby rock units, we can interpret the geologic processes that have affected the region in the past. Also, we can forecast, in general, the impact of such processes on any repository site for long periods of future geologic time.

Because of the complexity of geologic phenomena, each repository site must be selected on its own merits and must be considered unique. General characteristics of the geologic environment that govern the overall suitability of salt deposits for waste disposal were discussed in an International Atomic Energy Agency (1977) report. Johnson and Gonzales (1978) also summarized the regional geologic characteristics important for the disposal of radioactive wastes in salt deposits, and much of that discussion is summarized in the following paragraphs since it is also applicable to shales.

Structure and Geologic Framework. The regional geology and geologic history of any area containing a thick shale unit must be known to understand the processes that have

acted on the potential host rock in the past, processes that will influence containment of the waste in the future. Regions that have been tectonically stable for tens of millions to hundreds of millions of years are likely to remain stable over the next several hundred thousand years. Where rapid uplift or strong deformation is anticipated, the potential for waste disposal is less promising because radionuclides in such settings might escape as a result of such uplift and the accompanying denudation or structural disruption of the host rock. Some of the more important structural elements that should be studied for each shale or clay deposit include (1) dip or inclination of the strata, (2) presence or absence of faults and joints, and (3) nature and extent of adjacent rock units.

In thick shale deposits, an inclination of a few degrees is preferred so that it is possible to design nearly horizontal underground workings within the same rock unit over fairly large areas. Steep dips or tight folds with frequent reversals in dip are to be avoided because they indicate that the rocks were subjected to deformation or tectonic stresses that may still be active and may have produced complex geologic structures that could serve as conduits for groundwater movement.

Faults and joints are not desirable in host rocks. The plastic behavior of most shales at moderate depths would probably seal most such fractures in the repository interval proper, but fractures in adjacent, more brittle rocks might be troublesome as pathways for circulating groundwater. Faults and joints may also cause physical discontinuities in the shale that could adversely affect subsurface excavation. On a regional basis, a few faults or joints might be acceptable if they can be located and subsequently avoided or circumvented at the actual repository site.

Containment of radioactive wastes within shales and clays depends primarily on the properties of the argillaceous strata themselves, but additional protection may be provided by adjacent strata located above and below the host rock. The presence of other thick beds of shale, salt, or other plastic rocks with low permeability would help protect the repository unit from circulating groundwater. These strata would also tend to deform without fracturing if there were subsequent structural disturbance at the site. The least desirable adjacent strata would be those containing large quantities of flowing groundwater that might enter the repository and transport radionuclides from it.

Shale Deposits as Repository Host Rocks. The geometry, physical nature, thickness, depth, and stability of any shale are critical to the long-term containment of radionuclides in a repository. Stable shales and other argillaceous strata are present in almost all major geologic provinces in much the same form as that acquired after diagenetic changes occurring relatively soon after deposition.

A repository should be placed deep enough below the present land surface to guarantee that the waste will not be exposed through erosion or denudation during its hazardous period. To negate the slow removal of the land surface through erosion, which generally proceeds at an average rate of 2.5 to 7.5 m/100,000 yr in the continental United States (Ritter, 1967), and to avoid the shallow circulation of fresh groundwater that might come into contact with the upper portions of a repository host rock, we should consider a minimum depth of at least 300 m. The rate of plastic flow in clays and shales resulting from overburden pressure increases markedly with depth; therefore the mechanical

excavation of repository space within these rocks should be restricted to depths of no more than 1500 m, and preferably less than 900 m. Thus the most feasible depth range for repositories developed in argillaceous rocks is from 300 to 900 m. In this paper, shales and clays occurring within that depth range are designated as being at moderate depth. Those occurring at lesser depths are referred to as shallow, and those found at greater depths are termed deep.

In general, any shale formation must be of sufficient vertical and lateral extent to represent an adequate impermeable barrier by itself and to assure that any fractures [artificial (from excavation) or natural] emanating from the repository will be sealed so as not to jeopardize containment. The host rock must also be extensive enough to provide for adequate heat dissipation and to permit construction of sufficiently competent pillars that will support the excavated mine rooms. A thickness of at least 75 m of shale is preferred, but a lesser thickness might be suitable under certain circumstances.

A high degree of lithologic homogeneity or consistency is desirable for shale and clay deposits considered for radioactive waste disposal. Layers or irregular masses of some non-shale rocks encountered during the excavation phase can adversely affect mining operations. Also, heat dissipation may be adversely affected if large quantities of certain impurities occur within the disposal horizon. Lateral or vertical variations in lithologic expression may also have subsurface fluids associated with them; these are to be avoided.

Seismic Activity. Areas of low seismicity are favored for repository sites. Violent earthquakes could damage surface facilities and entrance shafts to the repository and lead to severe disruption of operations. The

major seismic risk to the long-term containment of wastes would be an earthquake-induced fault that might extend into the disposal zone in the future. Although the plastic behavior of shales and clays would likely assist in closing fractures, groundwater could possibly circulate more freely in adjacent rocks along such a fault.

Hydrology. Special attention must be paid to the hydrology of any prospective waste disposal site because of the extreme importance of keeping circulating water away from the repository. A comprehensive geohydrologic study of the entire region or basin must identify recharge and discharge areas and should establish spatial relationships, interconnections, and fluid characteristics of all aquifers above and below a prospective host rock.

The mere existence of surface streams, lakes, and ponds above an otherwise acceptable repository site should not necessarily rule out its selection. Whether such surface water would interfere with the short-term operation of the disposal facility or compromise the long-term containment of any emplaced wastes is the critical issue. Prospective sites lying beneath flood plains or other areas prone to flooding are to be avoided because extreme conditions could lead to the flow of water into underground excavations through open shafts or boreholes. Surface streams can also undergo marked changes in their flow regimes during geologic time; thus future hydrologic behavior as a function of the rate of incision and shifting of the alluvial channels must be predicted to guard against breaching of the repository by erosional processes.

Any repository, regardless of rock type, must clearly be free of circulating groundwater since this represents the main threat to containment of radioactive waste placed within geo-

logic formations. The nature and characteristics of water-bearing strata near a potential disposal zone are critical elements in establishing overall suitability. Investigations need to ascertain the nature and occurrence of groundwater flow, as well as its direction, velocity, and volume. In many areas, groundwater is an important resource for man's activities; obviously special care must be taken to protect these water resources.

Mineral Resources. Important mineral deposits, such as petroleum, coal, salt, potash, or mineralized brines, are present in the subsurface of many principal sedimentary basins in the United States. These and other minerals can occur in formations overlying or underlying a prospective shale host rock, or at some locations they may be interbedded with the shale. Weighing the need for a particular repository site against the present or potential need for extracting mineral resources at that site then becomes an important evaluative exercise. As a rule, any region would be viewed more favorably for repository siting if it had little or no potential for the discovery of scarce or valuable mineral resources. Another aspect of mineral-resource investigations is the need to locate and identify all existing boreholes, mine shafts, solution cavities, and other man-made excavations in the vicinity of a proposed repository. These artificial openings represent potential migration paths for groundwater into the repository. Again, areas with fewer such man-made openings are preferred. Effective plugging and sealing of those openings present represents an essential complementary action.

Assessment of Principal Shales in the United States

Shales and other argillaceous strata are among the most common

and widespread rock types throughout the United States. Thick deposits of these rocks that warrant regional evaluation are present in 38 of the 48 conterminous states (Fig. 2). Unlike salt deposits, which tend to be confined primarily to specific geologic basins, several shale units of interest are thick and occur at moderate depth both within geologic basins and across extensive interbasin and platform regions (Fig. 3).

Geologic conditions favoring the formation of thick shale and clay units were repeated many times in various sedimentary basins and interbasin regions of the United States. As a result, thick deposits embrace a wide range of geologic time and range in age from Precambrian through Tertiary.

Principal shale units within the Eastern Interior of the United States include the Upper Ordovician shales of Ohio, Pennsylvania, and New York and the Devonian-Mississippian shales of the Appalachian, Illinois, and Michigan Basins. These widespread units are locally as much as 1000 m thick and contain illite and chlorite as their dominant clay minerals.

Triassic fault-block basins along the Eastern Margin contain thick sequences of continental strata; several of these basins have thick shale units that deserve further study.

The most significant argillaceous unit within the Gulf Coast Region is the Paleocene age Porters Creek Clay, which varies from 150 to more than 300 m in thickness and is characterized by a montmorillonitic clay mineralogy. Other units of Paleocene and Eocene age are also important and deserve further consideration.

Shales of importance found within the Great Plains include a number of Paleozoic units in the Midcontinent Region and several Cretaceous units in the northern part of the Great Plains proper. Midcontinent shales include Devonian-Mississippian black

Figure 2 Map of the United States showing the distribution of principal shales and clays by general geologic age and the regions under which each unit is discussed in this paper.

Figure 3 Map of the United States showing the location and extent of principal and selected smaller sedimentary basins.

shales, as well as thick sequences of shale interbedded with other strata of Late Mississippian, Pennsylvanian, and Permian age. Many of these shales are 75 to 150 m thick, and, locally, some units are more than 1000 m thick. Illite and chlorite are the principal clay minerals.

The northern Great Plains is underlain by the Pierre Shale and other thick shales of Cretaceous age. The Pierre Shale typically is 100 to 750 m thick, locally reaching as much as 1800 m thick, and occurs at moderate depth throughout most areas in the region. The dominant clay mineral is montmorillonite.

Basins and platforms within the Rocky Mountains Region contain several thick shales of Cretaceous and Tertiary age, and these same units are generally undeformed in the non-mountainous portions of Wyoming and adjacent states. Several thick units of Devonian-Mississippian-Pennsylvanian age are also present in structurally complex areas of Idaho.

The Colorado Plateau contains thick Cretaceous and Tertiary shales distributed within several specific geologic basins. The Mancos Shale is as much as 1800 m thick throughout the region, whereas the Green River Formation contains oil-shale units as much as 400 m thick.

The Eleana Formation and other units of Devonian and Mississippian age are exposed in block-faulted areas of the Great Basin of Nevada and Utah. Because of the structural complexity of this region, identifying any area for further study at this time is difficult.

Thick clays and shales of Cretaceous and Tertiary age also underlie the Great Valley of California. Individual units are as much as 1500 m thick, although petroleum production and interbeds of sandstone within this region detract from the apparent utility of these units.

Several thick Tertiary shales are known from small and structurally complex coastal areas of the Pacific Northwest. Ongoing seismic and volcanic activity in this region reduces the value of these shales even further.

Precambrian argillites and associated rocks are present in outcrops and in the subsurface of the northern part of the Rocky Mountains and in central Arizona. Although these units are thick in outcrops, there are few data to indicate their character and distribution throughout their subsurface extent.

Eastern Interior. The Eastern Interior Region is an extensive area characterized by nearly horizontal to gently dipping Paleozoic bedrock, broad regional structures, and a long history of tectonic stability. The Appalachian, Illinois, and Michigan Basins, which are both structural and depositional in nature, are the principal tectonic features; they are separated by intervening broad uplifts, such as the Cincinnati Arch system. With the exception of the eastern margin of the Appalachian Basin (i.e., the Valley and Ridge Province) and the Kentucky River-Rough Creek-Shawneetown fault zone, which extends westward from the east-central Appalachian Basin to the southern margin of the Illinois Basin, significant zones of structural deformation are rare. Thus there are large regional tracts where geologic structure does not appear to be a limiting factor, but more detailed studies on regional and localized joint systems appear warranted.

Seismic activity within the region has also been minimal. The Michigan Basin has had very little seismicity inside its boundaries or adjacent to it. Although portions of the Appalachian Basin, such as the trend through northern Ohio and west-central New York, have a slightly higher level of earthquake frequency, overall seismic-

ity is quite low here as well. The Charleston, SC, seismic center, although lying outside the basin proper, might extend its area of influence into the southern part if any recurring event of sufficient magnitude were generated in the future. Only the New Madrid zone, south and southwest of the Illinois Basin, represents an area of historically significant seismicity lying close to this region. Because of structural complexities as a result of faulting and the proximity of the New Madrid seismic zone, the southern part of the Illinois Basin is not considered favorable with regard to any promising shale unit.

Within the Eastern Interior Region, there is a significant development of Paleozoic strata both inside the three basins where the units are thickest and across the intervening regional uplifts. Although there are numerous shales throughout the region and throughout the overall stratigraphic column, many are too thin or too deep to be considered promising. Shales that show definite potential and can be found over large expanses in the accepted depth and thickness ranges include: (1) the Upper Ordovician Maquoketa Group, especially along the eastern margin of the Illinois Basin; (2) the Upper Ordovician Cincinnati Series and equivalent shales located eastward into eastern Ohio and Western Pennsylvania; (3) the Upper Devonian-Lower Mississippian New Albany Shale Group in the northwestern part of the Illinois Basin; (4) the Upper Devonian-Lower Mississippian Antrim-Ellsworth Shale sequence in the western half of the Michigan Basin; (5) the Lower Mississippian Coldwater Shale in the Michigan Basin, especially to the west, where the Marshall Sandstone aquifer is not present; and (6) the Upper Devonian-Lower Mississippian Upper Olentangy and Huron Shales and possibly the Middle Devonian Sonyea

Group (Cashaqua Shale), all of which occur in the north-central to northern parts of the Appalachian Basin. Other shales, such as Floyd Shale in the Black Warrior Basin, and other individual shale formations within the Devonian-Mississippian sequence may also be important, but more detailed investigations are needed to evaluate conclusively the potential of these second-priority shale units.

The production (including anticipated future recovery) of natural resources, most particularly petroleum, coal, natural gas from shales, and groundwater, represents the most likely source of conflict of use for any of these proposed shale formations. The entire Eastern Interior Region has been extensively drilled; oil and gas production exists stratigraphically above and below the shales (and in some cases within the shale-bearing interval), and future petroleum exploration is expected to add to the number of existing boreholes. For any given shale unit, however, there are regions where the level of petroleum exploration has been low, commercial successes have been few, and the potential for conflict is low. Even in these cases, studies need to be undertaken to determine borehole density, especially of wells penetrating the shale in question; locate old boreholes; and assess the undiscovered hydrocarbon resources.

Coal mining is all done at shallower depths than any of the proposed shale formations, but large tracts of land leased for future coal mining coincide with areas of promising shale units. Land availability, as well as assessment of the coal value, are resource-related questions that would have to be addressed in future studies, despite the fact that coal mining itself does not present a direct conflict.

Groundwater, although not as widely used as surface water, is nonetheless a valuable resource at

present and can be expected to become even more valuable in the future. Even though bedrock aquifers are not generally the most widely used sources of potable groundwater, there are important exceptions. The most notable is the Lower Mississippian Marshall Sandstone in the eastern part of the Michigan Basin. Because this aquifer lies in contact with Coldwater and other shales, consideration of the Coldwater Shale may have to be restricted to the western half of that basin. The relative role of certain carbonate aquifers in the eastern Illinois Basin and aquifers within the Mississippian sequence of the Appalachian Basin are other examples where aquifers may prove restrictive to a given shale even if the latter possesses the other attributes being sought here.

With regard to the Devonian-Mississippian shale sequence, and to a lesser degree to the other shales, black shales whose high carbon content clearly indicates a close association to the generation of hydrocarbons are to be avoided. Residual methane or, in the case of the eastern gas shales, commercial amounts of natural gas are problems to be avoided in the context of this report. Thus dark gray, gray, and gray-blue or green shale zones, which generally have much lower contents of organic matter, become the more favored units or parts of units to pursue.

Other resource recovery or applications of subsurface space [disposal wells, subsurface storage caverns for liquified petroleum gas (LPG)] do not appear to pose any conflicts for the shales identified because the number of examples are comparatively few and the amount of space so allocated is quite small.

One possible advantage of the two Upper Ordovician sequences is that neither contains gas-bearing shales, as is the case with the Devonian-Mississippian sequence, and the

occurrence or discovery of commercial petroleum in associated strata is somewhat less than for the younger shale intervals. Both of these Upper Ordovician units also have a very successful history of LPG-storage cavern construction and operation; this experience has clearly demonstrated the low permeability and homogeneous nature of the shales involved in these units.

Eastern Margin. As a simple definition, the region designated here as the Eastern Margin includes all the terrane east of the Appalachian Basin in the Eastern Interior. The geology across this extensive region is very diverse and embraces (1) folded and faulted Paleozoic strata of the Valley and Ridge Province (Central Folded Appalachians), (2) metasedimentary-metavolcanic rocks within the Blue Ridge Province, (3) igneous and metamorphic rocks of the Piedmont-New England trend, (4) Cretaceous and Tertiary sedimentary units, which outcrop along and underlie the Atlantic Coastal Plain, and (5) Triassic continental strata that fill fault-bounded basins developed within the crystalline Piedmont and/or the subsurface beneath Coastal Plain sediments. Although argillaceous units can be found in all these areas, interest is centered here on the Triassic basins and shallow subsurface of the Coastal Plain. Complex and widespread geologic structures rule out any shales within the Central Appalachian Fold Belt, and pronounced structural deformation and metamorphism eliminate rock units in the Blue Ridge. Igneous intrusives, complex structure, and extensive metamorphism rule out further consideration of the New England subregion and most of the central-southern Piedmont. Possible exceptions are the several low-grade metasedimentary sequences of tuffaceous argillite, siltstone, and mudstone that comprise the so-called

Carolina Slate Belt within the easternmost part of the Piedmont. Granitic plutons, some semiregional faults, folded structures, and interbedded coarse-grained sedimentary and metavolcanic rocks; however, all represent negative aspects. Even though interest in this Piedmont trend is significant with regard to metallic-mineral exploration, relatively few data on the subsurface are available.

The Triassic basins extend from northern Florida to Nova Scotia, and all are narrow, elongate structural troughs oriented northeast-southwest and filled with sedimentary strata whose continental origins included deposition in deltaic-alluvial systems, lakes, and swamps. Several of these basins show clear evidence of two normal faults as borders; others reveal a single border fault, and in still others the position of border fault(s) is concealed. Several basins are partially or completely buried by coastal plain strata; included in this category are the Florence and Dunbarton Basins in South Carolina.

There is a significant lack of meaningful subsurface data on almost all the Triassic basins that are shale bearing and large enough to be considered further. The major exception is the Dunbarton Basin, which lies beneath the Savannah River Laboratory and has been specifically explored by means of geophysics, boreholes, and hydrologic testing. Major concerns about this basin are that it is overlain by water-bearing coastal plain strata and that certain Triassic units within the basin contain pore water that is overpressured (Weaver, 1976).

The extent and homogeneity of argillaceous units in these basins are virtually impossible to establish. Faulting, dike intrusions, and joints are common in several basins, but the screening of specific areas that avoid

these geologic features is likewise not possible at this time. Some Triassic units are also sources for local groundwater; other mineral resources pose little possible conflict. Despite these limitations, four southeastern basins contain shale-claystone-siltstone intervals that might qualify after appreciable further investigation. These include the Danville-Dan River Basin in Virginia and North Carolina, Durham and Wadesboro Basins in North Carolina, and the buried Dunbarton Basin astride the Georgia-South Carolina border.

The strata that underlie the Atlantic Coastal Plain dip toward the ocean in an eastward-thickening wedge and are principally Cretaceous and Tertiary in age. Within the deep subsurface, pre-Cretaceous strata of Paleozoic and possibly Triassic-Jurassic (?) age are also present.

Because of pronounced lateral facies changes; abundant carbonate and sand aquifers, which are major groundwater sources; and the general absence of any thick clay-rich zones that are laterally persistent, the Tertiary section of the coastal plain is not promising. Although some clay-rich zones of sufficient thickness occur at moderate depth within the Cretaceous section of eastern Maryland and North Carolina, these are marginal candidates. Silt and sand interbeds are also known to occur; the actual vertical expression of the clay horizons is toward the lower end of the thickness range, and groundwater aquifers lie above the clay units. Both clay zones lie below 450 m, and the expectation is strong that rock-mechanical problems would be experienced in these less-than-fully-indurated sediments at these depths.

Thus, although the Atlantic Coastal Plain contains an extensive and fairly thick stratigraphic sequence and a few clay-rich zones with some attractive features can be located, the

overall potential of argillaceous units in this province is poor. The best possibilities within the Eastern Margin Region appear to be certain shales and claystones within several Triassic fault basins, but so much more data are needed that any definitive statement on the real potential of these Triassic strata cannot be made at this time.

Gulf Coast. The Gulf Coast Region extends from the Mexican border across Texas, Louisiana, and Mississippi into southern Alabama and northwestern Florida. Its stratigraphic units, dominated throughout this extent by clastic lithologies, interfinger with sequences that become progressively more carbonate rich along the transitional area with the Atlantic Coastal Plain. Within the Texas-Louisiana portion of this region, the Cenozoic section is very well developed and thick, reaching an overall thickness of more than 9000 m along near-offshore Louisiana. The northward extension of this Tertiary-dominated stratigraphic succession to either side of the Mississippi River is known as the Mississippi Embayment. Older Cretaceous and Jurassic strata underlie the Tertiary sequences and extend gulfward from outcrop areas along the northern margin to depths of more than 7000 m in southern Louisiana. In fact, the general regional trend is for the entire stratigraphic wedge to thicken and dip toward the Gulf of Mexico. Localized reversals in dips are the result of regional domal features, such as the Sabine and Monroe Uplifts; regional and localized zones of faulting; and geologic structures caused by the flowage of deeper rock salt. The most significant of the salt structures are the several hundred salt domes (diapirs) that occur in five sub-basins across the region. Also important are various low-relief folds where the plastic salt

has not actually penetrated the overlying strata. Faulting is known from several regional zones that fringe the entire Gulf Coast Basin, from major down-to-the-basin systems, and in association with the other structural elements cited, especially salt domes.

Seismicity within the Gulf Coast Region is especially low; earthquake events are neither abundant nor of significant magnitude. Thus the region can be assigned to the two zones of lowest seismic risk. The only exception to this favorable seismic picture is the proximity along the northern border of the Mississippi Embayment of the New Madrid seismotectonic zone. Several large earthquakes centered in this area have been destructive throughout the northern embayment, and the felt areas of a few major quakes have extended far to the south. Nevertheless, much of the Gulf Coast Region known to contain thick clays does not appear to be greatly jeopardized by the seismic zone in the central United States.

The Cenozoic sedimentary record in this region is characterized by the regional influence of numerous large-scale deltaic systems. These have produced complex wedge-shaped deposits with pronounced changes in grain size and lithologies; lateral facies changes are, thus, very common. In contrast, several marine clays are fairly uniform and traceable for several hundred kilometers without appreciable variation. The most important of these persistent units from our point of view are the Porters Creek and Yazoo Clays; also of some interest are the Cane River and Cook Mountain Formations, where they are principally carbonaceous clays.

The Porters Creek Clay is the thickest and oldest of these Tertiary marine argillaceous units. Electric-log analysis shows that the unit within

the subsurface is consistently rich in clay and relatively free of silt and sand zones. The younger clays are less extensive and thinner, tend to be less compacted, and have a higher content of pore water. These younger clays are also more likely to be in direct contact with freshwater aquifers. Except for the Yazoo Clay, the Cane River and Cook Mountain Formations also tend to contain permeable silts and sands within their extents in the subsurface.

In all cases, the most favorable areas from a structural geology standpoint are in the central portion of the Mississippi Embayment and along the southern flank of the Sabine Uplift. Other areas generally coincide with complex geology imposed by regional fault systems and salt domes. Throughout much of these tectonically suitable areas, the Porters Creek Clay is more than 150 m thick at moderate depth. In parts of northern Louisiana and eastern Arkansas the unit thins slightly, but it is still more than 100 m thick at depths from 300 to 900 m. Throughout an east-west belt across the embayment and into Texas, the Yazoo Clay ranges from 75 to 300 m thick at depths less than 900 m. Not all of that thickness range represents pure clay, however; the unit contains some sand lenses. Clay intervals in the Cane River Formation across the embayment reach 120 m in thickness, and those within the Cook Mountain vary from 120 to 150 m in northeastern Texas.

On the basis of limited data on physical properties, the Porters Creek Clay, as the most lithologically uniform, most compacted, and least porous permeable clay horizon, appears to offer the most potential. Smectite (montmorillonite) clays dominate its clay mineralogy, however, and little is known about its rock-mechanical properties at the depths being considered.

Although the direct use (for nonmetallic purposes) of any of these four clays is limited to small surface mines that pose no resource conflict, the development of groundwater and petroleum resources clearly present possible conflicts. Also related is the density and nature of the numerous boreholes that reach and/or penetrate these units.

Each of these Tertiary clays that are deep and thick enough to be acceptable lies below important groundwater aquifers either currently used or potentially useable in the future. Although the few published accounts report that hydraulic conductivity values are low, much more data are needed to assure the impermeability of these clays and to ascertain whether heat or thermal differences might induce groundwater flow into these clays from the nearby aquifers.

Drilling for hydrocarbons has produced numerous boreholes that penetrate these clays to reach deeper exploration targets or develop commercial fields. Central Louisiana, central Arkansas, and northern Mississippi are three areas where the production of hydrocarbons is minimal, but where some numbers of exploratory boreholes have been drilled.

On the basis of regional geology, mineral resource development, thickness and depth factors, lithologic continuity, and the general absence of complicating geologic structures, the northern part of Louisiana and Mississippi and adjacent southern to eastern Arkansas appears to be the primary area in which further detailed evaluation ought to be conducted. The Porters Creek Clay throughout this semiregional trend appears also to be the most promising unit, and the Yazoo Clay slightly further to the south also exhibits some potential. Although the Cane River and Cook Mountain Formations are less attractive, there may be small

areas throughout this trend and into northeastern Texas where more specific investigations would demonstrate some level of promise.

Great Plains. Since the Great Plains is a vast region with diverse geology, evaluations of its suitability for the disposal of radioactive waste must be somewhat more generalized. Thick marine shales of interest are mainly late Paleozoic in age within the Midcontinent and adjacent portions, whereas those within the northern part of the Great Plains are Cretaceous. These shales are thick and extensive and lie at moderate depths in various parts of the region. They warrant further study for waste disposal.

The Great Plains Region is part of the stable cratonic interior east of the Rocky Mountains and has been generally tectonically stable since Pennsylvanian time. Most tectonic movements have been broad epeirogenic upwarps or downwarps. Seismic activity is generally low; almost all parts of the region are in seismic risk zone 1, the principal exception being the small area of seismic risk zone 2 along the Nemaha Uplift in Oklahoma, Kansas, and Nebraska. Most lands within the Great Plains are sparsely populated and are used mainly for agriculture and pasture.

A significant number of major groundwater aquifers underlie large portions of the Great Plains, serving as an important water supply for municipal, irrigation, industrial, and domestic purposes. Because of the sparse rainfall and runoff in most parts of the region, the surface-water supply is somewhat limited. Therefore the potential impact of repository siting on the local groundwater supply must be fully evaluated.

Petroleum is the major mineral resource that might compete with repository siting in the Great Plains.

Large areas within the region are major petroleum provinces, particularly in the Midcontinent and Permian Basin. Oil and/or gas are being produced and actively explored for within and around such important petroleum provinces as the Williston, Powder River, Denver, Anadarko, Arkoma, Ardmore, Fort Worth, Delaware, and Midland Basins. Petroleum exploration and production also are important on and near some of the arches and uplifts, e.g., Sweetgrass, Bearpaw, Central Kansas, Nemaha, Las Animas, Wichita-Amarillo, Bend, and Concho positive features.

The Permian Basin, including the Palo Duro and Dalhart Basins on the north, contains several thick shale units, but in most places they are more than 900 m deep and are in areas characterized as major petroleum provinces. The Woodford and Barnett Shales are more than 75 m thick in different areas but in all such cases are more than 900 m deep. Where the Woodford Shale is locally thick and at moderate depth, the unit is complexly folded. Missourian and Virgilian shales range from 75 to 300 m thick in the Permian Basin but generally are more than 900 m deep. Thick Missourian shales do occur, however, 400 to 1200 m below the surface in parts of the Eastern Shelf. Permian shales are more than 75 m thick in parts of the Val Verde Basin in the southeast and along the Eastern Shelf, but typically these shales are more than 900 m deep. Because the Permian Basin is important as a major petroleum province, a full assessment of the local petroleum potential will be needed before any shale in this basin can be considered for radioactive waste disposal.

The Fort Worth Basin of north central Texas contains several thick Pennsylvanian shales at moderate depths. Shale units in the Atokan, Desmoinesian, Missourian, and Virgilian Series are locally 75 to 600 m

thick and occur at depths of 300 to 900 m, chiefly in the northern part of the basin. Large quantities of oil and gas are found in the basin, especially in the northern part. Further study is needed to resolve the potential conflict between mineral resources and waste disposal involving any of the shales in this area.

Several basins of Oklahoma and Arkansas contain the thickest Paleozoic shale units within the Great Plains Region, but because of the structural complexity throughout much of this area and the importance of present and future oil and gas production, these shales appear to have little potential for the disposal of radioactive wastes. Thick shale intervals are present in the Woodford Shale and Upper Mississippian units, along with each of the series of Pennsylvanian and Permian age. In most areas where Woodford Shale is 75 to 200 m thick, the unit is structurally complex, fractured, cherty, and either less than 300 m deep or more than 900 m deep. Areas where the unit is found within acceptable depths are narrow and usually structurally complex. Upper Mississippian units, such as the Delaware Creek and Goddard Shales, are 100 to 1200 m thick, but they are more than 900 m deep in most basins of the area or are shallow and in structurally complex portions of the Southern Oklahoma Folded Belt, where the units typically are fractured and jointed.

Pennsylvanian shales in the basins of Oklahoma and Arkansas include Morrowan units that are 100 to 1800 m thick, typically more than 900 m deep and mainly present in the Southern Oklahoma Folded Belt. Atokan shales vary from 90 to more than 500 m thick in many areas and are found at depths from 300 to 900 m locally within the Arkoma Basin of Oklahoma and Arkansas. Desmoinesian shales, ranging from 75 to 300 m

in thickness, are present at depths of 300 to 900 m in the shelf areas of the Anadarko and Arkoma Basins and locally in other basins of southern Oklahoma. Missourian shale units up to 300 m thick extend to depths of 100 to 2000 m from central Oklahoma into the Anadarko Basin and reach a thickness of 910 m in parts of the Ardmore and Marietta Basins. Virgilian shales are more than 75 m thick and occur locally at moderate depths in central and western Oklahoma, but, in most parts of the area, the shales are more than 900 m deep. In western Oklahoma, Permian shales are 75 to 1000 m thick and range in depth from about 100 to 900 m; however, these argillaceous units are typically interbedded with such other rocks as sandstones, siltstones, and evaporites.

The Salina and Forest City Basins contain several thick shale units at moderate depths. The Chattanooga Shale is 60 to 85 m thick at depths of 600 to 850 m in the western part of the Forest City Basin. Although it is thicker farther east in Iowa, the Chattanooga Shale is generally less than 300 m deep. Pennsylvanian shales of the Atokan and Desmoinesian Series are more than 75 m thick and are at depths of 300 to 900 m in parts of both basins. Shales in the Virgilian Series are as much as 350 m thick in the Forest City Basin but typically are less than 300 m deep. Petroleum is being produced from the southern and western portions of both these basins, but thick shales in other parts of either basin may possibly be locally amenable to waste disposal without significant conflict with geohydrology or non-petroleum mineral development.

Central and western Kansas contains a number of scattered small areas where Desmoinesian, Missourian, and Virgilian shales are more than 75 m thick at depths of 300 to 900 m. Thick Permian shale units are more widespread within this area, occur at moderate depth, and extend

into parts of southeastern Colorado. Important oil and gas production is widespread in central and western Kansas but is minimal in southeastern Colorado. There may be areas in northwestern Kansas or southeastern Colorado where groundwater resources and/or non-petroleum mineral development would not serve as conflicts with the use of thick shales for waste disposal.

The Pierre Shale and other argillaceous units of Cretaceous age are of major importance as potential host rocks for waste disposal in the northern part of the Great Plains. Areas underlain by Cretaceous shales are characterized by simple structure with little deformation. The few faults, flexures, and folds are widely scattered, and there are vast areas that are structurally undisturbed.

The Pierre Shale is 100 to 1800 m thick in the northern Great Plains, and, throughout most parts of the region, it is typically 100 to 750 m thick and 300 to 900 m below the land surface and lacks borehole penetrations. Thus, this formation definitely warrants further study. These areas embrace substantial parts of the western halves of Nebraska, South Dakota, and North Dakota; portions of northeastern Colorado and southeastern Wyoming; and large portions of Montana.

Other Cretaceous shales are also thick and at moderate depths in parts of the central and northern Great Plains. Lower Cretaceous shales, such as the Skull Creek, Kiowa, and Mowry Shales, warrant additional investigation throughout northwestern Kansas, western Nebraska, northwestern South Dakota, central North Dakota, and scattered areas in Montana. The Upper Cretaceous Colorado Shale (locally termed the Belle Fourche, Carlile, and Marias River Shales) is also worthy of further study in northwestern Nebraska, central and

western South Dakota, central North Dakota, and much of Montana.

The Pierre Shale and other Cretaceous shales typically have mixed-layer illite-montmorillonite and montmorillonite as their dominant clay minerals, but they also contain interbeds of volcanic ash and bentonite. The Upper Cretaceous shale sequence furthermore contains some sandstone interbeds, mainly to the west, and they disrupt the homogeneity of these thick shales and should be avoided. Other discontinuities include joints and fractures, which are mainly concentrated in the weathered zone at and near the outcrop.

Although groundwater is locally present in these sandstone interbeds and weathered zones of the Pierre and other Cretaceous shales, the water is typically present only at and near the land surface and should not interfere with development of a disposal facility at greater depths. Other aquifers are present in the overlying Tertiary, Pleistocene, and Holocene sequences, as well as in underlying units of Late Cambrian through Cretaceous age. These aquifers must be investigated in greater detail to establish the geohydrology of any potential site.

Excavation of the Pierre Shale can lead to swelling and deterioration of the shale if the rock is not protected from alternate drying and wetting cycles. Both instantaneous and long-term rebound occur as a result of excavation, but the expansion or rebound of unweathered shale can be minimized by maintaining a high humidity in the underground openings. Experience has shown that tunnel-boring machines would be effective in underground mining of the Pierre Shale.

The Pierre Shale and other Cretaceous shales are relatively free of conflicting land use for development of mineral resources. Major petroleum provinces in the region include the

Denver, Powder River, and Williston Basins, along with portions of northwestern Kansas and southwestern Nebraska and the Bowdoin, Bearpaw, Sweetgrass, and Central Montana uplifts of Montana. Petroleum is being produced chiefly from rock units within or below the Cretaceous System, although locally there is production from overlying Upper Cretaceous and Tertiary sandstone reservoirs. Potential disposal sites within these provinces will have to be evaluated carefully to avoid areas with numerous boreholes and to avoid conflict with present and future production of hydrocarbon resources.

Coal seams stratigraphically above and below the Pierre and other Cretaceous shales are important energy resources that have been or may be recovered locally by strip mining. Development of this resource or of sand and gravel, stone, bentonite, or other surface-mined minerals, should have little effect on selecting a potential waste disposal site.

Rocky Mountains. Several aspects of the Rocky Mountains are generally favorable for the disposal of radioactive wastes, but a number of other characteristics greatly restrict areas that might eventually qualify. Favorable aspects of the region include the (1) presence of thick shales, mainly of Cretaceous and Tertiary age, over fairly large expanses, (2) low seismicity throughout, with most areas being assigned to seismic risk zone 1, (3) sparse population in most parts, and (4) ownership and/or administration of large tracts of land by the federal government.

Adverse aspects in many parts of the Rocky Mountain region that are underlain by thick shales include (1) structurally complex geology, including folds, faults, thrust faults, and fractured rock, mainly along the margins of the basins where the shales commonly are at shallow to

moderate depths, (2) sedimentary structural basins that are structurally simple principally in their central areas where the thick shales typically are more than 1000 m deep, (3) poor knowledge of the geohydrology of most basins, (4) extensive and large deposits of energy and other mineral resources that are extremely important to the nation's future, particularly such resources as petroleum, uranium, coal, oil shale, trona, and bentonite, (5) common occurrence of bentonite and montmorillonite, particularly in the Cretaceous shales (these clay minerals typically contain interlayer water that might be released upon heating); and (6) soft and plastic shales (little is known about their physical behavior when mined underground). The only underground storage cavern in the region was constructed in strong yet brittle and fractured Upper Cretaceous shale at a depth of 130 to 136 m. Although it withstood the stress of construction, it had to be abandoned because of a significant inflow of water and failure to pass the final air-pressure testing.

Despite these several generally unfavorable characteristics for many parts of the Rocky Mountain Region, several local shale units deserve further examination to better assess their potential for waste disposal. Lower and Upper Cretaceous shales may be at suitable depths and have little structural complication within certain areas around the margins of the Big Horn or Wind River Basins. The Upper Cretaceous Cody Shale is quite thick and lies at moderate depths over a large part of the Casper Arch, and the Lewis and Steele Shales appear to be moderately thick and at appropriate depths in parts of the Laramie and Hanna Basins and along the eastern side of the Great Divide and Washakie Basins. The Upper Cretaceous Baxter Shale also is quite thick and is found at moderate depths on and near the Rock Springs Uplift.

A Tertiary shale deserving more study is the Waltman Shale in the central and southern parts of the Wind River Basin. This unit will be of particular interest if it is at least 75 m thick in the southwest, where it rises out of the deep basin to depths as shallow as 900 m. Further study should also be made of the Green River shale, especially around the perimeter of the Green River Basin and in the Washakie Basin, where the formation contains little or no oil shale and is geographically removed from important trona deposits.

The Milligen Formation and Copper Basin Group of Idaho appear to be too complex structurally to warrant further study at this time. Other shales that have been considered in the Rocky Mountain region are generally at great depths within the central parts of the various basins or are structurally disturbed where they are at moderate depths along the margins of the basins.

Colorado Plateau. The Colorado Plateau is a tectonically stable region with several sedimentary and structural basins containing thick sequences of Upper Cretaceous and Tertiary shales that are flat lying to gently folded and at moderate depths over fairly large areas. In particular, the Upper Cretaceous Mancos Shale, which is a thick, blanket-like marine shale extending over the entire Colorado Plateau, warrants additional consideration as a shale that may locally be suitable for disposal of radioactive wastes.

Basins containing thick shales are the Uinta, Piceance, Henry, Kaiparowits, Black Mesa, and San Juan, which are all characterized by arid to semiarid climate. The quality and quantity of groundwater in each basin is not well understood, but water is known to occur in sandstone aquifers that commonly overlie and/or underlie the shales. Thus a study of

geohydrology is an important part of any further examination of shales in this region. Current and future development of major energy resources is also especially important in the Uinta, Piceance, and San Juan Basins, but the potential for developing significant mineral deposits is much less in the Henry, Kaiparowits, and Black Mesa Basins.

The Uinta and Piceance Basins contain thick shales of both Cretaceous and Tertiary age. The Mancos Shale is typically 1200 to 1800 m thick in both basins, and thick sections of this formation are present at depths from 300 to 900 m in a wide, undisturbed belt about 500 km long along the southern side of both basins. To the west, the Mancos Shale is divided by sandstone interbeds into Tununk, Blue Gate, and Masuk Shales, which collectively range in thickness from 100 to 600 m. On the northern and eastern sides of the basins the strata dip rather steeply into the basins, thereby limiting the Mancos Shale at moderate depths to a relatively narrow belt. In most other parts of these basins, the Mancos is too deep, from 1000 to 6000 m below the surface.

Tertiary shales in the Uinta and Piceance Basins belong to the Green River Formation and include so-called oil shales, which are actually marlstones rich in kerogen. Individual members of the Green River Formation typically are 100 to 400 m thick, and most of them contain shale, marlstone, or oil-shale units that are locally more than 75 m thick. The depth to the top of the Green River Formation is commonly from 150 to 1000 m in the Uinta Basin but only from 150 to 400 m in the Piceance Basin. The strata are generally flat-lying, and faulting is a very localized phenomenon. There are, however, well-developed sets of fractures in both basins; these small-scale structures locally are filled with solid hydrocarbons (gilsonite) or serve as

potential pathways for meteoric water to migrate into the subsurface.

Mineral resources of the Uinta and Piceance Basins are important, and their present and future development may conflict with the use of either the Mancos or Green River Shales for radioactive waste disposal. Both basins are major petroleum provinces, with production coming mainly from strata of Pennsylvanian, Cretaceous, and Tertiary age. The Green River formation in both basins also contains the major oil-shale reserves of the United States, and the formation in the Piceance Basin contains potentially valuable deposits of nahcolite and dawsonite. Coal, asphaltite, tar sands, and other mineral resources are also important in various parts of both basins, but their development should not conflict with waste disposal.

The Henry Basin is tectonically stable but has a sharp flexure along its western margin, and Tertiary intrusive rocks occur on its eastern flank. The basin is located near the boundary of seismic risk zones 1 and 2. The Tununk, Blue Gate, and Masuk Shales are 150 to 450 m thick; in the central part of the basin these shales are flat-lying and undisturbed at depths of 300 to 900 m. Important coal deposits are found here, but mining of these coals or of the bentonite and other identified mineral deposits should not conflict with the use of these shales for waste disposal.

Petroleum has not been discovered in the basin.

The Kaiparowits Basin contains 150 to 300 m of the Tropic Shale (equivalent to the lower part of the Mancos Shale) at depths of 300 to 900 m. The formation typically displays gentle dips, consistent with the simple structure of the basin, which consists of broad folds and several sharp monoclines. The basin falls within seismic-risk zone 2. Coal resources are also locally important in this basin,

but mining coal or other known mineral resources should not pose any conflict. Oil has been produced, but only from a small area, and the basin is not regarded as an important petroleum province.

A single shale unit, the Tununk Shale, reaches a thickness of 120 to 210 m within the Black Mesa Basin. In most parts of the basin the shale is less than 300 m below the land surface, but in some areas the lower half of the shale is 300 to 450 m below the surface. Strata in the basin are nearly flat-lying amid a few gentle folds. The basin lies near the boundary of seismic-risk zones 1 and 2. Coal deposits are locally important in the basin, but, again, development of coal or other mineral resources in the area should not interfere with the possible disposal use of the Tununk Shale. Petroleum has not been discovered in the basin.

The San Juan Basin contains several thick, relatively undisturbed Upper Cretaceous shales at moderate depths. The Mancos Shale is up to 600 m thick and from 300 to 900 m deep in the southern and western parts of the basin, and the Lewis Shale is from 180 to 250 m thick and from 700 to 900 m deep throughout the central and north-central parts of the basin. In the north-central part, the Kirtland Shale is 100 to 450 m thick, divided by a medial sandstone, at depths of 300 to 900 m. The San Juan Basin is a major petroleum province, with most of the production coming from the northern half. Past, present, and future exploration for petroleum in and around the basin represents a possible conflict with the use of any of these Cretaceous shales for waste disposal. Coal, uranium, and other minerals also are locally important within the basin, but their continued development is not seen as a similar conflict.

Great Basin of Nevada and Utah. Several of the shales and

argillites in the Great Basin are thick enough and extensive enough to be of interest for radioactive waste disposal, but the structural complexity of the region in general and of the mountain ranges containing these shales in particular greatly reduce the likelihood that a favorable recommendation can be made at this time. Uplift, folding, and thrust faulting during late Paleozoic, Mesozoic, and Cenozoic time have segmented the originally continuous blankets of shale into a series of fault-bounded blocks wherein lateral continuity of an undisturbed mass cannot be assured.

The Eleana Formation is the best known of the argillaceous units in the region because of extensive and ongoing studies by the Department of Energy and the USGS on the geology and hydrology at the Nevada Test Site. Although data on the thickness, mineralogy, and hydrology of the Eleana Formation show it to have favorable potential for waste disposal, the structural complexity of the unit in the areas where it has been examined is not encouraging. The argillite-shale sequence has been folded, thrust faulted, and fractured in most areas, and localized volcanic activity has further complicated this complex setting.

The Pilot and Chainman Shales are the most widespread of the argillaceous units in the Great Basin, extending over most of eastern Nevada and nearby parts of Utah. These shales are exposed in many of the elongate mountain ranges, but almost no subsurface data are available on them within these mountains or where they are deeply buried in the intermontane basins.

Available data on the groundwater as it relates to any of these shales are limited, and much more investigation would be needed if any area were to receive serious consideration for waste disposal.

Principal mineral resources of the region are gold, silver, lead, zinc, copper, and other metallic and nonmetallic materials. Petroleum has been discovered at only a few places.

Although the regional structural complexity detracts from the value of areas studied to date, more detailed investigations might identify other areas where these potentially promising shales are not so disturbed structurally.

Great Valley of California. The Great Valley of California contains a number of thick Cretaceous and Tertiary shales and clays at moderate depths, but certain geologic, seismic, and human activities of the region reduce the value of these rock units as potential hosts for subsurface waste disposal. Individual shales range from 75 m to as much as 1500 m thick in areas where the top of the shale unit is 300 to 900 m below the land surface.

Within the central part of the Sacramento Basin the Cretaceous Forbes Formation consists of 600 to 1200 m of argillaceous strata at moderate depths. Throughout most of the basin, the Eocene Capay Shale is 90 to 360 m thick. Other shales that are sufficiently thick in this northern basin are also Eocene in age; these include the Nortonville Shale, Markley Formation, and several thick units that represent fillings of buried alluvial gorges.

Within the San Joaquin Basin to the south, all the thick shales are Tertiary in age, but the areas where they occur at moderate depths are largely limited to Kern and Fresno Counties in the southern part of the basin. Included here are the following shales: Kreyenhagen of Eocene age; Media (Freeman), Antelope, McClure, and Reef Ridge of Miocene age; and Etche-goïn and San Joaquin of Pliocene age.

The Great Valley Region has undergone four major tectonic

episodes since the Late Cretaceous, and the most intense of these occurred in the mid Pleistocene. Because all the marine shales considered here are older, they have been affected by a large number of faults and folds, mainly along the western margins of the Great Valley, but also in the central parts of the Sacramento and San Joaquin Basins. Tectonic activity remains active within these basins, as demonstrated by seismotectonic movement along the White Wolf Fault as recently as 1952. All of the Great Valley is assigned to either seismic-risk zone 2 or 3, a designation resulting from the many large, historical earthquakes that have occurred adjacent to this region.

The Great Valley is also a major petroleum province, and this further detracts from the value of the shales here. Natural gas is being produced from many fields throughout most of the Sacramento Basin and from some fields in the San Joaquin Basin. In contrast, crude oil production is virtually limited to the southern part of the San Joaquin Basin, where most activity occurs in Kern, Fresno, Kings, and Tulare counties.

Groundwater is another resource in the Great Valley that constitutes a potential conflict to the use of shales for waste repositories. Water is critical to the continued growth of the region, and aquifers are heavily relied on to supply this resource, especially in the San Joaquin Valley.

Although a number of thick shales are present at moderate depths throughout the Great Valley, their value as host rocks for radioactive waste is greatly reduced in most areas because of seismic activity, structural complexity, petroleum exploration and production, and appreciable use of groundwater. Some areas where these constraints are at a minimum could probably be found through additional, detailed studies.

Pacific Northwest. Several Tertiary shales and argillaceous units are thick along localized coastal areas within the Pacific Northwest, but a number of adverse features limit the potential of these rock units. The areas underlain by these thick shales are typically long narrow strips along the coast, where the strata dip seaward beneath the Pacific Ocean or the Strait of Juan de Fuca. Knowledge of the shales is based on outcrop information only; there are few data on the subsurface character and distribution of the shales.

Many areas underlain by thick Tertiary shales are structurally complex, with the shale units being folded and faulted and dipping as much as 85° in some places. The region is characterized by a high level of seismicity, with much of the region being in seismic-risk zones 2 and 3. This seismicity and historically recorded vulcanism indicates that the Pacific Northwest is still tectonically active. Thus the shales of this region have little potential as horizons for the disposal of radioactive waste and should be given no further serious consideration.

Precambrian Argillites. Some of the Precambrian (Y-age) Belt Series within the northern Rocky Mountains Region appears to exhibit some potential for further consideration. Several stratigraphic units contain appreciable thicknesses of argillite or related, slightly metamorphosed argillaceous strata and are of interest despite large expanses underlain by each sequence where unfavorable conditions are present. Portions of the Belt Series that have experienced a higher level of metamorphism (greater than greenschist grade), are within belts of high seismic risk (zone 3), and/or are affected by major regional tectonic features are excluded. The area where Belt strata appear promising lies north and east

of the Purcell Anticlinorium and west of the Montana Disturbed Belt in the northeastern part of the Series' outcrop belt.

Several formations contain substantial thicknesses of argillite, but subsurface data on these units are inadequate to characterize their physical distribution fully. Measured outcrop thicknesses indicate that both the Ravalli and Missoula Groups contain thick argillaceous strata. The Burke and Spokane Formations contain more than 1000 m of argillite along the eastern part of this more favorable region. Toward the west, the argillites of the Burke Formation even increase in thickness. The subsurface depths of these strata cannot be determined from the available data, however.

Within this same region, the younger Missoula Group, especially in the Snowlip and Shepard Formations, contains nearly 2000 m of predominantly argillaceous strata. Again, data are insufficient to characterize these units fully in terms of their depth distribution.

Although the Prichard Formation, especially its upper part, is reported to contain thick argillites, data from areas to the west show that these units would be too highly metamorphosed in this eastern region.

Because potentially commercial copper mineralization has been found in the Revett Formation (which is equivalent to the Upper Burke Formation), the possibility exists that this mineral resource extends eastward within strata of the Burke Formation. This possible conflict needs more study; likewise, more subsurface data are needed for the several argillite-containing intervals.

Within central Arizona, the Pioneer Shale of the Apache Group is more than 150 m thick, and at least the upper half of this unit is argillite. Contact metamorphic effects to the Pioneer Shale from abundant diabasic

intrusives and regional faulting complicate the geology in this part of the Southern Basin and Range province. Few data are available on the subsurface depth relationships of the Pioneer Shale; thus detailed exploration is needed to exclude areas affected by these igneous-structural complications. The Pioneer Shale is regionally extensive and sufficiently thick, and detailed investigations might identify small areas that would lack complex geology.

Knowledge of the shale-rich strata found in the region of the Grand Canyon is largely restricted to this nationally famous feature. Several units dominated by argillaceous strata collectively reach a thickness approaching 1300 m. The Galeros and Kwagunt Formations of the Chuar Group and the Hakati Shale of the Unkar Group represent the principal shale-bearing stratigraphic units. Data on the lithologic character and thickness-depth relationships of these shale units extending northward beneath the Colorado Plateau are very limited, however. At the Grand Canyon itself, the top of the Precambrian sequence lies at a depth of more than 1000 m. If this shale-bearing sequence does occur within the subsurface at moderate depths away from the Grand Canyon, exact locations and regional extent are not known at the present time.

Thus, although Precambrian strata in Arizona contain thick to very thick units of shale and/or argillite, the Pioneer Shale of central Arizona is plagued by complex geology, and units known mainly from the Grand Canyon region are too deep. Also, little is known about their characteristics away from the Grand Canyon.

On the basis of very limited data, the argillite-rich units of the Belt Series, especially the Missoula Group, appear to be the only Precambrian supracrustal sequence deserving additional study. Similar strata in Arizona

show promise but would require so much additional study that pursuit of these units is not recommended. Other argillite-bearing Precambrian sequences, mainly from scattered outcrops throughout the western United States and from eastern Tennessee, have been eliminated because they are either too highly metamorphosed or very severely deformed structurally, or both.

Summary and Conclusions

On the basis of the data available and because of the summary nature of this paper, we make no effort to rank the promising shale and clay units discussed here. Because of the large number of argillaceous formations considered and the sizeable subsurface extent of many with acceptable depth, thickness, and physical property limits, this assessment clearly has had to emphasize the regional aspects of these units. No shale or clay cited as having potential can be viewed as a nominee for site consideration; any that is to be pursued further will require additional regional and detailed areal study before even smaller study areas can be designated. No effort has been made to incorporate nontechnical factors; these surely would have to be factored into the decision process when certain rock units are being chosen for continuing investigation.

Because water is such a pivotal factor in safeguarding the retention of radionuclides within a repository and because the protection of fresh groundwater is a concern commonly expressed anytime subsurface activities are planned near aquifers, areas containing promising shales but in close association with freshwater aquifers may require a more restrictive approach. Probably the most noteworthy examples would be the Porters Creek and Yazoo Clays in the Gulf Coast Region. Similarly,

portions of the Pierre and Coldwater Shales have important aquifers near where these shales are thick and at moderate depth over large areas. Although the presence of such aquifers does not preclude further consideration of any shale or clay unit, it does tend to lower the potential of such argillaceous strata on a local basis because of the concerns related to groundwater.

Surveys of groundwater hydrology indicate that there are several geotechnical areas where data about argillaceous rocks are meager to nonexistent. To a degree, this situation was created by the fact that shales and clays within the subsurface are generally not the focus of attention in any drilling or exploration program. Neither are they typically tested for their hydrologic properties. Therefore very little information is available on hydraulic conductivities in clay-rich rocks; it is a property whose measurement is more aligned to porous-permeable rocks, such as aquifers. More hydrologic testing needs to be conducted on shales and clays, not only to gather reliable geotechnical data but also to establish that such units can or would act as impermeable intervals as is commonly perceived. Properties such as vertical vs. lateral hydraulic conductivity should be specifically measured. The impact of differential heads between deeper and shallower aquifers flanking any candidate shale or clay, the effects of thermal gradients on the groundwater regime relative to these impermeable units, the nature of osmotic pressures on these rocks, and the passage of fluids through them also need study and evaluation.

More information is also needed in the area of rock-mechanical properties. This is especially necessary for argillaceous units because, historically, rock-mechanical testing has not been conducted at depths of 300 to 900 m except for certain deep mines

where shales form the back. The thermal-mechanical response of clay-rich strata to in situ heater testing needs also to be analyzed, especially at depths greater than those in tests to date.

Ion-exchange capacities of clay minerals in soils and as pure mineral separates are well established. The capacity of indurated shales and clays in place, vis-à-vis their adsorption capability, has not been widely pursued as a research topic, but it should be. Other than studies about the swelling and heaving nature of bentonite-rich materials, little has been done on equating various physical properties in shales and clays and specific clay-mineral assemblages or compositions. Ion-exchange capacity, preferential absorption of elements, especially radioisotopes, and the effect on clay-rich rocks of wetting-drying cycles, such as might be imposed from subsurface excavations, all require additional study relative to the actual clay mineralogy present.

Although several shales appear to offer promise, a major point that cannot be overemphasized is that relatively little is known about shales and clays in the geotechnical subject areas that are most important in making decisions about radioactive waste disposal in these rocks. We must again underscore the fact that no study areas and certainly no sites are suggested in this paper. A very considerable amount of data was investigated, but, because a strongly regional focus was necessary even to approximate assimilating that much information, no individual shale is being recommended more highly than any other. This paper has not answered the basic question of whether shales and clays truly represent acceptable host media for high-level radioactive wastes. More detailed field, laboratory, and subsurface investigations are necessary. This paper's major contribution has been to narrow the choices

of units and areas to large regions where it would be prudent and technically sensible to concentrate future work.

If any argillaceous rock is to ever house a subsurface waste repository in the United States, much additional investigation of this group of rocks in general and in particular of some of the regionally screened units discussed must be undertaken. We feel that some level of ongoing investigation of these abundant and widespread rocks is definitely warranted.

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The Use of Radiogenic Noble Gases for Dating Groundwater

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The accumulation in groundwater of products from the radioactive decay of elements naturally found in rocks offers a potential for measuring the time that the groundwater has been in contact with the rock. This method of dating groundwater has an advantage over using decay products from atmospheric radionuclides in that the amount of decay product becomes greater with increasing age rather than less. Different decay products accumulate at different rates, however, and, thus, have a different potential usefulness in age determinations.

The most useful decay product is helium, which is produced from uranium and thorium. The use of argon-40 produced from potassium is limited because it is abundant in meteoric water. Neon, xenon, and krypton can be used, but only with great difficulty because they are produced in extremely small quantities. In general, the potential for error increases when a long time is required to produce a small quantity of the dating nuclide.

An example is given of the use of helium dissolved in groundwater to obtain an age of 840,000 yr for water in crystalline metamorphic rock beneath the Savannah River Plant near Aiken, SC. Combined with other information, this water age can be used to measure the hydraulic conductivity of a large mass of rock (tens of kilometers in length). The hydraulic conductivity

so calculated compares favorably with that obtained from hydraulic tests.

Introduction

Any study of the subsurface to demonstrate the safety and feasibility of storing radioactive waste in the geologic environment must include investigations in many subject areas, e.g., rock properties, structural geology, hydrogeology, geochemistry, seismicity, and resource development. In all these investigations, a degree of certainty is required which exceeds that required in most geologic siting studies. Thus scientists pursuing these investigations must apply many techniques of measurement. Each different method that provides independent but coinciding results contributes to the certainty of the final understanding and conclusions.

The water velocity in the vicinity of a proposed geologic storage site is one but by no means the only subject of key interest. The hydrologic studies commonly made (Table 1) to predict the water velocity suffer because neither the time nor the space scale is comparable to the scale of interest in waste repository considerations. Tests of much longer duration are needed.

Studies of natural processes that have been under way for a very long time can be used to supplement the usual procedures for determining water velocity (Table 1). These studies are almost always of a geochemical nature.

Table 1 Methods of Determining Groundwater Velocity for a Large Region*

Hydraulic conductivity	Gradient	Porosity	Regional velocity
Laboratory measurements	Piezometric maps and cross sections	Laboratory measurement	Calculated (Darcy's Law)
Instantaneous injection (slug) tests	Piezometric maps and cross sections	Laboratory measurement	Calculated (Darcy's Law)
Drawdown or recovery tests	Piezometric maps and cross sections	Laboratory measurement	Calculated (Darcy's Law)
Aquifer tests using observation wells	Piezometric maps and cross sections	Laboratory measurement	Calculated (Darcy's Law)
Two-well tracer test (from velocity measurement)	Piezometric maps and cross sections	Two-well tracer test	Calculated from velocity
Multiwell tracer test under natural gradient (from velocity measurement)	Piezometric maps and cross section	Laboratory measurement	Calculated from velocity

*Listed in order of increasing length of extrapolation and increasing time for collecting test data.

The "age" of groundwater can be defined as the length of time it has been out of contact with the atmosphere. A workshop was held in Tucson, AZ, on Mar. 16-18, 1978, on methods that might be used to date very old groundwater (Davis, 1978). This workshop was sponsored by the Department of Energy, whose interest was in methods to evaluate the safety of proposed subsurface repositories for nuclear waste. The age of groundwater is a critical aspect of such an evaluation because it gives an indication of past rates of water movement, which, in turn, can be used to evaluate the likelihood of future migration of radionuclides from a given repository.

At this conference six methods of estimating age were discussed:

1. *Hydraulic methods* use the hydraulic gradient, fluid conductivities, effective porosities, and Darcy's Law and related equations to estimate the velocity and, thus, the total travel time (Table 1).

2. *Geologic history*, such as previous stands of the ocean or a hot, cold, dry, or wet climate, may leave a trace on the groundwater, e.g., distinctive isotopic ratios or dissolved solids content.

3. *Atmospheric radionuclides* that decay after entering the ground include tritium and carbon-14. These isotopes are commonly used in today's dating methods. Other possibilities exist for determining much older ages by using chlorine-36 or krypton-81.

4. *Decay products* of some radionuclides begin to accumulate after the water comes in contact with rocks. These accumulated decay products increase in concentration as the water becomes older, unlike the decay products of atmospheric radionuclides, which decrease as the water becomes older.

5. *Structural molecular changes* of dissolved material, such as amino acids, in the groundwater might be useful indicators of water age.

6. *Radionuclide disequilibrium* between parent and daughter elements, as, e.g., uranium-234 and uranium-238, may be an index to groundwater age.

This paper focuses on *decay products* (method number 4) and carries out one recommendation of the Tucson conference, i.e., to evaluate the potential usefulness of the noble gases for dating groundwater. In addition, the

paper presents an example of the use of helium to date water beneath the Savannah River Plant near Aiken, SC, and compares this method to hydraulic methods.

Principles

Natural precipitation is virtually devoid of the decay products of uranium, thorium, or potassium. This water recharges the ground and flows with the groundwater. Because uranium, thorium, and potassium are nearly ubiquitous in rocks and undergo continual radioactive decay, the decay products are generated continuously within the rock. Some of the decay products will be retained by the rock, but some will enter the groundwater. If the generation rate of the decay product and the parent radionuclide element content of the rock are known, a minimum residence time for the water in contact with this type of rock can be calculated from the amount of decay product present in the water.

The principal assumption involved in this calculation is that the transfer rate of the decay product from the rock to the water is the same as the generation rate. For a hydrologic system subject to new conditions, such as initial saturation or a radical change in salinity, this assumption may be suspect. If the hydrogeological history of the region shows that the groundwater system has not undergone significant change, however, the release rate of the decay products from the rock to the water may have reached a steady state that is proportional to its generation rate.

If the decay product continues to accumulate in the rock-forming minerals or diffuses through the rock and is lost to the atmosphere, the water may be older than the age calculated. If the decay product migrates into the aquifer of interest from deeper zones in the earth, the calcu-

lated age may be too old. Independent hydrogeological knowledge of the groundwater system is obviously required for this method of dating, as it is for all other methods.

Another assumption in using decay product dating of groundwater is that the parent element content of the rock is known along the entire flow path. If the geology is relatively homogeneous over the flow path, this is not a complicating assumption. Even if the geology is unknown, minimum ages can be calculated from the literature on assumed parent element contents of rock.

Helium, a decay product of uranium and thorium, has been used to date water in crystalline rock beneath the Atlantic Coastal Plain (Marine, 1976, 1979), in outcropping crystalline rock (Fritz, Barker, and Gale, 1979), and in sandstone (Andrews and Lee, 1979), but other decay products are not known to have been used.

Potential for Dating Groundwater by Using the Accumulation of Radiogenic Noble Gases

One of the suggestions of the Tucson meeting (Davis, 1978) was that the usefulness of various radiogenic noble gases should be evaluated in terms of their generation rates. The noble gases (helium, xenon, krypton, neon, and argon) are particularly useful for dating purposes because they are nonreactive with earth materials. The purpose of this paper is to evaluate the potential usefulness of these radiogenic noble gases in terms of the quantity produced. No discussion is presented on the transfer of the accumulated gases from the rock minerals to the surrounding groundwater.

Uranium and thorium are present in detectable amounts in most rocks. Decay of ^{238}U , ^{235}U , and ^{232}Th by α

emission leads to the formation of ^4He . A very small fraction of the uranium and thorium disintegrations occurs by spontaneous fission, yielding fission products that include isotopes of xenon and krypton. In addition, neutrons are produced which are absorbed by certain constituents of the rocks to form activation products. In a small fraction of the alpha decays, the α particle interacts (α, n) with light elements, such as ^{18}O and ^{19}F , to form additional neutrons and two isotopes of neon. Argon-40 is formed by decay of the long-lived radioisotope ^{40}K , a minor constituent of natural potassium.

Helium-4. The present composition of natural uranium is 99.3% ^{238}U and 0.7% ^{235}U . Eventually ^{238}U decays to stable ^{206}Pb , with a half-life ($T_{1/2}$) of 4.51×10^9 yr (Lederer, Hollander, and Perlman, 1967) and the emission of eight α particles; ^{235}U decays to stable ^{207}Pb , with a $T_{1/2}$ of 7.1×10^8 yr and the emission of seven α particles. Thorium-232 decays to stable ^{208}Pb , with a $T_{1/2}$ of 1.41×10^{10} yr and the emission of six α particles. Ultimately the vast majority of the α particles (He ions) are converted to neutral ^4He atoms by the capture of two electrons. Helium-4 is formed continually from the time of original formation of the rock.

The number of ^4He atoms formed as a function of time can be expressed as

$$^{232}\text{Th}: ^4\text{He atoms} = 6N_0(1 - e^{-\lambda_{232}t})$$

$$^{235}\text{U}: ^4\text{He atoms} = 7N_0(1 - e^{-\lambda_{235}t})$$

$$^{238}\text{U}: ^4\text{He atoms} = 8N_0(1 - e^{-\lambda_{238}t})$$

where N_0 is the original number of atoms and λ is the radioactive decay constant ($4.92 \times 10^{-11}/\text{yr}$ for ^{232}Th , $9.76 \times 10^{-10}/\text{yr}$ for ^{235}U , and $1.54 \times 10^{-10}/\text{yr}$ for ^{238}U). Time t is in years. Assuming that the time of decay (perhaps up to 3×10^8 yr) is

short in comparison with the half-lives involved, we can replace the $(1 - e^{-\lambda t})$ term with λt . This assumption is strictly valid for ^{232}Th and ^{238}U , but a small correction would be necessary for ^{235}U at long decay times. Because of the low abundance of ^{235}U in natural uranium, however, the correction can be ignored without introducing any significant error.

Conversion of the helium atoms to microliters of ^4He gas at standard temperature and pressure yields the following rates of formation of ^4He :

$$^{232}\text{Th}: 2.84 \times 10^{-5} \mu\text{l}/(\text{yr} \cdot \text{g Th})$$

$$\text{Natural U}: 1.20 \times 10^{-4} \mu\text{l}/(\text{yr} \cdot \text{g U})$$

Accumulation of ^4He from decay of natural uranium and ^{232}Th is shown in Fig. 1 as a function of decay time. The quantity of ^4He produced would be the sum from both sources. Actual quantities expected from a given rock can be calculated from the percent of uranium or thorium in the rock.

Neon-21 and Neon-22. One of about every 10^6 α particles interacts with light elements in the rock matrix to form another isotope with the emission of a neutron. Two such reactions that produce ^{21}Ne and ^{22}Ne are

The neon isotopes, which are stable, are produced in quantities of about one millionth of the ^4He formed. The principal isotope of atmospheric neon is ^{20}Ne (90.5%) (Knolls Atomic Power Laboratory, 1972). The significant aspect of neon produced as the result of radioactive decay is that no ^{20}Ne should be formed. Thus the amount of ^{21}Ne and ^{22}Ne should indicate the time the water has been out of contact with the atmosphere. Estimated quantities of ^{21}Ne and ^{22}Ne produced as a func-

Figure 1 Radiogenic production of noble gases as a function of time.

tion of time are also shown in Fig. 1 (per gram of uranium).

Xenon and Krypton. Several isotopes of xenon (${}^{131}\text{Xe}$, ${}^{132}\text{Xe}$, ${}^{134}\text{Xe}$, and ${}^{136}\text{Xe}$) and krypton (${}^{83}\text{Kr}$, ${}^{84}\text{Kr}$, and ${}^{86}\text{Kr}$) are formed as fission products in the spontaneous fissioning of ${}^{238}\text{U}$, ${}^{235}\text{U}$, and ${}^{232}\text{Th}$. Spontaneous fission half-lives are 1.9×10^{17} yr for ${}^{235}\text{U}$, 6.8×10^{15} yr for ${}^{238}\text{U}$, and $>10^{21}$ yr for ${}^{232}\text{Th}$. Thus significant amounts of fission occur only in ${}^{238}\text{U}$, and fissioning of ${}^{235}\text{U}$ and ${}^{232}\text{Th}$ can be ignored.

Fission yields for the isotopes of xenon and krypton were estimated (Argonne National Laboratory, 1963), and volumes of xenon and krypton per gram of uranium were calculated. Results are shown in Fig. 1. Quantities are very small in comparison with quantities of ${}^4\text{He}$. We should note that all the xenon and krypton isotopes are stable. In each case natural xenon and natural krypton contain stable isotopes that are not formed as fission products and, thus, would not be formed in rocks.

Argon-40. Argon-40 is the principal constituent (99.59%) of natural argon, but it is also formed by the decay of ^{40}K , a minor constituent (0.012%) of natural potassium. Potassium-40 decays with a half-life of 1.26×10^9 yr; in 11% of its disintegrations, it decays by electron capture to form ^{40}Ar .

The volume (STP) of ^{40}Ar formed per gram of ^{40}K can be expressed as

$$^{40}\text{Ar}/\text{g } ^{40}\text{K} = 6.16 \times 10^4 (e^{\lambda_K t} - 1)$$

where λ_K is the decay constant of ^{40}K , or $5.50 \times 10^{-10}/\text{yr}$.

This ratio of argon produced to potassium present is reduced by a factor of 0.00012 if the amount of ^{40}Ar is expressed per gram of natural potassium ($^{39}\text{K} + ^{40}\text{K} + ^{41}\text{K}$).

Estimates of the amounts of ^{40}Ar (per gram of natural potassium) as a function of time are shown in Fig. 1. The other noble gases shown in Fig. 1 are all the result of uranium decay, and thus the total quantity of each is in the same ratio as shown in Fig. 1 irrespective of the amount of uranium present. Argon, however, is produced from potassium, which is about 10,000 times more abundant than uranium (Clark, 1966). Zartman and Wasserberg (1961) estimated that the ratio of radiogenic ^4He produced to ^{40}Ar is about 7.

Although the $^{40}\text{Ar}/^{40}\text{K}$ method is quite useful in dating rocks and minerals, it does not appear to be useful in dating water. A mineral date by this method requires a closed system, i.e., a mineral grain for which the assumption that no parent or daughter product has been added or lost is valid. Obviously, if argon is collected from the water, a closed system cannot be assumed. Because of the very small quantity of ^{40}K in natural potassium (0.012%) and the great abundance of ^{40}Ar in natural argon (99.59%), the amount of ^{40}Ar that orig-

inated from decay of ^{40}K is almost impossible to determine.

Helium-3. Small amounts of ^3He can be produced in rocks as an indirect result of radioactive decay. It has been estimated (Rankama, 1963, p. 92) that about 6% of the neutrons liberated in rocks as the result of spontaneous fission or (α, n) reactions result in the formation of ^3H , which decays to ^3He . The amounts of ^3He formed are probably insignificant. Calculated ratios of ^3He to ^4He formed from natural uranium and thorium are about 1.2×10^{-7} in each case. The ^3He -to- ^4He ratio in atmospheric helium is about 1.3×10^{-6} .

Ratios of ^3He to ^4He from 10 to 15 times the atmospheric ratio have been found in oceanic basalts and in volcanic gases from Lassen and Yellowstone Parks (Lupton and Craig, 1975; Craig and Lupton, 1976; Craig et al., 1978).

Conclusions on the Potential for Dating Groundwater by Accumulation of Radiogenic Noble Gases. The decay product that appears most promising for dating groundwater is ^4He . This isotope is formed in reasonable quantities by direct α decay of uranium and thorium. Direct use of other isotopes of noble gases for groundwater dating does not appear promising.

Methods using argon, xenon, krypton, and neon entail significant difficulties. All these elements except argon are formed in smaller quantities than corresponding amounts of ^4He . Spontaneous fission half-lives determining the production of xenon and krypton are very long. Considerable uncertainty is introduced in calculating ages with neon isotopes because of inaccuracy in predicting how many α particles react to produce the neon isotopes. In general, the potential for error increases when a long time is required to produce a small quantity of the isotope. Mean-

Figure 2 Location of the Savannah River plant and nearby geologic provinces. The line of section for Fig. 2 is also shown.

ingful use of any of the decay products discussed here as indicators of age requires the assumption that either the isotopes involved are absent or their compositions are known at the start of the period of decay. Since this is not a valid assumption for ^{40}Ar , the usefulness of ^{40}Ar for groundwater dating is limited.

The Use of Helium to Date Groundwater

The following discussion presents an example of the use of helium to date water in the crystalline metamorphic rock beneath the Savannah River Plant (SRP) near Aiken, SC.

This study was part of a broader study at SRP from 1961 to 1972 to evaluate the safety of storing radioactive waste in metamorphic bedrock. The bedrock is buried beneath 300 m of coastal plain sediments at the plant site. This investigation was deferred in 1972 pending a more detailed evaluation of alternative concepts of waste storage and management.

Hydrologic System at the Savannah River Plant. The Savannah River Plant is located on the Atlantic coastal plain about 32 km southeast of the outcrop of the crystalline metamorphic rock at the Fall Line, which separates the Piedmont and Coastal Plain physiographic provinces (Fig. 2). There are three separate geologic and hydrologic systems (Fig. 3) at SRP: (1) coastal plain sediments (Miocene, Eocene, and Late Cretaceous sediments, Fig. 3) in which water occurs in porous unconsolidated to semiconsolidated sand and clay; (2) crystalline metamorphic basement rock, consisting of chlorite-hornblende schist and hornblende gneiss with lesser amounts of quartzite, where water occurs in small fractures; and (3) a buried Triassic basin, consisting mostly of red consolidated mudstone with some poorly sorted sandstone, where water occurs in the intergranular space but is very restricted in movement because of the extremely low hydraulic conductivity.

The water in the coastal plain sediments is separated from the water in

Figure 3 Generalized northwest to southeast geologic profile across the Savannah River plant.

the crystalline metamorphic rock by a layer of dense clay or sandy clay, called saprolite. This layer is the residual weathering product of the crystalline rock from the period when the rock was last exposed to the atmosphere before being covered by Cretaceous sediment, perhaps 100 million years ago. The hydrologic separation of these two systems is suggested by the following observations: (1) Water in the coastal plain sediment contains about 30 mg/l of dissolved solids as opposed to about 6000 mg/l for the water in crystalline rock. (2) Pumping tests in the crystalline rock (up to 1 yr in duration) show no indications of leakage from the sediments above.

(3) Water in the crystalline rock contains dissolved gas, including helium, which is far in excess of the amount in the atmosphere. The presence and composition of dissolved gas indicate that it does not escape to the sediments at a significant rate.

From water injection and removal tests on packed-off sections of rock, Marine (1966) concluded that there are two types of fractures in the crys-

talline rock. The first consists of minute fractures that pervade the entire rock mass but transmit water extremely slowly. Rock that contains only this type of fracture is called "virtually impermeable rock." The other type of fracture is restricted to definite zones and has larger openings that transmit water at a faster rate. Rock that includes this type of fracture is called "hydraulically transmissive rock."

The hydraulic conductivity of both types of crystalline rock was discussed by Marine (1967, 1975), and representative values are 1.2×10^{-5} m/d for virtually impermeable rock and 3.3×10^{-2} m/d for hydraulically transmissive rock.

A flow path can be inferred by applying hydrologic principles to the geometry of the groundwater system in the crystalline rock. This flow path is supported by the piezometric map (Fig. 4) constructed from water levels in the wells that penetrate the crystalline rock. It is 51 km long from the recharge area to well DRB6 near the center of the plant site.

Figure 4 Piezometric map of water in crystalline metamorphic rock and inferred flow paths.

Helium Content of Water from the Crystalline Rock. The water from the crystalline rock contains sufficient dissolved gas to effervesce when brought to the surface. This gas is 91% nitrogen by volume (Table 2). The most significant constituent, however, is dissolved helium. A minimum residence time for the water in the rock can be calculated from the quantity of helium collected and the uranium and thorium content of the rock.

Table 2 shows wide differences in the amount of gas recovered and the percent helium in the gas in samples collected from different wells. The helium content of individual samples varies approximately as the electrical conductivity of the water (Fig. 5). This relationship suggests that all the freshwater used to drill the wells was

not removed at the time the gas was sampled. Several methods of explaining this variation in helium content were suggested before it was realized that it was caused simply by inadequate sampling procedures. Because of the large amount of water pumped from well DRB6, it is believed that the gas analyses of samples from this well are representative of those which would be obtained if the drilling water were removed from the other wells.

The gas samples were collected by pumping water from the wells through a water-filled plastic bottle inverted in a tub of water. As the gas evolved from the water passing through, it displaced the water in the bottle. At a pumping rate of 78 l/min (well DRB6), the water that leaves the rock at a depth of 544 m takes about 2 h to travel up the well and pass

Table 2 Selected Analyses of Effervesced Gas from Wells in Crystalline Metamorphic Rock

Well	Date of collection	Water removed,* m ³	Pumping conditions at time of sampling	Number of samples averaged	Gas evolved through sampler, ml gas/l H ₂ O
Crystalline rock					
DRB 2	5/23/63	12	Pumped at 9.8 l/min		10.5
	5/24/63	13	about 1 hr each day for 8 d		5.3
DRB 3	4/29 to 5/3/63	888	Continuous at 7.5 l/min for 3 d	7	0.82
	5/1/63	865	Continuous at 7.5 l/min for 1 d		
DRB 5	5/7 to 5/10/63	98	Continuous at 22.7 l/min for 3 d	6	0.90
DRB 6	11/9/62	3175	Continuous at 77.5 l/min for 28 d		2.07
	1/21 to 1/24/63	3855	Continuous at 77.5 l/min for 3 days	8	0.60
	1/22 to 1/23/63	3742	Continuous at 77.5 l/min for 2 d		
	1/23 to 1/24/63	3855	Continuous at 77.5 l/min for 3 d		
DRB 7	6/27/63	19	Pumped at 9.1 l/min about 1 hr every 3 d over a period of 1 month		14.00
Tuscaloosa formation		Very large	Continuous; about 3780 l/min		0.1

(Table 2 Continued)

	Gas composition, mol %							Helium evolved from water, ml He/l H ₂ O	
Well	Nitrogen	Argon	Helium	Hydrogen	Oxygen	Carbon dioxide	Carbon monoxide		
Crystalline rock									
DRB 2	93.00	1.27	1.49	3.05	1.19	0.01	<0.01	0.156	SRL
	91.74	1.33	1.41	1.45	4.08	0.01	<0.01	0.074	SRL
DRB 3	94.98	1.32	1.75	1.16	0.77	<0.01	<0.01	0.014	SRL
	95.6	1.1	1.6	1.7	Trace				Bureau of Mines; hydrocarbons, 0.0 mol %; hydrogen sulfide, 0.0 mol %
DRB 5	95.96	1.45	2.21	0.17	0.18	<0.01	<0.01	0.20	SRL
DRB 6	92.53	1.03	5.28	0.26	0.74	0.04	0.11	0.11	SRL
	91.00	1.10	6.00	0.30	1.00	0.2	0.4	0.036	SRL
	94.6	1.1	4.2	0.1	0	0.1			Bureau of Mines; hydrocarbons, 0.0 mol %; hydrogen sulfide, 0.0 mol %
	94.7	1.1	3.7	0.1	0.3	0.1			Bureau of Mines
DRB 7	91.32	1.18	0.26	5.87	1.37	<0.01	<0.01	0.036	SRL
Tuscaloosa formation	93.20	1.09	<0.01	<0.01	4.14	1.61	<0.01		SRL

*Total quantity of water released from well from completion of drilling and packer tests to time of sampling.

Figure 5 Relationship between helium content and electrical conductivity in water samples from crystalline rocks at the Savannah River plant.

through the sample bottle. Because wells DRB2 and DRB7 would not yield water at a rate sufficient to pump continuously, they were pumped intermittently, drawing the water level down to the pump suction (187.5 m below surface) each time. Then the wells were left idle for periods that varied from 1 to 8 d before being pumped again. At first it was thought that this intermittent movement of water up the wells may have accounted for the different gas volumes shown in Table 2, but, when the solubility of the gas at various depths of water was calculated, it was realized that no gas came out of solution until it was within a few meters of the surface.

It was also believed initially that gas collection was not complete because of the short residence time of the water in the inverted bottle. The gas in solution in the water should have come to atmospheric equilibrium within a few seconds, however. Thus the gas remaining in solution and not analyzed is only that which remains in solution at atmospheric pressure.

Table 3 shows the calculations of total gas in solution in the water from

DRB6 using Henry's law. The second column is the gas analysis. The volume collected was calculated (column 3) on the basis of 0.60 ml of gas for each liter of water passing through the sample collector (Table 2). After the total volume of gas collected per liter of water was obtained, the mole fraction of each gas (column 4) was calculated. Because atmospheric pressure is 760 mm Hg and the vapor pressure of water is 24 mm, the total pressure of the five gases is 736 mm (760 - 24). The partial pressure of each gas (column 5) is equal to its mole fraction multiplied by 736 mm. Multiplying the partial pressures (column 5) by the Henry's law constants (column 6) and dividing by 760 mm/atm yields the amount of each gas that remains in solution (column 7). The total amount of gas in solution (column 8) is obtained by adding the volume of gas collected (column 3) to that remaining in solution at atmospheric pressure (column 7).

The validity of this method of calculating total dissolved gases was tested by collecting two samples of water under a pressure of about 274 m of water, driving off the gas, and analyzing in the laboratory. The analyses of two such collections are shown in Table 3, column 9. There is good agreement between the calculated values of total gas (column 8) and the measured values (column 9). This agreement supports the argument that the original gas collections were in equilibrium at atmospheric pressure.

Table 3, column 10, shows the volume of the various gases that would be in solution if air were in solution at atmospheric pressure. These values were calculated by multiplying the solubilities of various gases in water at atmospheric pressure, as given by Linke (1958), and the mole

Table 3 Calculated and Measured Values for Total Gas in Solution and Partial Gas Pressures for Gas Dissolved in Water from DRB6*

Gas	Mole %	Volume collected, cm ³ /l H ₂ O	Mole fraction	Partial pressure 0.25°C, mm Hg	Henry's law constant 0.25°C, cm ³ /(l H ₂ O · atm)	Volume left in solution, cm ³ /l H ₂ O	Total gas in solution, cm ³ /l H ₂ O	Volume of gas in two samples collected under pressure, cm ³ /l H ₂ O June 16, 1971 June 28, 1971		Volume of gas in equilibrium with normal atmosphere,† cm ³ /l H ₂ O	Partial pressure 0.25°C, mm Hg
Nitrogen	91.0	0.546	0.915	673.4	15.0	13.27	13.82	18.0	20.9	12.5	700.2
Argon	1.1	0.0066	0.011	8.1	31.0	0.33	0.34	0.40	0.43	0.32	8.3
Helium	6.0	0.036	0.060	44.2	8.6	0.500	0.54	0.50	0.57	4×10^{-4}	47.7
Hydrogen	0.3	0.0018	0.003	2.2	17.0	0.049	0.05	0.07	0.01	9×10^{-6}	2.2
Oxygen	1.0	0.006	0.010	7.4	28.0	0.273	0.28	0.50	0.79	6.45	7.6
Water				24.0							
Total		0.5964	0.999	759.3		14.42	15.03	19.5	22.7	19.3	790.0 (~1.04 atm)

*Samples collected Jan. 23, 1963, were used for calculations at standard temperature and pressure.

†Calculated from solubility given by Lanke (1958) and mole fractions given by Weast (1966)

fraction of the various gases in the atmosphere, as given by Weast (1966). In comparison with gases in the atmosphere, the gas dissolved in the bedrock water is greatly enhanced in helium and hydrogen, slightly enhanced in nitrogen and argon, and depleted in oxygen.

Using the total amount of dissolved gases (Table 3, column 8), we can calculate the partial pressure of each gas when all the gas was dissolved in the water (column 11) by dividing the amount (column 8) by Henry's law constant (column 6) and converting atmospheres to millimeters of mercury. The total pressure of all gases dissolved in the water, including the vapor pressure of water, is 790 mm. Not until the pressure drops below this value will the gases start to come out of solution. Since this pressure is only 30 mm Hg or 0.4 m H₂O above atmospheric, no gas will come out of solution in the well water until it is at very nearly atmospheric pressure.

The knowledge of the amount of helium in the water was used to calculate the minimum residence time for the water in the crystalline rock.

Calculation of Residence Time.

The helium generation rate from uranium was reported to be $11.0 \times 10^{-5} \text{ mm}^3/(\text{g U} \cdot \text{yr})$ (Levorsen, 1967) and that from thorium, $3.1 \times 10^{-5} \text{ mm}^3/(\text{g Th} \cdot \text{yr})$ at standard temperature and pressure. For the crystalline rock (well DRB6 data), the uranium and thorium contents average 1.5 and 8 ppm, respectively (Proctor and Marine, 1965). The helium generation rate from uranium is $1.5 \times 10^{-6} \text{ g U/g rock} \times 11 \times 10^{-8} \text{ cm}^3 \text{ He}/(\text{g U} \cdot \text{yr})$ or $16.5 \times 10^{-14} \text{ cm}^3 \text{ He}/(\text{g rock} \cdot \text{yr})$. The helium generation rate from thorium is $8 \times 10^{-6} \text{ g Th/g rock} \times 3.1 \times 10^{-8} \text{ cm}^3 \text{ He}/(\text{g Th} \cdot \text{yr})$ or $25 \times 10^{-14} \text{ cm}^3 \text{ He}/(\text{g rock} \cdot \text{yr})$. If we combine the uranium and thorium

data, the helium generation rate is $41 \times 10^{-14} \text{ cm}^3/(\text{g rock} \cdot \text{yr})$.

Assuming an average fracture and nonfracture porosity of 0.2% for the crystalline rock [0.08% for effective porosity of hydraulically transmissive rock (Webster, Proctor, and Marine, 1970) and 0.13% for intergranular porosity from laboratory measurements], we have $2 \times 10^3 \text{ cm}^3$ of water in 1 m^3 of rock. In well DRB6 (Table 3), there is 0.50 cm^3 of helium per liter of water ($0.50 \times 10^{-3} \text{ cm}^3$ helium per 1 cm^3 of water) or 1.00 cm^3 helium per 1 m^3 of rock. The average density of the crystalline rock is reported to be 178 lb/ft^3 or about $2.9 \times 10^6 \text{ g/m}^3$ (Christl, 1964); therefore the helium accumulated in the crystalline rock is

$$\frac{1.00 \text{ cm}^3 \text{ He/m}^3 \text{ rock}}{2.9 \times 10^6 \text{ g rock/m}^3 \text{ rock}} = 3.45 \times 10^{-7} \text{ cm}^3 \text{ He/g rock} \quad (1)$$

If we divide the accumulated helium by the generation rate determined for uranium and thorium, we get the minimum length of time necessary to accumulate the observed quantity of helium:

$$\frac{3.45 \times 10^{-7} \text{ cm}^3 \text{ He/g rock}}{41 \times 10^{-14} \text{ cm}^3 \text{ He}/(\text{g rock} \cdot \text{yr})} = 840,000 \text{ yr} \quad (2)$$

The length of the flow path (Fig. 4) from near the outcrop area through well DRB6 is inferred to be 51 km. If we assume that flow along this path constitutes the residence time for the water, the velocity of the water is $\sim 0.06 \text{ m/yr}$.

These calculations were made from analyses that show minimum helium content for DRB6, which provided the only reliable samples. Thus greater ages and smaller flow velocities might be obtained if other analyses had been used.

Table 4 Thorium, Uranium, and Helium Contents* of Selected Core Samples of Crystalline Metamorphic Rock

Well	Depth, m	Thorium, ppm	Uranium, ppm	Helium, nl/g		Percent of calculated helium measured‡
				Measured	Calculated†	
DRB6	558.9	5	1	4.2	77	5
DRB7	562.4	13	2	49.3	181	27
DRB8	394.2-394.7	13	2	47.0	181	26
DRB8	498.3-498.6	19	5	22.7	321	7
P6R	317.3	3	1	1.9	59	3
P8R	192.6	5	1	3.0	77	4
DRB8§	275.9-276.3	13	5	109.0	277	39
DRB8§	284.2-284.9	19	2	5.0	235	2
DRB8§	294.0-294.3	7	2	31.4	127	25

*Spark source spectrometry analyses by Lawrence Livermore Laboratory

†Calculated production in 2.9×10^8 yr (the krypton-argon age of the rock) from the thorium and uranium analyses and rates of 3.1×10^{-2} nl He/(g Th · yr) and 11×10^{-2} nl He/(g U · yr)

‡Does not include helium in water (<1% of calculated total)

§Clay and rock materials from the saprolite region.

Several assumptions involved in this calculation need explanation:

1. The water is assumed to contain 100% of the helium generated. This assumption cannot be true since some helium must reside in the rock where it was first generated. Table 4 shows helium analyses and uranium and thorium contents of the same rock samples. A definite correlation exists between the uranium, thorium, and helium contents of the rock specimens. The present-day helium in the rock represents from 3 to 27 vol.% of the helium formed in 2.9×10^8 yr, the potassium-argon age of the rock. The variation in the three clay samples is somewhat greater. If we assume 0.2 vol.% rock porosity, this amount of helium in water is 0.34 nl/g rock at well DRB6; this represents about 7.5% of the helium in the rock and water. Thus, if the helium in the water is 0.34 nl/g rock and the helium retained by the rock is 4.2 nl/g rock, the total accumulation is 4.54 nl/g rock. If we divide this accumulation by the helium generation rate [41×10^{-8} nl He/(g rock · yr)], we find that 11,000,000 yr is required to generate the helium, rather than the 840,000 yr

shown in Eq. 2, which is based on helium in water only. Since there is no evidence that the temperature and pressure conditions in the rock have been vastly different in the past 11,000,000 yr than they are now, the calculated values in Table 3 are probably applicable.

2. It is assumed that no significant changes have occurred in the rate of transfer of helium from rock to water during this 11,000,000-yr period. Helium is assumed not to have accumulated for long periods in the rock and then been released recently to the water either because the presence of water is recent or because of some change in the transfer mechanics or coefficients. The top of the crystalline rock is now about 198 m below sea level, and the geologic-hydrologic history indicates it has probably been below sea level at least since Eocene time (~50,000,000 yr ago). The crystalline rock has probably always been saturated with water since the beginning of the Cretaceous deposition, even before it sank below sea level. The extent to which changes in the dissolved solids concentration in the water may alter the mechanics of

helium release from the rock is not known, however.

3. The computations assume that the helium was generated by the same type of rock as that in the area in which it is found. This is a reasonable assumption, but it is possible that a granite intrusion with a higher content of uranium and thorium may have contributed some of the helium. For example, assume that the helium-generating rock contains 20 ppm uranium, a very unlikely value since it is the maximum reported (Clark, 1966) for 242 analyses of silicic igneous rock from all over the world. There is, on the average, four times more thorium than uranium in granite rocks (Clark, 1966). Therefore the helium-generating rock containing 20 ppm uranium would contain 80 ppm thorium. These concentrations would give this rock a helium generation rate of $370 \times 10^{-14} \text{ cm}^3 \text{ He}/(\text{g rock} \cdot \text{yr})$ and would still require 90,000 yr to generate the observed accumulation of helium in the water.

4. The volume and density of the rock in which the helium was generated are assumed to be equal to the volume and density of the rock in which it has accumulated although these two volumes need not consist of the same kind of rock. If the volume of rock in which the helium was generated were smaller than the volume of accumulation (the volume of rock explored), a longer period of accumulation would be required. Conversely, if the helium were generated in a large volume of rock and concentrated in the explored volume of rock, then a shorter time of accumulation would be indicated. The helium occurs in solution with water, however, and not as a free gas. Laboratory and field studies (Carter et al., 1959) showed that helium is a highly satisfactory tracer of water if there is little opportunity for loss to the atmosphere. This finding indicates that helium in solution moves with the water and could not

concentrate independently of the water.

5. The calculations assume that no helium has been lost from the rock during the past 11,000,000 yr. If helium has been lost, the length of time required to accumulate the observed quantity of helium must be correspondingly greater. It would be nearly impossible to observe leakage directly; the high porosity, permeability, and quantity of water naturally flowing in the Cretaceous sediments above the rock would make the slight amount of helium leaking from the crystalline rock into the sediments undetectable. If any significant quantity of helium were leaking out of the rock, however, the observed quantity of helium could not accumulate.

6. It is assumed that none of the accumulated helium is emanating from the mantle, but the discussions for assumptions 3 and 4 still apply whether the rock of origin is crust or mantle. In the SRP area, where the continental crust is very thick, it is unlikely that the mantle contributes any significant primordial helium. During the analyses reported in Table 2, ^3He was looked for, but none was found. This may reflect only that the methods used were not designed to detect ^3He -to- ^4He ratios. The amount of helium retained in the metamorphic rock at SRP ranges from 2 to $49 \times 10^{-6} \text{ cm}^3/\text{g}$, whereas that found by Lupton and Craig (1975) in oceanic basalts (mantle derived) was 1 to $148 \times 10^{-8} \text{ cm}^3/\text{g}$. Thus the crustal rocks at SRP contain about two orders of magnitude more helium than oceanic basalts. The groundwater in the crystalline rock at SRP contains $0.5 \text{ cm}^3/\text{l}$, whereas that found by Clarke, Beg, and Craig (1969) in oceanic water was $\sim 4 \times 10^{-5} \text{ cm}^3/\text{kg}$ (STP). Thus the groundwater in the metamorphic rock at SRP contains about four orders of magnitude more helium than oceanic waters. Therefore, even if some of the helium at

SRP was from the mantle, the quantity would not be sufficient to alter the age calculations previously given.

Conclusions on the Use of Helium to Date Groundwater.

During investigations of natural water velocity in geologic material of low permeability, the common field investigative techniques should be supplemented by geochemical and isotopic analyses to explore the possibility of using natural water constituents to develop groundwater velocity information. One such analysis involves measuring the concentration of helium to determine groundwater velocities. This method has the advantage that the concentration of helium (the non-radioactive, stable, daughter product of naturally occurring actinides) increases with the increasing age of the water rather than decreasing as does the concentration of radioactive isotopes. Another advantage is that the helium is not of atmospheric origin; therefore the method involves no assumption about the past composition of the atmosphere. Also, since helium is nonreactive with other elements in the rock-water system, the method uses fewer assumptions about the past chemical history of the system.

Comparison of Hydraulic Conductivity Values Developed by Hydraulic and by Dating Methods

The following discussion compares hydraulic conductivity values derived from laboratory, packer, pumping, and tracer tests with that developed from the helium dating method.

Laboratory Tests for Hydraulic Conductivity. Hydraulic conductivity was measured on 29 samples of unbroken rock core from well DRB1 (Fig. 6) by the U. S. Army Corps of Engineers. About two-thirds of the

samples were unmeasurable, i.e., values were less than 3.8×10^{-11} cm/s, which was the lowest value that could be recorded by the testing equipment and procedure (145 Kpa differential pressure for 30 d). Maximum hydraulic conductivity of the measurable one-third of the samples was 9.2×10^{-8} cm/s, with an average of 2.3×10^{-8} cm/s (Table 5). The water leakage through the samples that had measurable hydraulic conductivity occurred at some inhomogeneity in the sample, e.g., a minute fracture, a healed fracture, a chlorite seam, or the contact between schist and gneiss. In the mass of crystalline rock, these inhomogeneities probably occur so commonly that they render large sections of apparently sound rock nearly homogeneous with respect to permeability.

These laboratory tests were illuminating but were thought to be nonrepresentative of the hydraulic conductivity of the metamorphic rock because hydraulically transmissive rock could not be transported to the laboratory. Later testing on a more regional scale showed that the laboratory tests were more representative than was first believed.

In Situ Borehole Tests. A series of packer tests were made in eight boreholes (Fig. 6) that penetrated 300 m of metamorphic rock within a circle 2760 m in diameter. These consisted of both instantaneous injection tests (slug tests) and instantaneous water removal tests (swabbing tests). A number of the tests were specifically designed to include hydraulically transmissive rock. Apparent transmissivities were obtained in the testing, but, because of the discrete nature of the water-transmitting fractures, hydraulic conductivity was not obtained (Marine, 1967).

For the in situ tests in virtually impermeable rock, the minute frac-

Figure 6 Location of exploration wells cored through crystalline rock (deep rock borings). $\odot$ DRB2, etc., indicates location and number of deep rock boring.

Table 5 Comparison of Laboratory, In Situ, and Rock Mass Measurements of Hydraulic Conductivity of Metamorphic Rock at the Savannah River Plant*

	Virtually impermeable rock		Hydraulically transmissive rock		Rock mass
	Laboratory measurements	In situ packer tests	Pumping test	Tracer test	
Maximum	9.2×10^{-8}	1.8×10^{-7}			
Average	2.3×10^{-8}	1.4×10^{-8}	3.3×10^{-5}	1.6×10^{-5}	2.5×10^{-7}
Minimum	3.8×10^{-11}	9.4×10^{-10}			

*All values are centimeters per second.

tures were assumed to be sufficiently distributed for the concept of hydraulic conductivity to be applied. For 25 tests on virtually impermeable rock (most packer tests were about 30 m in length), the average hydraulic conductivity was 1.4×10^{-8} cm/s. The range was from a minimum of 9.4×10^{-10} cm/s to a maximum of 3.8×10^{-8} cm/s. However, in two other tests on what was considered to

be virtually impermeable rock, the hydraulic conductivity was 1.8×10^{-7} and 9.4×10^{-8} . Thus, as shown in Table 5, the average value for the hydraulic conductivity of virtually impermeable rock obtained by both laboratory and in situ tests are almost the same.

The maximum value from each testing method is also almost the same. The minimum value for the

Figure 7 Results of slug tests in wells DRB5 and DRB6.

laboratory tests is almost two orders of magnitude lower than the minimum value from the in situ tests because, indeed, smaller specimens are less likely to incorporate even virtually impermeable fractures.

Pumping Tests. Pumping tests were not and, in a practical sense, could not be made on virtually impermeable rock. Several were performed on hydraulically transmissive rock, however. The resulting transmissivity from a pumping test of 30-d duration was equal to the summation of the transmissivities obtained from packer tests on two wells exposed to the hydraulically transmissive zone (Fig. 7). This pumping test gave a transmissivity of $2.0 \text{ m}^2/\text{d}$ for hydraulically transmissive rock that averaged 68 m in thickness. Thus, if

homogeneity is assumed for this zone, the apparent hydraulic conductivity would be $3.3 \times 10^{-5} \text{ cm/s}$.

In a later pumping test of 1-yr duration, as the drawdown cone extended in space, the rock appeared to become less permeable (discharge boundary). The water level graphs of observation wells, shown in Fig. 8, indicate that equilibrium was not achieved while pumping 57 l/min for 1 yr. This feature implies that the hydraulically transmissive zone is not semi-infinite in extent but gives way to virtually impermeable rock at some distance from the pumping well.

Two-Well Tracer Test. A tritium tracer test was conducted in two wells in a zone of hydraulically transmissive rock (Fig. 9). In this test the tracer

Figure 8 Graph of water levels in observation wells while DRB6 was being pumped at 57 l/m from Aug. 7, 1968, to Aug. 7, 1969.

Figure 9 Geologic section showing the wells and fracture zone used in the two-well tracer test. Arrows show the generalized direction of water flow.

was forced to flow through the hydraulically transmissive zone from an injection well to a pumping well. The pumped water was then returned to the injection well through a plastic pipe on the ground surface. Analysis of the arrival of this tracer at the pumping well (Webster, Proctor, and Marine, 1970) gave a value for hydraulic conductivity of 1.6×10^{-5} cm/s. As shown in Table 5, the value obtained from the two-well tracer test was very close to that obtained from the pumping test.

Rock Mass Hydraulic Conductivity from Age of Water. The water from the metamorphic rock contains a dissolved gas that is as much as 6% helium. The helium content was used by Marine (1979, also earlier in this paper) to determine that the age of the water was 840,000 yr. This is the length of time that the water was in contact with the metamorphic rock. From piezometric information, the inferred flow path in this type of rock is 51 km long (Fig. 4). If flow along this path constitutes the residence time for the water, the velocity of the water is about 0.06 m/yr.

The hydraulic gradient over this flow path is 6×10^{-4} m/m. The fracture (effective) porosity in a hydraulically transmissive fracture zone is 0.08% (Webster, Proctor, and Marine, 1970). These values can be used to determine the effective hydraulic conductivity for the rock mass averaged over the entire flow path:

$$K = \frac{VE}{I}$$

where K = hydraulic conductivity
 V = velocity
 E = effective porosity
 I = hydraulic gradient

For the metamorphic rock upgradient from SRP

$$\begin{aligned} K &= \frac{0.06 \text{ m/yr} \times 0.0008}{6 \times 10^{-4} \text{ m/m}} \left(100 \text{ cm/m} \right) \\ &\times \frac{1}{365 \text{ d/yr}} \times \frac{1}{86,400 \text{ s/d}} \\ &= 2.5 \times 10^{-7} \text{ cm/s} \end{aligned}$$

Conclusions on Comparison of Hydraulic Conductivity Values Developed by Hydraulic and Dating Methods. Table 5 compares five methods of measuring hydraulic conductivity. Laboratory tests gave values similar to those obtained for in situ tests on virtually impermeable rock. Analyses of pumping tests gave values similar to a tracer test for hydraulically transmissive rock. The hydraulically transmissive rock is about three orders of magnitude more permeable than the virtually impermeable rock. The hydraulic conductivity obtained from the age of the water and the inferred gradient and flow path represents a composite average of a large mass of rock consisting of both virtually impermeable and hydraulically transmissive rock. This value is two orders of magnitude less than values from hydraulically transmissive rock, an order of magnitude greater than the average values of laboratory and in situ tests, and about the same as the maximum laboratory and in situ values.

Fracture zones in the metamorphic rocks are not infinite in extent but terminate in virtually impermeable rock. Thus the regional average hydraulic conductivity is dominated by the conductivity of virtually impermeable rock so that, for this study, laboratory measurements of hydraulic conductivity provide values that are indeed applicable to calculations of regional flow within an order of magnitude.

Conclusion and Summary

The "age" of groundwater can be defined as the length of time the water has been out of contact with the atmosphere. The most common methods of dating groundwater are calculation from measured hydraulic characteristics, such as gradient, hydraulic conductivity, and porosity, or calculation from the abundance of some radioactively decaying isotope of known abundance in the atmosphere and in the recharge water, such as tritium or carbon-14. Both of these methods have shortcomings in determining ages that can be used to investigate an area for a radioactive waste repository. One method that is useful for greater ages is the determination of dissolved stable noble gases produced radiogenically by decay or other interactions with elements in the rock minerals.

Of the several stable noble gases, helium-4 is probably the most useful because it is among the most plentifully produced and is essentially absent in the atmosphere and in recharging water.

The accumulation of dissolved helium-4 in groundwater was used to determine an age of 840,000 yr for water in crystalline metamorphic rock beneath the Savannah River Plant near Aiken, SC. In combination with hydraulic information, such as the inferred flow path, gradient, and porosity, this age could be used to determine the average hydraulic conductivity. This value for hydraulic conductivity compares favorably with values obtained from hydraulic tests, such as laboratory measurements, packer tests, pumping tests, and tracer tests.

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Theoretical and Laboratory Investigations of Flow Through Fractures in Crystalline Rock

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A theoretical model developed for flow through a deformable fracture subject to stresses was successfully tested against laboratory experiments. The model contains no arbitrary parameters and can be used to predict flow rates through a single fracture if the fractional fracture contact area can be estimated and if stress-deformation data are available. These data can be obtained from laboratory or in situ tests. The model has considerable potential for practical application.

The permeability of ultralarge samples of fractured crystalline rock as a function of stresses was measured. Results from tests on a pervasively fractured 1-m-diameter specimen of granitic rock showed that drastically simplifying assumptions must be used to apply theoretical models to this type of rock mass. Simple models successfully reproduce the trend of reduced permeability as stress is applied in a direction normal to the fracture plane. The tests also demonstrated that fracture conductivity increases as a result of dilatancy associated with shear displacements. The effect of specimen size on the hydraulic properties of fractured rock was also investigated. Permeability tests were performed on specimens of charcoal black granite containing a single fracture subjected to normal stress. Results are presented for tests performed on a 0.914-m-diameter specimen and on

the same specimen after it had been reduced to 0.764 m in diameter. The data show that fracture conductivity is sensitive to stress history and sample disturbance.

Introduction

The potential for escape of hazardous material to the biosphere by groundwater transport is one of the most important factors that must be considered in the siting and design of facilities for underground disposal of nuclear waste. The hydrologic regime in crystalline rocks is usually dominated by flow through fractures in the rock mass. Thus, to develop analytic models of flow and transport through these media, we must investigate the laws of fluid flow in fractures. The construction and operation of a waste repository produces changes in the state of stress in the surrounding rock because of the excavation of the underground openings and the heating and subsequent cooling that results from the decay of the radioactive material. These changes in the state of stress in the rock mass include variations in effective stress caused by perturbations of fluid pressures, which result from changes in total stress in the groundwater flow regime. Changes in the state of stress produce displacements in the rock mass which can affect the hydraulic properties of the fractures as a result of changes in aperture, contact area, and other characteristics of the flow path. Models used to predict the

movement of groundwater must, therefore, be able to account for changes in rock mass permeability resulting from these effects. Interpreting data from well tests, pressure tests, and other techniques designed to measure the hydraulic properties of a rock mass also requires an understanding of the laws governing flow in fractures.

Traditionally laboratory tests designed to measure the hydraulic properties of fractures in crystalline rock have been performed on specimens with dimensions of several centimeters. Although tests performed at this scale provide useful insights into the phenomenology of flow through discrete fractures, their ability to represent accurately the conditions in situ is open to question. The hydraulic properties of a natural fracture are determined by the geometric and physical properties of the fracture. These properties are not homogeneous, and therefore there is some minimum sample size below which results obtained from laboratory specimens are not representative of the mean hydraulic characteristics of the in situ fracture. Although the magnitude of these effects has not yet been determined experimentally, the potential for a significant size effect has been observed in laboratory data from tests performed on specimens of different dimensions. Thus, to reduce uncertainty in parameters and to make reliable comparisons between empirical results and theoretical models, we must obtain measurements from specimens containing fractures with dimensions closer to those of practical concern—namely, meters rather than centimeters.

Models of Flow Through Fractures

Models of flow through fractures in crystalline rock have been based on

solutions of the Navier-Stokes equation for steady, laminar, isothermal flow between smooth parallel plates (Boussinesq, 1868; Bear, 1972). For plates separated by a constant distance (b), the flow rate is proportional to b^3 . This relationship, called the cubic law, has been shown to be valid for flow between optically smooth plates of glass down to apertures of $0.2 \mu\text{m}$ (Romm, 1966). Lomize (1951) showed that the cubic law also applied to laminar flow between glass plates with variable, curvilinear profiles. He defined the distance between the plates as the mean aperture and introduced a roughness factor to account for local variations in aperture. Independent investigations by Louis (1969) and others (Baker, 1955; Huitt, 1956; Parrish, 1963; Rayneau, 1972; Gale, 1975) on flow in fractured rock support Lomize's findings for laminar flow under conditions where the Reynolds number is less than 2400. These studies established the validity of the cubic law for flow in rough, open fractures (i.e., fractures where the parallel surfaces are not in contact).

In their natural state, fracture surfaces usually have some degree of contact, and the aperture and contact area depend on the stress acting across the discontinuity. In this type of closed fracture, flow occurs along the paths that are not blocked by asperities bridging the fracture surfaces. In the nearly impermeable rocks that would be suitable sites for disposal of nuclear waste, closed fractures will predominate. Witherspoon et al. (1980) expressed the cubic law for flow in a rough fracture in a simplified form by introducing a factor (f) to account for deviations from ideal conditions. Thus, when $f \geq 1.0$ (i.e., for a rough fracture):

$$\frac{Q}{\Delta h} = \left[\frac{C}{f} \right] b^n \quad (1)$$

where Q = flow
 Δh = difference in hydraulic head
 C = a constant depending on flow geometry and fluid properties
 $n = 3$

The results of laboratory investigations by Iwai (1976) on the hydraulic properties of tension fractures induced in basalt, granite, and marble samples are used to study the validity of the cubic law for flow in closed, deformable fractures. Iwai measured the change in conductivity of single fractures during loading and unloading under normal stresses up to 20 MPa and measured the normal displacements across the fractures. Typical results from his experiments on radial flow through a fracture in granites are given in Fig. 1, which plots flow

Figure 1 Experimental and theoretical flow through a fracture in granite as a function of normal stress.

per unit head ($Q/\Delta h$) vs. normal stress for one complete cycle of loading and unloading. To check the validity of Eq. 1, we must know the true fracture aperture (b). Witherspoon

et al. (1980) developed an expression for the true aperture:

$$b = (b_d + b_r) \quad (2)$$

where b_r is the residual aperture after a given stress history and b_d is the apparent aperture obtained from

$$b_d = \Delta V_m - \Delta V \quad (3)$$

where ΔV is the net deformation caused by the stress history and ΔV_m is the maximum fracture deformation caused by applying a high stress. The term b_d is not the true aperture appropriate for use in Eq. 1 because, unless the fracture is subjected to extremely high stress, the flow paths through the fracture are not closed, and the hydraulic properties of the fracture do not become similar to those of intact rock (Kranz et al., 1979). As illustrated in Fig. 2, in prac-

Figure 2 Stress deformation behavior of a fracture.

tical experiments ΔV_m is measured at a stress under which the fracture has some residual aperture, b_r . From Eqs. 2 and 3, Eq. 1 can be rewritten:

$$\frac{Q}{\Delta h} = \frac{C}{f} (\Delta V_m - \Delta V + b_r)^n \quad (4)$$

This equation has three unknowns, f , b_r , and n . For the cubic law to be valid, n must take the value 3. Witherspoon et al. (1980) initially assumed that $f = 1.0$; this implies that the fractures are, in fact, smooth and the surfaces are not in contact. The unknowns n and b_r were then evaluated by applying a least-squares curve-fitting procedure to Iwai's data (1976). Values of n obtained in this way ranged from 3.01 to 3.10. The values of b_r obtained from Eq. 4 for $f = 1$ differed from those computed from Eqs. 1 and 2 with $f = 1.0$ by less than 3%. Thus it was concluded that, for closed deformable fractures, $n \approx 3.0$. Then, assuming $n = 3.0$ in Eq. 1, we obtain values of f ranging from 1.0 to 1.21. These values are all greater than 1.0 and agree with Lomize's (1951) findings. Using these values of f in Eq. 1, Witherspoon et al. (1980) found good agreement with Iwai's experimental data and concluded that, at least for the range of conditions in Iwai's experiments, the cubic law is valid for closed, deformable fractures.

Gangi (1978) and Tsang and Witherspoon (1981) developed models of fractures which explicitly consider the geometry of the asperities and the deformation of the fracture under load. Gangi's "bed-of-nails" model treated the asperities as a series of elastic rods of varying heights and cross-sectional areas occupying the space between two flat parallel plates. By selecting appropriate functions for the height and cross-sectional distributions of the rods, he was able to model the nonlinear deformation of

the fracture aperture in response to applied normal stress, and, assuming the cubic law to hold, he predicted the resulting changes in fracture conductivity. Using these techniques, Gangi obtained good agreement with the experimental data of Nelson (1975) from Navajo sandstone and reasonable agreement with the results of Jones (1975) from fractured carbonate rocks.

Tsang and Witherspoon (1981) developed the model shown in Fig. 3, which, like Gangi's, describes the fracture surface conditions as a series of asperities of various heights and cross sections. However, when they modeled the closure of the fractures in response to applied normal stress by analyzing the elastic deformation of the asperities, they found poor agreement with Iwai's data for flow through fractures in granite. Iwai (1976), measuring the contact areas on the fracture surface at a stress of 20 MPa, found them to be 10 to 20% of the total surface area. Contact areas computed from the asperity model amounted to only 0.1% of the total area unless Young's modulus of the asperities was assumed to be two orders of magnitude less than that of the intact rock. This discrepancy was considered unreasonable, and Tsang and Witherspoon (1981) developed an alternative method to evaluate the deformational characteristics of a fracture and the influence of applied normal stress on fracture conductivity.

As shown in Fig. 4, Tsang and Witherspoon's model considers the fracture to be composed of a series of voids with lengths $2d_j$. When the normal stress (σ) is increased, the number of asperities in contact with the fracture surfaces increases and the width of the voids between contact points decreases. Walsh (1965) derived an expression for the effective modulus (E_{eff}) of rock containing a

Figure 3 Schematic representation of a fracture by an asperity model.

Figure 4 Deformation of voids under increasing normal stress. (a) At normal stress σ_1 . (b) At normal stress $\sigma_2 > \sigma_1$. (c) At normal stress $\sigma_3 > \sigma_2$.

number of voids oriented normal to the direction of loading. As shown in Fig. 5, E_{eff} is given by

$$\frac{1}{E_{\text{eff}}} = \frac{1}{E} + \frac{4\pi \langle d^3 \rangle}{E \langle u \rangle} \quad (5)$$

where the half void length cubed (d^3) and the small volume of rock ($u = \Delta x \Delta y \Delta z$) immediately surrounding each void have been averaged over all the voids in the sample and where E is the intrinsic modulus of the rock containing no voids. Equation 5 describes a system of sparse voids where the perturbation of the stress field caused by the presence of one void does not influence conditions in the near field of another void. As shown in Fig. 4, however, a fracture is more accurately represented by a large number of voids in close proximity, and the total fracture area in contact is small so that if there is a spa-

Figure 5 Geometry of a flat elliptical void in a rock under stress.

tially random number of voids (M) in the fracture

$$\langle (2d)^2 \rangle M \approx A \quad (6)$$

and

$$\langle d^3 \rangle \approx \langle d^2 \rangle \langle d \rangle \quad (7)$$

where A is the total area of the fracture surface. For these conditions Tsang and Witherspoon (1981) proposed that the deformation modulus of the fracture is best represented by E_{eff} ; thus Eq. 5 can be modified to

$$\frac{1}{E_{\text{eff}}} = \frac{1}{E} + \frac{4\pi \langle d^3 \rangle}{E_{\text{eff}} \langle u \rangle} \quad (8)$$

and, from Eqs. 6 and 7, further simplified to yield the approximation

$$\frac{E_{\text{eff}}}{E} \approx 1 - \frac{\pi \langle d \rangle}{\Delta z} \quad (9)$$

where Δz is the distance across the fracture plane over which E_{eff} applies. Values for E and E_{eff} can be obtained from stress-displacement data from intact and fractured specimens of the same rock type, such as those shown in Fig. 6.

Figure 6 Typical normal stress displacement behavior for intact and jointed rock.

As illustrated in Fig. 4, increasing normal stress on the fracture reduces the average void length ($2\langle d \rangle$) and increases the number of contact points (N_c) where asperities bridge the surfaces of the opening. In Fig. 3 the fracture roughness is represented by an array of asperities with varying heights (h_j). At zero applied stress the maximum aperture is b_0 , corresponding to an asperity height of zero. Applying normal stress produces fracture closure ΔV , and the correspondence between aperture and asperity height is

$$b =$$

$$\begin{cases} (b_0 - \Delta V - h) & h < (b_0 - \Delta V) \\ 0 & h \geq (b_0 - \Delta V) \end{cases} \quad (10)$$

If $n(h)$ is the characteristic asperity height distribution function before loading, the total number of asperities in contact is given by

$$N_c(\Delta V) = \int_{b_0 - \Delta V}^{b_0} n(h) dh \quad (11)$$

Thus the asperity height distribution $n(h)$ can be computed from the derivative of N_c . However, because b_0 is not known and Eq. 9 only provides the change in $\langle d \rangle / \Delta z$ relative to conditions at zero stress, $n(h)$ can be determined only to some constant multiplier. If, however, a functional form exists for $N_c(\Delta V)$ and if the fractional areas (ω) of the total fracture surface occupied by the contact points is known at a specified deformation (ΔV), b_0 can be determined because

$$\omega = \frac{N_c(\Delta V)}{N_c(b_0)} \quad (12)$$

On the basis of the asperity model shown in Fig. 3, Tsang and Witherspoon (1981) expressed the cubic law in the form

$$Q/\Delta h = C\langle b^3 \rangle \quad (13)$$

where C is a proportionality constant that depends on the macroscopic fracture dimensions and the properties of the fluid. The statistical average of the variation of aperture is then obtained from

$$\langle b^3(\Delta V, \delta) \rangle = \frac{\int_0^{b_0 - \Delta V} (b_0 - \Delta V - h)^3 n(h) dh}{\int_0^{b_0} n(h) dh} \quad (14)$$

Thus, if an estimate of the contact area of the fracture can be made for any stress and if stress-displacement data are available for the intact rock and for a specimen containing a fracture, the flow through the fracture can be obtained from Eq. 14.

Flows predicted by Eq. 13 were compared with the experimental data of Iwai (1976) from radial flow tests on a normally loaded fracture in a granite specimen. The theoretical and experimental relationships between flow per unit head and normal stress are compared in Fig. 1 for one cycle of loading and unloading. Stiffness properties in Eq. 9 were obtained from the deformation measurements made on the fractured specimen and the deformation properties of intact specimens of the same rock. On the basis of Iwai's measurements (1976), which indicated that ω is between 10 and 20%, the contact area (ω) at maximum applied stress was assumed to be 15% of the total surface area. No curve fitting was involved in making the flow predictions, and the good agreement between the theoretical and experimental results suggests that the analytic procedure reliably models the phenomena controlling flow through a rough, deformable fracture under applied normal stress.

Tests on Ultralarge Specimens of Fractured Rock

Permeability tests on an ultralarge specimen of rock containing a fracture were first performed by Gale (1975), who investigated the hydraulic properties of an artificially induced fracture in a 1-m-diameter by 2-m-high cylindrical specimen. This work was performed using the very large triaxial testing machine shown in Fig. 7. This equipment, originally designed to study the constitutive properties of rock-fill materials (Becker, Chan, and Seed, 1972), has an axial load capacity of 17.8 MN, and the vessel is rated for 5.2 MPa working pressure. The facility has been adapted for fracture conductivity and permeability experimentation on ultralarge specimens of rock. To evaluate the feasibility of sampling, instrumenting, and testing a very large volume specimen of a fractured rock mass, we obtained the 1-m-diameter by 2-m-high cylindrical specimen of granitic rock (quartz-monzonite) from the Stripa mine in Sweden. The Stripa mine is the site of a series of large-scale, in situ, hydrologic and geotechnical experiments that are part of the Swedish-American Cooperative Program on Radioactive Waste Storage in Mined Caverns in Crystalline Rock (Witherspoon and Degerman, 1978). The specimen (see Fig. 8) was recovered from the rib of a mine entry by drilling a circular pattern of horizontal holes around its periphery while it was held in compression by a rock bolt through the central axis (Andersson and Halén, 1978). After it was shipped to the laboratory, the specimen was prepared for testing by capping with reinforced concrete. As shown on the fracture map of the surface of the specimen (Fig. 9), the rock was pervasively fractured with two sets of principal discontinuities, one oriented normal to the long axis (A, B, and C) and one steeply inclined (D, E,

Figure 7 Large triaxial testing machine.

Figure 8 Ultralarge core of granitic rock from Stripa, Sweden.

and F). The fracture filling material was predominantly chlorite and sericite, with lesser amounts of epidote, calcite, and other minerals.

The specimen was tested in the large triaxial machine (Fig. 7). The test procedure took the form of a modified unconfined compressive strength test in which the axial loading, at a rate of 0.5 MPa/min, was interrupted and held constant at several stages. At each constant load stage, permeability tests were performed by injecting water into (divergent flow) and withdrawing water from (convergent flow) a borehole drilled through the axis of the specimen. The test configuration is shown

schematically in Fig. 10. The triaxial vessel was filled with water at a pressure of 1400 kPa throughout the test to ensure saturation of the sample and to keep air in solution. Linear variable differential transformers (LVDTs) and strain gauges were mounted on the specimen to measure overall axial deformation, circumferential strain at mid-height, deformation of the principal fractures, and strains in the rock matrix. The locations of these instruments are shown in Fig. 9.

The results of these experiments on the Stripa specimen were reported in detail by Thorpe et al. (1980). A peak stress of 7.4 MPa was attained

Figure 9 Fracture map showing locations of instrumentation on Stripa granite specimen.

at 0.06% axial strain before the onset of generalized failure of the specimen. This peak stress was much lower than the average unconfined compressive strength of 100 MPa measured from small 5.2-cm-diameter samples of granitic rock obtained from the Stripa mine. However, the tangent modulus of deformation measured before failure of the large specimen was 52.3 GPa, which is within the range obtained from small diameter samples. The failure kinematics were complex, involving tilting of the top of the specimen, creep deformation, and nonlinear shearing motions. New fractures were developed in previously intact portions of the specimen, and pre-existing fractures were opened, as shown in Fig. 9.

Results from the permeability tests on the Stripa specimen are shown in Fig. 11 in the form of hydraulic conductivity vs. applied axial stress. The results from the Stripa rock are compared with results of previous laboratory and in situ tests in which normal stresses were applied to a single fracture. Although the permeability of pervasively fractured specimen was much greater than that of the others, it initially exhibited the characteristic reduction in permeability with increasing axial loading. As the axial stress was increased from zero to 5.56 MPa, the permeability decreased from 14.64 to 3.04 cm/s. Before generalized failure of the sample, however, there was a rapid increase in permeability to 7.67 cm/s; this was

Figure 10 Schematic of test arrangement for Stripa specimen.

associated with shear dilatancy and fracture opening. Increased permeability was not unexpected but has not previously been observed in laboratory tests. Similar changes in rock mass permeability caused by shear deformations can be expected to occur in the near field of a nuclear waste repository as a result of perturbations of the stress field caused by excavation and thermal loading.

Because of the complexity of the flow regime through the pervasively fractured specimen, it was not possible to establish a simple relationship between permeability and fracture deformations. There was evidence, however, from preliminary falling-head permeability tests that the horizontal fracture B (see Fig. 9) was the dominant flow path. The inclined

fracture D showed the second highest conductivity but carried only about 10% of the flow through fracture B. Flow through fracture C, the third most conductive, was less again by an order of magnitude. On the basis of these observations, Thorpe et al. (1980) performed an analysis of flow through fractures B and D only and investigated the ability of a simplified model to predict the changes in hydraulic properties of the rock mass as a result of fracture deformation. The model assumed that all flow occurred through fractures B and D and that they could be treated as hydraulically independent systems of flow in which the cubic law for laminar flow between smooth parallel plates is valid. Total flow through the model was the sum of the flows through B and D. Estimates of the absolute aperture of the fractures were made in two ways. In one method the initial apertures at zero

Figure 11 Changes in conductivity in response to applied stress.

applied stress were estimated from the asymptotes of the load-displacement data obtained from the LVDT instrumentation. Absolute apertures at higher loads were then computed by subtracting the observed fracture displacements from these values. In the second method initial apertures were estimated by applying the cubic law to flow data obtained in preliminary falling-head permeability tests performed under zero axial load. Figure 12 compares values of flow measured in the laboratory tests with those estimated from the simplified two-fracture model using both methods to calculate the initial apertures of fractures B and D. Although there is considerable discrepancy between the measured and estimated flows, the general characteristics of the relationship between permeability and applied stress are predicted by the simple two-fracture model. The initial decrease in permeability caused by application of axial stress is reproduced by the model, as is the rapid increase in permeability associated with the onset of shear dilatancy and

Figure 12 Flow through the Stripa specimen compared with flows estimated from simplified model.

fracture opening that occurred during failure of the specimen. Considering the complexity of the fracture system in the Stripa specimen and the gross simplifying assumptions made in the analysis, the correlation between measured and computed values, although they differ by approximately an order of magnitude, is surprisingly good. This suggests that, in rock masses containing well-defined systems of fractures, analytic procedures based on available models of flow through discrete fractures could be used to predict changes in rock mass permeability caused by thermomechanical loading. It must be recognized, however, that, in rock masses where flow is not dominated by a few discrete discontinuities, analytic methods based on a continuum model may be more appropriate (Hubbert, 1956; Witherspoon et al., 1981). In practice, analysis of the hydrologic aspects of site selection and design of nuclear waste repositories will rely on data obtained by a variety of techniques, including not only laboratory and in situ test programs but also important contributions from the disciplines of geology and geophysics (Watkins and Thorpe, 1981).

Witherspoon et al. (1979) compiled the data from tests on the single, normally loaded fractures presented in Fig. 11. Because the conductivity of fractures under high normal stress obtained from large specimens was considerably greater than conductivities measured from small specimens, it was concluded that there may be a significant size effect that influences the measured hydraulic properties of fractures in rock. An experimental program has been initiated to test single natural fractures with areas up to 0.66 m² to investigate this phenomenon further and to make more detailed studies of the relationships between fracture conductivity, stress, and deformation. Cylindrical specimens containing a natural frac-

Figure 13 Fractured block of Charcoal Black granite.

ture at mid-height oriented normal to the long axis have been prepared from large blocks of Charcoal Black granite quarried near Cold Spring, MN. Figure 13 shows a massive block of granite from which the 0.914-m-diameter by 1.83-m-high specimen shown in Fig. 14 was prepared. A rock bolt was called in a hole drilled through the granite block before it was reduced to cylindrical form with the wire saw jig shown in Fig. 15 with the purpose of minimizing disturbance to the natural fracture (Watkins, 1981). Figure 16 is a map of the periphery of the finished specimen showing the location of the principal fracture (B) that passed through the diameter and the LVDT and strain gauge instrumentation used to monitor the deformations caused by

applied axial load. Preliminary tests showed that secondary fractures A, C, D, and E did not have significant hydraulic connectivity with fracture B. The test procedure used to study the hydraulic characteristics of the fracture was similar to that used in the experiments on the Stripa specimen, except that the central borehole was packed off immediately above and below fracture B to minimize flow through the rock matrix and measurements of conductivity were made through several cycles of loading and unloading.

Experiments on the ultralarge specimens of Charcoal Black granite are still in progress, but Fig. 17 summarizes the relationships obtained to date between fracture conductivity

Figure 14 Instrumented specimen of Charcoal Black granite.

Figure 15 Cutting a granite specimen with a wire saw. (Photograph courtesy of Cold Spring Granite Co.)

Figure 16 Map of the surface of the Charcoal Black granite specimen showing fractures and locations of instruments.

Figure 17 Relationship between flow through a natural fracture and axial stress for specimens of Charcoal Black granite.

and axial stress. Results are presented from two series of tests. One series of experiments was performed on the 0.914-m-diameter specimen, and a second series was performed on the same specimen after it had been reduced in size to 0.764 m in diameter. In each case the data show the effect of successive cycles of axial loading and unloading. The conductivities of the fracture in the 0.764-m-diameter sample were typically two orders of magnitude greater than those in the specimen when its diameter was 0.914 m. This result appears to contradict the observation of decreasing conductivity with decreasing specimen size from the data com-

piled in Fig. 11. However, a careful analysis showed that the fracture had suffered small but significant disturbance while the sample was being reduced in size. This sensitivity of the hydraulic properties of fractures to disturbance illustrates the importance of mining-induced changes in rock mass permeability which can occur around underground openings constructed for disposal of nuclear waste.

As shown in Fig. 17, the effect of repeated cycles of loading and unloading on fracture conductivity is to progressively decrease the conductivity. Figure 18 illustrates unit flow rates measured at similar levels of normal stress after application of different numbers of load cycles. These data illustrate a number of phenomena that reflect the effects of cyclical loading on the constitutive properties of the material forming the walls of the fracture. The permanent reduction in conductivity as a result of hysteresis is greatest after the first loading cycle, and the change caused by each successive cycle is progressively less. Decreased conductivity per cycle of loading is significantly reduced after the fracture has been subjected to high normal stress, as is shown by the relatively flat curve on Fig. 18, which shows unit flow rates measured at a normal stress of 13.5 MPa. These findings are compatible with the stress-deformation data obtained from the LVDTs mounted across the fracture and are further evidence that permeability is a function of the stress history of a rock mass. Cyclical changes in stress in the rock surrounding a waste repository will occur as a result of the construction of openings and the temperature changes caused by ventilation and the heating and subsequent cooling that accompanies radioactive decay of the waste. The results shown in Figs. 17 and 18 indicate that cyclical changes in the normal stress on fractures in a rock

Figure 18 Change in unit flow rate with cycles of loading and unloading (0.914-m-diameter specimen).

mass should not result in increased permeability if the stress at the end of the loading cycle is at least equal to the initial in situ stress.

Conclusions

The cubic law of flow through fractures in rock is based on the analogy of flow through smooth parallel plates and states that the flow per unit head is proportional to the cube of the fracture aperture. By introducing suitable parameters to account for fracture roughness and contact area, we have shown that the cubic law is valid for flow through rough deformable fractures in crystalline rocks subjected to normal stresses over a wide range of practical interest (0 to 20 MPa). A model for flow through deformable fractures that explicitly incorporates fracture roughness and contact area has been developed and successfully tested in laboratory experiments. The model accounts for changes in conductivity as a result of changes in normal

stress by treating the flow paths as a series of interconnected deformable voids. The model can be used to predict flow rates through natural fractures if an estimate of the fractional contact area of asperities that bridge the fracture aperture can be made and if stress-deformation data for the intact rock and a specimen containing the fracture is available. These data can be obtained from laboratory or in situ tests so that the model has considerable potential for practical application in modeling flow through fracture systems of the type expected to be encountered in the rock mass surrounding a deep underground nuclear waste repository constructed in crystalline rock.

Measurement of the permeability of a rock mass and the conductivity of fractures can be influenced by the size of specimens used in laboratory experiments. Sample gathering, preparation, and testing techniques have been developed to investigate these effects and to study the basic phenomenology controlling flow through fractures by testing naturally fractured cylindrical specimens up to 1 m in diameter by 2 m high. Work completed to date has shown that the hydraulic properties of fractures are sensitive to sample disturbance and stress history. Although gross simplifying assumptions must be made to apply theoretical models to a pervasively fractured rock mass, comparing model predictions with experimental results from an ultralarge specimen of fractured granite showed that simple models successfully reproduce the trend of reducing permeability caused by initial application of axial stress and also reflect the increase in fracture conductivity associated with dilatancy caused by shear displacements. On the basis of these studies, it appears reasonable to expect that, with further refinement of the theoretical models and experimental techniques, reliable procedures can be developed to

analyze the flow regime in a crystalline rock mass surrounding a nuclear waste repository and to predict the effects of changes of stress that are induced by construction and the heat generated by the waste form.

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Nomenclature

A	Total area of fracture surface
b	Fracture aperture
b_d	Apparent aperture
b_r	Residual aperture
C	Proportionality constant
d	Half length of a void
b_0	Maximum fracture aperture
E	Young's modulus of intact rock
E_{eff}	Effective modulus of fractured rock
f	Factor accounting for fracture roughness, etc.
k_f	Fracture conductivity
M	Number of voids
$N_c(\Delta V)$	Number of areas of contact in fracture
$n(h)$	Asperity height distribution function
Q	Flow
$Q/\Delta h$	Flow per unit head
x, y, z	Cartesian coordinates
ΔV	Normal deformation of fracture
ΔV_m	Maximum normal deformation of fracture
σ	Normal stress
ω	Fractional contact area of fracture

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Part II Repository Perturbations of the Natural System

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Thermomechanical Studies in Granite at Stripa, Sweden

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Media other than rock salt are being considered for the deep, geologic disposal of nuclear wastes. The disposal of high-level nuclear waste in a deep, underground repository will subject the rock to a thermal pulse that will induce displacements, strains, and stresses in the rock. Thermomechanical experiments, with electrical heaters simulating the thermal output of waste canisters, were carried out in granite at a depth of 340 m below surface adjacent to a defunct iron ore mine at Stripa, Sweden. Changes in temperature, displacement, and stress in the rock around these heaters were measured, and the measurements were compared with predictions calculated from the theory of linear thermoelasticity. Measured temperature changes agreed well with predictions, but measured displacements and stresses were consistently less than those predicted with constant values for the coefficient of thermal expansion and elastic properties of the rock. A laboratory test program to measure these coefficients over ranges of stress and temperature representing those in the field experiment has been initiated. Test specimens were taken from cores recovered from the instrumentation holes in the Stripa experiments. Preliminary results from laboratory tests on specimens free of joints

indicate that the values of Young's modulus and Poisson's ratio increase from about 60 to 80 MPa and from 0.15 to 0.22, respectively, as the confining stress is increased from 2 to 55 MPa; these values decrease with increasing temperature, more so at 2 MPa than at 55 MPa. The linear coefficient of thermal expansion at a confining stress of 30 MPa increases from about $10 \times 10^{-6}/^{\circ}\text{C}$ at 40°C to about $14 \times 10^{-6}/^{\circ}\text{C}$. The magnitudes of these changes are not sufficient to resolve the disparity between measured and predicted results. Perhaps the properties of test specimens containing joints will show greater variations in the values of the thermomechanical coefficients with temperature and pressure.

Introduction

Geological disposal of nuclear wastes within excavations made at depth in suitable media has long been and continues to be favored as the currently most practicable means of isolating wastes from the biosphere over the long term (National Academy of Sciences, 1957; Interagency Review Group on Nuclear Waste Management, 1978). The significant body of experience that exists concerning underground excavation does not include the effects of heat generation on

excavations and the geologic media. Some of the effects on salt have been assessed in Project Salt Vault (Bradshaw and McClain, 1971), but it is now agreed that other media must be examined (Interagency Review Group on Nuclear Waste Management, 1978). Access to tunnels driven into the granite country rock 340 m below surface adjacent to a defunct iron ore mine at Stripa, Sweden, provided a unique opportunity for experimenting in granite without delay and at minimal cost at a depth where conditions of stress, jointing, groundwater, and other factors likely to be encountered at the site of an actual waste repository exist.

In Situ Experiments

The disposal of high-level nuclear waste deep underground will cause the geologic media in the vicinity of such a repository to undergo a thermal pulse, which will induce thermo-mechanical displacements and stresses in the rock. In general, the displacements will be directed away from the source of the heat while the temperature is increasing and then will tend to return as the temperature decreases. Likewise, the thermo-mechanical stresses will add compressive stresses to the virgin state of stress in the rock within the heated zone and shear and tensile stresses outside of it.

Transport by groundwater is the most probable mechanism by which components of the wastes may find their way back to the surface. The intrinsic permeability of many granites is so low that the only hydraulic conduits of concern arise from joints and fractures in rock masses. Clearly the thermomechanical perturbations may have significant effects on the hydraulic transmissivity of such features. Accordingly, it is necessary that the effects of these perturbations be understood if the utility of a geo-

logic formation as a site for a potential waste repository is to be evaluated properly. Furthermore, a repository cannot be designed and its performance in the long term cannot be predicted without such an understanding (Cook and Witherspoon, 1978).

The value of field experiment depends on the extent to which they provide sufficient understanding of the phenomena involved to enable transferral of results to other sites where repositories may be built. The Stripa program involves collecting sufficient field and laboratory data to ensure that their analyses will provide either a high degree of understanding of the behavior of the rock mass or an identification and definition of crucial issues requiring further research.

Three different thermomechanical experiments were carried out at Stripa (Cook and Hood, 1978). The first was designed to study the short-term, near-field effects around an electrical heater simulating a full-size canister of reprocessed high-level waste. The second was a similar experiment designed to study the long-term, near-field effects. The third experiment was time-scaled and designed to simulate the interaction of canisters placed either 9.6 or 22.4 m apart over a period equivalent to about two decades, as a function of the quadratic relationship between time and distance in linear thermo-elasticity (Carslaw and Jaeger, 1959).

The power levels of the two full-scale heaters were 3.6 and 5 kW, which correspond to levels projected for reprocessed fuel 5 and 3.5 yr after discharge from the reactor (Office of Waste Isolation, 1976). These power levels, in combination with the peripheral heaters used in the second stage of the 5-kW heater experiment to simulate the effects of increasing the temperature of the rock containing a waste canister, produced thermal stresses on the walls of the

boreholes containing the heaters below, at, and above those sufficient to cause decrepitation (Hood, Carlsson, and Nelson, 1979). This enabled researchers to define the conditions causing decrepitation (Fig. 1).

Power to the heaters was turned off in June 1979. Continuous measure-

ments were made during the cool-down period, as they were during the heat-up period. It is expected that a substantial amount of additional information, especially concerning nonlinear phenomena, will be obtained by analysis of hysteresis over the full thermal cycle.

Figure 1 Axial section through the 5-kW full-scale heater, with sketches of bore scope views of portions of the hole containing this heater at 7, 97, 211, and 232 d after the start of heating, illustrating the decrepitation of the borehole wall caused by thermally induced stresses, the magnitudes of which are given. Note that the gross decrepitation caused by the additional stress induced by turning on the eight peripheral heaters on day 204 impeded the radiant heat transfer from the heater to the rock, causing the temperature of the heater to increase by about 100°C.

Thermal and Thermo-mechanical Analysis

On the basis of the theory of linear thermoelasticity and properties of the granite measured in conventional small-scale laboratory tests, the results of all three experiments—i.e., the expected temperature, displacement, and stress fields as functions of time—were predicted in advance of the collection of field data. The field data were collected in such a way as to allow comparisons between theoretical predictions and underground measurements made continuously during the experiment. To date the comparisons have shown that the use of simple linear heat conduction provides an adequate prediction of the temperature fields around the experiments (Figs. 2 and 3). According to the theory of linear thermoelasticity, displacements should be related to temperature fields by a simple factor, $\alpha_l[(1 + \nu)/(1 - \nu)]$, where α_l is the linear coefficient of thermal expansion of the rock and ν is Poisson's ratio for the rock. All the measured displacements differ significantly from predicted values in two different ways (Fig. 4). First, initial displacements, which are of the order 100 m/m, are highly nonlinear, reflecting possibly the effects of joints in the rock. Second, greater displacements than these appear to be linear but to have a magnitude only about half that expected from values derived from simple laboratory measurements. Likewise, the stresses appear to have values different from that given by the temperature field and a factor $\alpha E/(1 - \nu)$, where E is Young's modulus of the rock, and the other symbols are as defined for the previous factor (Fig. 5) (Cook, Gale, and Witherspoon, 1979; Hood, 1979).

Another possible contribution to the discrepancies between predicted and measured values may come from the fact that the temperature depen-

dence of the thermomechanical properties was not included in the predictive model. Subsequent work has been directed at studying the effect of temperature- and stress-dependent properties on predicted stresses and displacement. An indication of the improvement in displacement predictions is shown in Fig. 6 (Chan, Hood, and Board, 1980). These results indicated the importance of considering temperature-dependent properties, but they are preliminary in that the data base for the properties was incomplete and insufficient in a number of tests.

Figure 2 Horizontal plane through the middle of the 5-kW full-scale heater showing the predicted isotherms (dashed lines) and the actual temperatures (squares with numbers) measured along different directions at 190 d after the start of heating. Note the relatively good correlation between measurement and prediction and the high degree of axial symmetry. Scales on the x and y axes are in meters.

Figure 3 Horizontal plane through the middle of the array of eight time-scaled heaters (black squares) showing the predicted isotherms (dashed lines) and the measured temperatures (squares with numbers) at 190 d after the start of the experiment. Actual distances between the heaters are given in meters along the x and y axes. Spacing between heaters corresponds to 7 and 22 m for full-scale heaters, and temperatures correspond to those at 1938 d (5.3 yr) because of the time scaling.

Although an expanded data base is needed, discrepancies between measured and predicted values may continue. It is important to note that the disparities between measurement and predictions made by using simple theory and laboratory data should not be regarded as evidence of a lack of predictive capability but rather as a means for identifying and understanding the important difference in behavior between a rock mass and laboratory specimens of rock.

Thermomechanical Properties Investigation

A laboratory program to more thoroughly investigate the thermoelastic properties of the Stripa rock mass is presently under way. The core from every instrumentation hole at Stripa was kept. Thus properties can be obtained from specimens of core taken from the same holes in which measurements of displacements and stresses were previously made. Tests are performed over a range of tem-

perature and hydrostatic and deviatoric (unequal axial and radial) stresses to bracket stresses and temperatures experienced by the rock in the field. Planned tests include dry, wet, intact, and fractured samples, but only intact, dry specimens have been tested to date. Results of the test program will be used to refine the predictive models, incorporating any non-linear properties revealed by the tests.

The laboratory program began with the development of a test facility emphasizing thermomechanical property measurement capabilities. Figure 7 is a photo of the test frame and power pack. The stiff triaxial test machine is capable of providing a maximum confining pressure of 70 MPa and a maximum axial load of 1.4 MN. Independent systems for heating and cooling the cell are provided, with a maximum sustained test cell temperature of 200°C. A core either 52 or 62 mm in diameter, with a length-to-diameter ratio of 3 to 1, can be accommodated by the test cell. Confining pressure and deviator stress

Figure 4 (a) Predicted (dashed line) and measured (solid line) displacements between anchor points situated 3 m above and below the mid-plane of the 5-kW heater and at a radial distance of 2 m as a function of time. (b) Plot of the ratio between measured and predicted values as a function of time. Note the initial non-linearity of the displacements and their subsequent linear, but lower than predicted, behavior.

loading paths are controlled by an electroserve control system using a PDP 11/44 computer to close the feedback control loop (Fig. 8). Such a sys-

Figure 5 Predicted (dashed lines) and measured (solid lines) changes in stress as a function of time, inferred from a vibrating-wire borehole strain gauge located 0.85 m above the midplane and 1.5 m radially from the 5-kW full-scale heater.

tem was necessary to maintain test control for the extended periods of time required for testing each sample. Automatic data acquisition was also integrated into the computer control system.

Bracketing the in-situ temperature and stress conditions by a test matrix in which one sample was tested at each selected pressure-temperature (P-T) state would require an exceedingly large number of samples for statistically meaningful data. Therefore each sample is subjected to a matrix of P-T states, with the test sequence designed to minimize sample damage (Fig. 9). Property measurements are begun at the highest pressure and lowest temperature, and sample temperature is increased by not more than $2^{\circ}\text{C}/\text{min}$. In addition, the maximum axial load applied for stress-strain measurements is 40% of the average strength at the given confining pressure and temperature, as determined by Swan (1978).

Figure 6 Measured and predicted rock displacements in the vertical plane between anchor points 2.24 m above and below the heater midplane for an extensometer at a radial distance of 1 m from the 3.6-kW heater. Predicted displacements for both temperature-dependent and temperature-independent material properties are shown, along with measured and predicted displacements during the cool down after the heater was turned off.

Laboratory testing is not complete, but preliminary results indicate general trends in the data. Elastic moduli were found to be somewhat dependent on stress state and temperature, as seen, for example, in Figs. 10 and 11. At confining pressures less than 30 MPa, increasing temperature resulted in lower moduli. Peculiarly, at high confining pressures, E increased somewhat at higher temperatures, whereas ν continued to exhibit a decreasing trend. Comparison of data at one temperature shows that the rock stiffness increased at the higher confining pressures. This effect was more pronounced at the highest test temperatures. Figures 10 and 11 also present data by Swan (1978) for Stripa granite, which exhibit some discrepancies as yet unexplained.

Thermal expansion measurements were made every 25°C during heat

up and cool down to determine the dependence of the thermal expansion coefficients on confining pressure and temperature. This dependence is illustrated by Fig. 12 for the volumetric coefficient of expansion, α_v , obtained during heat up for one sample. For a given confining pressure, there is a significant increase in the thermal expansion coefficient with increasing temperature. The effect was less, however, at higher confining pressures. For a given temperature, an increase in confining pressure resulted in a decrease in α_v for the data in Fig. 12, but it is not clear that this represents a general trend. The data points in Fig. 12 represent values of α_v determined by assuming a straight-line relationship between adjacent data points, whereas the curves represent values of α_v derived from a polynomial regression analysis of the thermal

Figure 7 Photo of test equipment showing the various components. From left, stiff testing frame with test cell in place, power pack with electric-motor-driven pumps, and instrumentation rack.

Figure 8 Schematic of test control system illustrating mechanism for independent control of axial load and confining pressure by computer. Abbreviations are LC, load cell, and PT, fluid pressure transducer. Computer adjusts electric-motor-driven pumps according to signals received from transducers in test system. Pumps can also be controlled manually from the motor control console.

Figure 9 Test sequence for property measurement. Arrows indicate the manner in which the testing proceeded from one pressure-temperature (P-T) state to the next. ○, thermal expansion measurements; ●, thermal expansion measurement and stress-strain test. Symbols represent the P-T state at which either elastic moduli or thermal expansion measurements were made.

Figure 10 Measurements of Young's modulus (secant modulus) at confining pressures of 55 and 2 MPa and test temperatures from room temperature to 200°C. Data are from one sample (No. E024.38-4.57). Data obtained by Swan (1978) for Stripa granite under unconfined conditions are shown for comparison.

Figure 11 Measurements of Poisson's ratio at confining pressures of 55 and 2 MPa and test temperatures from room temperature to 200°C. Data are from sample E024.38-4.57. Data obtained by Swan (1978) under unconfined conditions are shown for comparison.

Figure 12 Volumetric coefficient of thermal expansion determined at 55 MPa confining pressure over a temperature range from room temperature to 175°C. Data are from sample E020.32-0.51. Data points represent values of α_v calculated by assuming a linear relationship between strain and temperature for an incremental increase in temperature. Curves represent values of α_v derived from a polynomial regression analysis of the data.

expansion data. The shape of the curve is related to the degree of polynomial selected as the "best fit" of the data and does not have any particular physical significance. Curve fitting, though useful in smoothing and sometimes in defining trends, should not be considered a replacement for sound theoretical work in defining functional relationships between variables. Use of regression analysis of the thermal expansion data, in fact, reflects the need for further theoretical work in the area of thermomechanical constitutive relations for rock to better define the functional relationship between thermal expansion and temperature.

Figure 13 compares values of α_q for one test at a confining pressure of 30 MPa with those of Heard and Page (1982) and Board (1980), who also

studied Stripa granite. The values of α_q were significantly higher at low temperature than those of the other investigators, but the rate of increase with temperature was less. Further testing, now in progress, will aid in understanding these discrepancies, as well as lead to increased confidence in the trends observed thus far.

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Figure 13 Comparison of the one-dimensional coefficient of thermal expansion α_L at 30 MPa confining pressure for sample E020.32-0.51 with other data obtained for Stripa granite. Values of α_L calculated by assuming a linear relationship between strain and temperature for an incremental temperature increase.

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Dome-Salt Thermomechanical Experiments at Avery Island, Louisiana

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An overview is given of three heater tests at Avery Island, Louisiana. The design considerations and operating conditions are described relative to the stated objective of each of the tests, and the data obtained to date are presented. An analysis of the results will be presented in the future. Measurements of temperature, heat flux, and displacement are presented. These three categories of measured responses were the most reliable and also are readily comparable with calculated responses. Determinations of induced stress in the salt and backfill pressure measurements in the heater borehole were not considered successful. Results are not presented for these measurements. The information presented is important for understanding the response of salt to an imposed heat source.

Introduction

Three long-term heater tests were conducted at Avery Island, Louisiana, to acquire thermal and mechanical data that will aid in identifying and understanding various responses of domal salt to imposed heat sources. Knowledge of these responses is required to design a repository in rock salt for the ultimate disposal of nuclear waste. Because nuclear wastes generate heat, heat will be transferred into the surrounding rock. This will result in increased rock tem-

peratures that induce thermomechanical responses, such as thermal expansion, and possibly thermochemical responses, such as brine migration. Identifying and understanding the various responses of the formation are necessary to design a storage facility capable of providing environmentally and economically acceptable disposal for nuclear waste.

Previously, heater tests were performed in Project Salt Vault in bedded salt near Lyons, KS (Bradshaw and McClain, 1971). Project Salt Vault used both actual radioactive waste and electrical heaters to impose the heat load on the rock. The Avery Island heater tests are extensions of this previous work in bedded salt to domal salt. No nuclear waste or radioactive material of any kind was used in the Avery Island tests, however.

Each of the three heater tests at Avery Island used an electrically-heated simulated waste canister with a different power level. The simulated canisters were 3.5 m in length with an effective heating length of about 2.6 m. The heaters were located inside 30-cm-diameter steel sleeves situated in 41-cm-diameter boreholes, which were vertical and about 5.5 m deep, with the heater located in the lower portion of the borehole. The heater tests were separated from each other so that each installation simulated a single canister emplacement. Provisions in one of the heater tests allowed for a demonstration of the behavior of a multiple heater emplace-

ment by use of peripheral heaters. Measurements were made to provide data concerning temperature distributions, heat fluxes, displacements, and induced stresses.

Heater Test Description

The Avery Island heater tests consisted of three separate, but neighboring experiments. The location of the heater test was the 500-ft level (150 m below mean sea level) in the Avery Island Salt Mine operated by the International Salt Company. Although the heater tests were similar, sufficient differences existed in their configuration and objectives that each heater test is described separately.

The three heater tests, hereafter referred to as sites A, B, and C, encompassed two types of installations and three heater power levels. The differences in the installations and power levels were predicated by the objective for each test. The objectives for the tests were (Fairchild and Jenks, 1978):

1. Site A, to establish the thermal conductivity and heat capacity of domal salt and provide data for verifying methods of calculating temperatures and displacements in salt subjected to overdrive heating

2. Site B, to establish the thermal and mechanical properties and behavior of domal salt when heated to temperatures of interest for a waste repository in salt and provide information on the closure of an open disposal borehole and the degradation of the borehole surface during heating

3. Site C, to establish thermal and gas atmosphere exposure conditions simulating those expected for a sleeved, backfilled, high-level waste package and determine the corrosion characteristics of the crushed-salt backfill and the amounts of brine and certain gases that enter and are

trapped in the backfill during the heating period

Heater Test Geometry. The simulated waste canisters in each of the heater tests were identical, but the sleeve, borehole size, and annulus condition were different. A summary of the significant differences among the tests is presented in Table 1.

The heaters used at each site were 20-cm-diameter (8 in.) welded pipes (Schedule 40S, type 304L stainless steel) containing two Calrod electric tubular heaters surrounded by cast ALCOA type 443.2 aluminum alloy. The heated length of the canisters was about 2.6 m. The heaters were set on the bottom of the sleeves; thus the heaters were located at elevations 2.9 to 5.5 m below the floor of the test room. [Van Sambeek (1980) described the heaters and their layouts in detail.] Above the heaters, the sleeves were filled to the floor level with vermiculite insulation. The tops of the sleeves were capped to prevent the entrance of moisture from the mine atmosphere, but the caps allowed electrical and instrumentation leads to exit.

The annulus conditions between the outside of the sleeve and the wall of the heater borehole are specified in Table 1. The uppermost 1.5 m of annulus at site A was also filled with rock-wool insulation to reduce the heat loss by convection. At site B a Butyl rubber shroud was attached between the sleeve top (which extended about 0.5 m above the floor) and a metal ring attached to the floor to isolate the annulus from the mine air. The backfill used to fill the annulus at site C was crushed salt with a maximum particle size of about 1 cm.

Selection of Power Levels. The heater tests at sites B and C were designed to provide heating situations comparable to those expected for

Table 1 Key Differences in Heater Test Geometry and Conditions

Characteristic	Site A	Site B	Site C
Power level, kW	6	3	4 + peripheral heaters*
Heater borehole diameter, m	0.44	0.41	0.41
Sleeve size			
Schedule number	80	40S	40S
Inside diameter, m	0.289	0.305	0.305
Outside diameter, m	0.324	0.324	0.324
Annulus condition	Air†	Air	Crushed salt backfill

*The total peripheral heater power was slowly increased from 0 to 5.6 kW during the first 600 d of the test.

†The annulus above the heater elevation at site A became filled with recrystallized salt during the operation of the test. The condition of the annulus at the elevation of the heater is unknown at this time.

emplacement of spent fuel and high-level waste, respectively. Individual canisters containing spent fuel are expected to have power levels of about 0.55 kW; however, numerous emplacements in a regular pattern within a given area are also expected. Thus, although individual emplacements will have low heat input into the surrounding salt, the superposition of the heat input from many such emplacements will result in a temperature distribution across most of the salt. The power level for the site B heater test was selected to produce a temperature distribution approximating that expected for a spent fuel repository. The temperatures within the heater assembly at site B were not intended to be representative of those expected for the spent fuel waste canister.

The primary objective of the site C test was to study the effects produced within the sleeve-backfill-borehole region of an emplacement. The power level of the simulated canister was 4 kW, and the power level of the peripheral heaters was scheduled to produce a temperature field similar to that expected for a gross thermal loading of 37 W/m^2 (150 kW/acre). Thus the simulated waste canister, sleeve, backfill, and the portion of salt

between the central heater assembly and the peripheral heaters (which were located at a 1-m radius) experienced temperatures representative of a high-level waste repository. The portion of salt outside the peripheral heaters did not necessarily experience representative repository temperatures.

The site A heater test was designed to provide data to establish the thermal properties of salt and to verify the methods used to calculate temperatures and displacements in salt subjected to heating. Because both sites B and C heater tests involved heating the salt to expected repository temperatures, a test with a high power level was chosen to best provide these data. A power level of 6 kW was used for the site A test because this power level was the most that the existing power controller could supply to the heater. Peripheral heaters were not included in the test; thus the geometry of site A would be amenable to axisymmetric modeling.

Instrumentation. The numbers and locations of instrumentation in each of the heater tests were based on the objective for the test. At sites B

and C, most of the instrumentation was located within a 1-m radius of the heater centerline. This area encompassed the volume of salt that experienced temperatures representative of repository conditions. At site A the majority of the instrumentation was located within about a 3.5-m radius of the heater centerline. The instrumentation at site A was also closely spaced to provide enough data for comparison with the results of the various methods of predicting salt response.

The primary measurements and techniques used to measure the salt response were:

- Temperature, type K thermocouples
- Heat flux from the floor, surface heat-flux meters
- Differential floor expansion, multiple-point extensometers
- Floor heave, optical level survey
- Heater borehole closure, feeler gages
- Induced stress, vibrating wire stress meters
- Backfill pressure on the site C sleeve, strain gauges*

The actual numbers and locations of the instrumentation are specified in the tables included in the results section.

Results

Temperature Measurements.

Temperatures were measured at more than 200 locations within the three heater test areas. The majority of these readings were taken in the salt surrounding the heaters; however, 31 measurements were made within the heater assemblies. The thermocouples used to measure the salt temperature were deployed in vertical EX (38-mm-diameter) boreholes drilled at various radial distances from the centerlines

of the heaters. Seven thermocouples were included in each borehole at site A, and five or six were included at sites B and C. The temperature sensors within the heater assemblies were attached to the heaters (radial distance 0.11 m), the inside diameter of the sleeves (radial distances 0.14 m), or the outside diameters of the sleeves (radial distance 0.16 m) at each of the sites.

Temperatures measured after 1000 d of heating, are presented in Tables 2, 3, and 4 for the temperature sensors included in the three heater tests. Each table presents data for one of the sites and includes the channel numbers, the locations (specified in r-z coordinates), and the measured temperatures for each sensor in that heater test.

As an example of the temperature history within each of the heater tests, the measured temperatures at a radial distance of about 0.3 m are shown as a function of time in Fig. 1. A separate curve is shown for each elevation at which thermocouples were located.

At site A (Figure 1) the downward trend in the curves between days 100 and 250 is attributed to a gradual decrease in the power level of the heater because of a malfunction in the power controller. After the power controller was repaired and returned to a full 6-kW power level, the temperatures began to rise again. At site C the temperatures in the salt continued to increase for a longer time because of the increasing power level of the peripheral heaters. Temperatures, plotted as a function of radial distance from the heater centerlines for each of the heater tests, are presented in Fig. 2 for a period of heating of 1000 d.

Heat Flux Measurements. Three heat-flux meters attached to the floor near the site A heater test were used to measure both the heat flux through

*These gauges failed very early in the test and are not discussed.

Table 2 Measured Temperatures in the Salt After 1000 d at Site A

Channel number(s)	Radial distance from heater center-line,* ft	Nominal elevation,† ft						
		-0.17	-4.2	-9.2	-13.2	-17.2	-22.2	-27.2
		Temperature, °F						
T/C 108 to 114	0.99	95.8	132.2	253.8	312.4	257.8	121.5	99.7
T/C 115 to 121	1.03	94.9	128.4	238.1	302.9	238.1	118.1	99.9
T/C 101 to 107	1.24	95.2	128.9	231.3	284.8	233.4	118.6	100.2
T/C 122 to 128	1.30	93.5	129.7	221.3	282.4	237.9	120.3	100.4
T/C 94 to 100	1.52	93.9	126.1	215.3	259.6	213.7	117.4	100.1
T/C 129 to 135	1.54	94.3	123.7	207.9	257.8	210.4	118.1	99.9
T/C 136 to 142	1.90	90.6	121.3	191.0	231.8	194.5	117.7	99.6
T/C 87 to 93	1.98	93.4	122.8	193.3	227.3	190.4	116.9	99.6
T/C 143 to 149	2.30	88.0	119.1	179.3	217.9	181.3	116.7	99.5
T/C 80 to 86	2.35	92.7	120.4	182.0	208.4	178.5	116.4	99.6
T/C 73 to 79	3.15	92.3	116.5	162.8	182.0	159.2	114.2	98.8
T/C 150 to 156	3.27	90.7	114.7	157.3	178.0	156.6	115.0	99.1
T/C 66 to 72	4.74	88.3	108.4	136.6	147.5	136.2	110.7	98.0
T/C 157 to 163	4.88	88.8	109.0	136.9	146.5	136.7	110.1	97.6
T/C 164 to 170	10.69	83.3	93.7	102.9	105.8	104.4	98.6	93.2
T/C 59 to 65	11.08	81.6	91.5	100.4	103.5	102.2	97.3	92.4

*Potential error in radial location is $\pm 0.5\%$ of the depth.

†Actual elevations may vary ± 0.3 ft from listed nominal elevation.

Table 3 Measured Temperatures in the Salt After 1000 d at Site B

Channel number(s)	Radial distance from heater center-line,* ft	Nominal elevation,† ft					
		-0.17	-4.5	-9.5	-13.5	-17.5	-22.5
		Temperature, °F					
T/C 200 to 205	0.97	94.2	108.7	152.5	178.0	148.8	99.3
T/C 194 to 199	1.09	92.7	107.8	145.3	166.4	141.2	98.9
T/C 206 to 210	1.71	90.9	104.9	134.8	149.8	130.9	
T/C 179, 190 191, 192, 193	1.94	89.4	104.0	131.9	147.6	129.4	
T/C 211 to 215	2.32	89.1	102.2	124.9	134.8	120.7	
T/C 216 to 220	3.18	88.1	99.3	116.5	123.4	114.4	

*Potential error in radial location is $\pm 0.5\%$ of the depth.

†Actual elevations may vary ± 0.15 ft from listed nominal elevation.

the meter and the temperature of the floor. These data and the air temperature in the mine were used to calculate a convection film coefficient. The results of the calculation are shown in Fig. 3. The slope, h , in the

temperature-difference-heat-flux plot is the convection film coefficient.

The convection film coefficient can be used in thermal-modeling studies to account for the heat loss at the floor surface because of natural con-

Table 4 Measured Temperatures in the Salt After 1000 d at Site C

Channel number(s)	Radial distance from heater center- line,* ft	Nominal elevation,† ft					
		−0.17	−5.0	−10.0	−14.0	−18.0	−23.0
		Temperature, °F					
T/C 228 to 232	0.67	100.9	157.3	296.9	254.4	299.7	
T/C 244 to 249	0.90	99.7	150.1	271.5	314.3	249.4	143.6
T/C 238 to 243	1.13	97.4	147.4	260.0	296.4	240.1	143.9
T/C 250 to 254	1.51	98.9	147.2	246.5	279.9	230.6	
T/C 233 to 237	2.01	96.2	143.3	233.4	262.6	224.3	
T/C 255 to 259	2.22	97.7	144.3	225.4	251.7	214.7	
T/C 260 to 264	3.01	96.7	140.1	212.3	231.9	203.6	

*Potential error in radial location is $\pm 0.5\%$ of the depth.

†Actual elevations may vary ± 0.1 ft from listed nominal elevation.

Figure 1 Temperatures measured in the salt at a radial distance of 0.3 m. (a) Site A. (b) Site B. (c) Site C.

vection or forced ventilation. The range in the measured heat flux is attributed to the irregularities in the floor surface, which may have partially isolated the flux meters.

Displacement Measurements

Extensometer Measurements.

Differential floor expansion was measured near each of the three

heater tests with a total of 13 multiple-point extensometers set in NX (76-mm-diameter) boreholes. Each extensometer included six Invar steel rods, 3 mm in diameter, attached to anchors at various depths in the borehole and a reference head attached to the mine floor. The anchors were expansion-shell rock-bolt anchors sized for use in an NX

Figure 2 Temperature profiles after 1000 d of heating. (a) Site A. (b) Site B. (c) Site C.

Figure 3 Heat flux from the floor at site A.

borehole. In all the vertical emplacements, the anchors were located at depths of 2.44, 3.05, 4.27, 5.49, 6.1, and 11.0 m below the mine floor. Anchor depths for the inclined extensometers differed in each of the installations.

With an extensometer, the change in distance between a specific anchor

and the reference head can be measured. Thus the extensometer displacement data can be converted to strains. Converting the data to strain eliminates the effect of the moving reference head (movement caused by floor heave). As an example, the vertical strains at a radial distance of 0.5 m

Figure 4 Differential floor expansion expressed as vertical strain at radial distances of about 0.5 m.

Figure 5 Floor heaves measured near the heater boreholes.

are presented in Fig. 4 for each heater test after 1000 d of heating. The magnitude of the maximum vertical strain at each site is approximately proportional to the total power level at each site.

Floor Heave Measurements. The change in floor elevation around the three heater tests was measured by optical level survey at 50 selected locations around each test. The measurement points were round-headed bolts anchored in the floor with epoxy.

Figure 5 presents measured floor heave as a function of time for the points nearest the heater boreholes (radius, 0.3 m) from each of the heater tests. The floor heaved quite rapidly during the first 100 d of heating at each site. After about 150 d, the floor heave at site B leveled off and rose only slightly thereafter. At site A, the floor continued to rise through about 200 d of heating, and then it also leveled off to a near steady-state condition. At site C, the floor continued to rise over a longer

Figure 6 Floor heave profiles after 1000 d of heating.

duration because of the weekly increases in the power level of the peripheral heaters. After 600 d, when the peripheral heaters had reached their maximum power level, the floor at site C also reached a near steady-state condition.

Figure 6 presents heave profiles for 1000 d of heating at each of the sites. Points at the same radial distance were averaged to obtain the heave profiles. The differences in the heater power level caused large differences in floor heave near the heater borehole, but the heave profiles gradually merge with increasing radial distance.

Heater Borehole Closure Measurements. The closure of the heater boreholes was measured using different sized disks to determine the annulus size between the sleeve and borehole wall. The resolution of these measurements was 0.8 mm. The result of the measurements made during the 1000 d of heating was that no significant (>1.6 mm) closure was detected at site B. At site A, a recrystallization of salt filled the annulus and prevented long-term measurement of the borehole closure. No borehole closure measurements were made at

site C because the annulus was filled with crushed-salt backfill.

Stress Measurements. Historically the detection of stress changes in salt has been unsatisfactory. In Project Salt Vault three different "stress meters" were used (Bradshaw and McClain, 1971). Specifically, hydraulic stress meters, borehole deformation gauges, and borehole pressure cells were used at both ambient and elevated temperatures in the salt. None of the three types of gauges provided a quantitative value of the stress change. The trends in the data were qualitatively explainable. However, correlations could not be established to yield the magnitude of the stress change.

Vibrating-wire stress meters (Hawkes and Bailey, 1973) were installed in each of the Avery Island heater tests. Since this type of gauge had not previously been used in salt, the objective was to evaluate the capability of the gauge, particularly in heated salt.

The data obtained indicated that the gauges did not perform satisfactorily. Qualitatively, the data show some trends that are explainable and consistent. Quantitatively, dis-

crepancies exist both in spatial and time comparisons of the gauges' responses.

If vibrating-wire stress meters are to be used in future tests in salt, a rigorous calibration (and possibly some modifications in the gauge design) will be required.

Summary and Conclusions

Representative data and inferred response were presented for each of the Avery Island heater tests. The temperature, heat flux, and displacement measurements provided a data base that can be used for comparison with numerical predictions of salt response. Unfortunately, not all the measurements were as successful. The vibrating-wire stress meters and the strain gauges on the site C sleeve would have provided valuable information if they had performed as intended. The overall value of the tests was not compromised, however. The measurement of borehole closure in the site B heater test indicated that only insignificant closure occurred. This result is somewhat surprising but possibly realistic because of the shallow depth of the test area. The recrystallization of salt, which filled the annulus above the

heater at site A, is not yet understood. The post-test evaluation is expected to provide additional information on its extent and possibly on its origin.

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Domal Salt Brine Migration Experiments at Avery Island, Louisiana

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Three in-situ brine migration experiments were performed in domal salt in the Avery Island mine located in southwestern Louisiana. The primary measurements included temperature, moisture collection, and pre- and post-test permeability at the experimental sites. Experimental data are discussed and compared with calculations based on the single-crystal brine migration theory. Comparisons indicate reasonable agreement between experiment and theory.

Introduction

A series of in situ brine migration experiments were conducted in domal salt at the 168-m (550-ft) level in the Avery Island mine of the International Salt Company in southwestern Louisiana. The objectives of the experiments were to examine the migration of synthetic and natural brines in salt in a temperature field induced by emplaced electrical heaters and to develop requisite and more precise measurement techniques and procedures for use in future natural brine migration experiments. In a more general sense, these experiments were intended to address the question of the extent of liquid brine inclusion migration in the vicinity of emplaced radioactive waste canisters as induced by thermal perturbations in the salt. The resolution of this question will have considerable impact on the

design and emplacement of backfill materials and other protective measures for isolating waste canisters from natural brine in a repository in geologic salt.

This paper describes three in situ brine migration experiments and the temperature fields induced in the salt by the electrical heaters and briefly compares measured temperatures with temperatures obtained by a finite element simulation. The moisture collection data are discussed, and results obtained from a theoretical model of brine migration are compared with experimental results.

Background

Salt deposits contain small brine inclusions distributed throughout the halite crystals and possibly along grain boundaries. The thermal conditions resulting from the storage of nuclear wastes in a nuclear repository in rock salt could cause the inclusions to move through the salt. Observation of brine inclusion migration in single crystals indicates that liquid inclusions migrate up the temperature gradient and biphasic inclusions migrate down the temperature gradient. A summary of the theory related to the driving mechanism for all-liquid inclusions is given by Olander et al. (1980):

The solubility of salt in the brine inclusion increases with temperature. Consequently, in the presence of a temperature gradient across the brine inclusion, salt dissolves into the inclusion across the hot surface and crys-

tallizes out at the cold surface. Thermal and molecular diffusion of salt within the liquid phase from the hot to the cold faces causes the inclusions to move in the opposite direction.

The magnitude of the temperature gradient, as well as the temperature level in the salt surrounding the heat source, dictates the rate of inclusion migration toward the heat source.

According to Olander et al. (1980), brine could accumulate around a waste package and possibly cause deterioration and dissolution of the package components and waste form. Inclusions containing a gas phase are also present in halite crystals in rock salt. Such inclusions may form when the all-liquid inclusions reach the waste package. After reaching the waste-package-salt interface, the brine partially evaporates, and the inclusion may reveal with some insoluble gas trapped inside. Typically, the gas-liquid (or two-phase) inclusions migrate down the temperature gradient and could possibly provide a pathway by which radionuclides leached from the waste form by the brine can be transported away from the waste package. An understanding of the migration mechanism is necessary to predict the rate and amount of brine that may accumulate in the vicinity of a waste package placed in domal or bedded salt.

Stewart and Potter (1979) contended that an understanding of the nature of the chemical and physical interactions between the salt, canister, geogenic wastes, and any brine present is necessary to design for waste containment within a salt formation. They suggested that the brine contained within the salt around a heat-producing waste canister will migrate toward the canister as a consequence of the induced thermal gradient. Brine that enters the emplacement borehole and penetrates the buffer materials will enhance the corrosion of the metallic canister, thus

potentially exposing the waste form to leaching. Stewart and Potter also suggested that an abnormal presence of brine in the salt around the emplacement borehole might structurally weaken the salt and reduce its sorptive properties. In summary, their feeling was that any one or a combination of these circumstances could seriously hinder the retrieval of the nuclear wastes, if retrieval became necessary, and, in the worst case, could contribute to a loss of integrity of the repository and the long-term waste containment.

Whether or not these scenarios are valid for geologic salt and for the thermal gradients expected in a repository is as yet not fully known. Various experimental studies now being conducted should aid in the development of brine migration theory by providing basic data on actual rates of brine migration.

Review of Previous Investigations

Whitman (1926) and Kingery and Goodnow (1963) investigated droplet migration in solids and showed that salt is eliminated from sea ice when brine droplets in the ice migrate to brine drainage channels under the influence of the temperature gradient between atmospheric air and seawater.

Numerous papers on brine migration in salt crystals appeared in the 5-yr period from 1968 to 1973. During this time, Anthony and Cline (1970, 1971a, 1971b, 1972, 1973), Cline (1971), Cline and Anthony (1971a, 1971b, 1971c, 1972), and Anthony and Sigsbee (1971) published about a dozen papers dealing with the migration of both single-phase and biphasic droplets in solids, with either an impressed thermal gradient or an impressed accelerational field. With two exceptions, in which the investigators studied the interaction of liquid inclusions

within a grain boundary in a large accelerational field and in a thermal gradient, all the studies involved single-crystal KCl and NaCl. Also during this period, Wilcox (1968, 1969a, 1969b, 1972), Chen and Wilcox (1972), and Wilcox and Schlichta (1971) conducted similar studies involving the movement of liquid inclusions in crystals subjected to centrifugation and thermal gradients.

More recently, Jenks (1972, 1979) extended the single-crystal theory to predict the amount of brine inflow that could be expected to accumulate in the region of salt containing a typical waste canister. Jenks (1979) used the theoretical and experimental results of Anthony and Cline (1970, 1971a, 1971b, 1972, 1973), Cline (1971), Cline and Anthony (1971a, 1971b, 1971c, 1972), and Anthony and Sigsbee (1971) to correlate and explain the available data for rates of brine migration at temperatures up to 250°C in naturally occurring crystals of bedded salt from Lyons and Hutchinson, KS.

Russian workers, including Geguzin, Dzyuba, and Korzhanov (1975), developed inclusion migration theories similar to those of Anthony, Cline, and co-workers. Geguzin and co-workers conducted measurements in single crystals of KCl in a very narrow range of temperatures.

A limited number of brine migration studies have been conducted in the laboratory on polycrystalline rock salt. Hohlfelder and Hadley (1979), at Sandia National Laboratories, investigated brine migration in a 1-kg specimen of rock salt from southeastern New Mexico. This study provided measurements of moisture loss from the salt at elevated temperatures. They compared the experimental results with those obtained from a modified porous-medium flow model and found excellent agreement. The water motion (brine migration) within the salt specimen was assumed to be

Darcian flow, with a receding evaporation front for the water vapor.

Roedder and Belkin (1980) investigated the movement of liquid-filled inclusions in bedded salt samples from the proposed Waste Isolation Pilot Plant (WIPP) site in southeastern New Mexico. The thermal gradient, fixed at 1.5°C/cm, was maintained for 3 to 10 d at average bulk temperatures of 108 to 260°C. The sample size was 1 by 1 cm by 1 to 2 cm in length. Typically, for cubic inclusions 1 mm on an edge, the migration rate was 1.2 to 5.4 cm/yr; whereas inclusions 0.1 mm on an edge migrated 0.4 to 1.6 cm/yr. Increases in average bulk temperature and/or temperature gradient were correlated with increased migration rates. The variation in migration rates within a given sample was about a factor of three.

Laboratory studies conducted at RE/SPEC (Krause, 1981) determined that average brine inclusion migration rates are on the order of 1.5 to 6 cm/yr (approximate cubic inclusion sizes ranged from 0.05 to 0.30 mm) for temperature gradients of 3.5 to 10.2°C/cm, respectively, with mean bulk temperatures of 200 to 250°C. This range of data was obtained by examining 380 inclusions in rock salt from southeastern New Mexico. A typical sample weighed 250 g, with a core approximately 51 mm in diameter and 57 mm long.

Bradshaw and McClain (1971) demonstrated emplacement and retrieval techniques for spent fuel in salt mine during Project Salt Vault. During this field-scale experiment, brine-filled cavities migrated toward the drill holes containing the spent canisters and electrical heaters. Following this observation, Bradshaw and Sanchez (1969) measured a number of relatively pure salt crystals from the Carey Salt Company mine at Hutchinson, KS. The crystals were cubes about 2.5 cm on a side and con-

tained brine cavities 2 to 10 mm in maximum length. They were exposed to thermal gradients ranging from 4 to 34°C/cm, with mean bulk temperatures of 75 to 244°C. For these thermal conditions, the inclusion migration rates, for 31 measurements, ranged from about 10 to 100 cm/yr. Bradshaw and Sanchez concluded that the driving mechanism for the migration of the inclusions is the difference in solubility between the warm and cold faces of the brine inclusion. Following these observations, they developed a brine migration model based on the modified theory of Hoekstra, Osterkamp, and Weeks (1965) for the migration of liquid inclusions in ice crystals. Their model provided a means for predicting the rate and amount of brine migration in salt under nonambient temperature conditions.

As evidenced by these studies, scatter in the experimental data occurs in all the studies on laboratory-size samples of salt. Olander et al. (1980) pointed out that the origin of the scatter is not well understood, but "it is thought to be related to the sensitivity of the interfacial resistances to dissolution and deposition to impurities and to the detailed dislocation structure intersecting the moving inclusions." Olander concluded, however, that the theory of migration of liquid brine inclusions in single crystals is well substantiated. In experimental studies for NaCl, Olander et al. (1980) determined that, because of the lower temperature coefficient of solubility and the larger interfacial kinetic resistances to dissolution and precipitation for NaCl in comparison with those for KCl, observed brine inclusion velocities are about an order of magnitude lower for NaCl than for KCl.

In summary, the modest amount of literature reviewed here describes

studies of migration of single-phase and biphasic brine inclusions in single crystals and in polycrystalline salt. Gnirk, Krause, and Fossum (1980) pointed out that the presence of grain boundaries and induced stress levels in geologic salt will serve to retard the migration of brine. These thoughts suggest that perhaps a "threshold" gradient level is required to initiate migration along or across grain boundaries. At present, the mechanism of migration along and across grain boundaries is not well understood.

Description of the Avery Island Experiments

Scope of the Experiments. Three separate test configurations in domal salt in the Avery Island mine were addressed:

- The areal extent of liquid brine inclusion (both natural and artificial) movement for an induced thermal gradient
- The rate of brine inflow to the heat source for an induced thermal gradient
- The possible influence of thermally induced microfracturing in salt around the heat source

This series of in situ experiments examined the movement of natural or artificial brine inclusions either toward or away from a heat source. Evidence of artificial brine migration can be obtained by searching for deuterium oxide tagged patterns left in the salt after a prescribed heating period.

General Test Configuration. A plan view of the test configuration of a central heater borehole and surrounding brine and thermocouple boreholes is shown in Fig. 1. Figure 2 presents a cross-sectional view of the centrally located heater borehole with associated instrumentation. The brine and thermocouple

Figure 1 Orientation and layout of boreholes for brine migration sites AB, NB, and SB. Brine boreholes are B2, B4, and B8; thermocouple boreholes are TC2, TC4, and TC8. Distances from center are A, 50 mm; B, 100 mm; and C, 200 mm.

boreholes, which have diameters of 38 mm (1.5 in.), were dry-drilled to depths of 3.81 m (12.5 ft) and 5.64 m (18.5 ft), respectively.

Thermocouple assemblies (Type K—Chromel—Alumel with Inconel 600 sheaths) were placed in the boreholes designated TC, as illustrated in Fig. 1, and the boreholes were filled with crushed rock salt. The elevations of the thermocouple measuring junctions were the same as those of the heater borehole wall thermocouples shown in Fig. 2. A cross-sectional view typical of borehole thermocouples placed in the salt is shown in Fig. 3.

The brine boreholes were arranged to determine the influence of temperature and temperature gradient on brine movement at evenly spaced intervals from the heater borehole wall. The three brine boreholes were drilled at radial spacing distances ranging from 51 mm (2 in.) to 203 mm (8 in.) between the heater borehole wall and the brine borehole

wall. This spacing was a reasonable compromise to allow drilling of the brine boreholes in the vicinity of the heater borehole. Possible stress interactions might have occurred if the boreholes had been spaced at smaller center-to-center intervals. Since the temperature gradients decrease in a radial direction away from the heater borehole, placing the brine boreholes at too great a distance from the heater would have diminished the magnitude of possible brine migration within the experimental time period, which was originally planned to be 150 d.

Specific Test Configurations.

The following experiments were performed at the three separate site configurations (Krause, 1979):

1. Test AB, natural brine movement under ambient temperature conditions. This control experiment was designed to evaluate the movement of any natural brine in the domal salt as a consequence of stress perturbations caused by drilling the borehole configuration. The salt was not subjected to heating in this test.

2. Test SB, synthetic brine movement under elevated temperature conditions. This experimental configuration consisted of a centrally located, heated borehole within a pattern of other boreholes containing either thermocouples or synthetic brine. A 1.0-kW-rated electrical heater was placed in the heater borehole. The temperature in the surrounding salt was elevated to 75% of the expected steady-state distribution obtained in a finite element simulation. After this thermal condition was attained, synthetic brine and glass beads were introduced into the brine boreholes, which were then pressurized to 690 kPa. The glass beads were used to minimize thermal convection within the borehole. The synthetic brine was tagged with deuterium oxide so that the extent of the brine movement

Figure 2 Cross-sectional view of heated borehole and typical brine borehole at site SB. Drawing is not to scale. $\triangle$, surface thermocouple; $\bullet$, heater thermocouple; and $\times$, brine borehole thermocouple.

within the salt after a specified heating period could be determined by analysis of samples from post-test overcore drilling. The composition of the synthetic brine is given in Table 1. Figure 2 shows a cross-sectional view of the heated borehole and an adjoining brine borehole. Temperatures in the salt and moisture entering the heater borehole were monitored at this site.

3. Test NB, natural brine movement under elevated temperature conditions. This control experiment was designed to evaluate the movement of any natural brine in domal salt under elevated temperature conditions. A 1.0-kW-rated electrical heater was used to heat the surrounding salt.

The moisture within the heater hole was sampled periodically to determine if an influx of natural brine had occurred. The geometry and operation of test NB was identical to that of test SB, except that synthetic brine was not placed in the brine boreholes.

The three test configurations were operationally interrelated in the following manner. The test AB configuration can be considered a baseline, unheated condition in which moisture collection in the central unheated borehole was not influenced by temperature level and thermal gradient. Moisture collected as a result of elevated temperature conditions in test NB was obtained by subtracting the amount of moisture collected in

Figure 3 Cross-sectional view of the borehole thermocouple probes at sites NB and SB. Drawing is not to scale.

test AB (unheated) from that collected in test NB and, thus, determining the net moisture collection (natural brine migration) caused by heating. This general scheme was also applied to test SB. The moisture collected at test AB can be subtracted from that collected at test SB to determine the moisture gain from the heated SB configuration.

The moisture collection system used at sites SB and NB consisted of a series of desiccant canisters with a dry nitrogen purge through the heater borehole. A schematic of the moisture collection system is shown in Fig. 4.

Genesis of the Concept of the Large Synthetic Brine Inclusion. During the design of the experiments, it was postulated that the synthetic

Table 1 Composition of WIPP-A Tagged Synthetic Brine*†

Component	Concentration, g/l	Wt. %
MgCl ₂	137.08	11.42
NaCl	101.55	8.46
KCl	57.20	4.77
CaCl ₂	1.71	0.14
Na ₂ SO ₄	5.175	0.43
D ₂ O	25.00	2.08
H ₂ O	872.345	72.6

*Data are from Clynné et al., 1981.

†Weights are for the anhydrous salts. Brine density at 20°C is 1.2021 ± 0.0002 g/cm³.

brine in the boreholes could perhaps be perturbed by a convection cell caused by the small radial thermal gradient across the brine. To reduce the possibility of convective circulation of the synthetic brine, we placed glass beads in the boreholes. Even though the synthetic brine borehole (large-scale inclusion) is much larger than typical geologic brine inclusions, the possible movement of synthetic brine from this borehole toward the heat source could provide preliminary data on:

- Possible movement of untagged or tagged synthetic brine and also natural brine inclusions through domal salt.
- The concentration (gradient) of the synthetic brine as a function of radial position measured from the heater borehole center line.
- Possible movement of synthetic brine through microcracks within the domal salt surrounding the heater borehole.

Operational History for Sites SB and NB. The primary experimental sites (sites SB and NB) began operation on Oct. 4, 1979. Site SB operated at an average power level of about 925 W for 325 d, after which heating was terminated with a stepped power reduction (20% per day for 5 d). The

Figure 4 Schematic of moisture collection system for sites SB and NB. Components are 1, 6, large desiccant filters; 2, 3, 4, small desiccant filters; 5, flowmeter/metering valve; and 7, pressure regulator and dry nitrogen supply bottle.

post-test evaluation activities at site SB were initiated on Sept. 4, 1980, and all the on-site activities (with the exception of site SB overcore) were completed before October 1980. Site NB operated at an average power level of about 890 W, and power reduction was initiated on Apr. 1, 1981. After a gradual reduction in power (about 30 W/d), heating at site NB was terminated on Apr. 30, 1981. Because a gradual power reduction was applied at site NB, the salt surrounding the heated borehole experienced smaller thermal perturbations. During power reduction at both sites SB and NB, moisture was collected to assess the influence on brine inflow. It was determined during power reduction that site SB experienced a moisture "surge"; site NB did not experience a significant increase in the moisture collection rate. At this date, the heater and packer assemblies have

been removed from site NB, and over-coring is not planned at this site.

Experimental Temperature Measurements

Temperature Profiles at Sites SB and NB. The measured temperature profiles for the heater borehole wall at sites SB and NB are presented in Figs. 5 and 6. The maximum indicated temperature (at both sites) on the mid-height of the heater borehole wall is about 51°C (124°F). The temperatures in the salt surrounding the heater boreholes are presented in additional profiles in Figs. 7, 8, and 9 for site SB and in Figs. 10, 11, and 12 for site NB. The salt temperatures were measured with thermocouple probes emplaced within the thermocouple boreholes designated as TC2, TC4, and TC8 (as shown in Figs. 1 and 3).

Figure 5 Heater borehole wall temperature profiles at site SB. Heater power is 0.925 kW, and days of heating are $\square$, 0.02; $\circ$, 1; $\triangle$, 5; $+$, 10; $\times$, 50; $\diamond$, 200.

Figure 7 Salt temperature profiles at site SB measured with TC2 located at a radial distance of 0.11 m from the heater center line. Heater power is 0.925 kW, and days of heating are $\square$, 0; $\circ$, 0.02; $\triangle$, 1; $+$, 5; $\times$, 10; $\diamond$, 50; and ∇ , 100.

Figure 6 Heater borehole wall temperature profiles at site NB. Heater power is 0.890 kW, and days of heating are $\square$, 0.02; $\circ$, 1; $\triangle$, 5; $+$, 10; $\times$, 50; $\diamond$, 200.

Figure 8 Salt temperature profiles at site SB measured with TC4 located at a radial distance of 0.16 m from the heater center line. Heater power is 0.925 kW, and days of heating are $\square$, 0; $\circ$, 0.02; $\triangle$, 1; $+$, 5; $\times$, 10; $\diamond$, 50; and ∇ , 100.

Figure 9 Salt temperature profiles at site SB measured with TC8 located at a radial distance of 0.26 m from the heater center line. Heater power is 0.925 kW, and days of heating are $\square$, 0; $\circ$, 0.02; $\triangle$, 1; $+$, 5; $\times$, 10; $\diamond$, 50; and ∇ , 100.

Figure 11 Salt temperature profiles at site NB measured with TC4 located at a radial distance of 0.16 m from the heater center line. Heater power is 0.890 kW, and days of heating are $\square$, 0; $\circ$, 0.02; $\triangle$, 1; $+$, 5; $\times$, 10; $\diamond$, 50; and ∇ , 100.

Figure 10 Salt temperature profiles at site NB measured with TC2 located at a radial distance of 0.11 m from the heater center line. Heater power is 0.890 kW, and days of heating are $\square$, 0; $\circ$, 0.02; $\triangle$, 1; $+$, 5; $\times$, 10; $\diamond$, 50; and ∇ , 100.

Figure 12 Salt temperature profiles at site NB measured with TC8 located at a radial distance of 0.26 m from the heater center line. Heater power is 0.890 kW, and days of heating are $\square$, 0; $\circ$, 0.02; $\triangle$, 1; $+$, 5; $\times$, 10; $\diamond$, 50; and ∇ , 100.

Figure 13 Radial temperature distribution for site SB at the heater mid-elevation (-3.35 m). Heater power is 0.925 kW, and days of heating are $\square$, 0.02 ; $\circ$, 1 ; $\triangle$, 5 ; $+$, 10 ; $\times$, 50 ; and $\diamond$, 200 .

The temperature profiles indicate vertical symmetry about the heater mid-elevation and hence relatively small vertical temperature gradients. The 50- and 200-d profiles have essentially the same magnitudes; this implies near steady-state thermal conditions.

Radial Temperature Distribution at Sites SB and NB. Radial temperature distributions are shown in Fig. 13 for site SB and Fig. 14 for site NB. These temperature distributions, which are for the mid-elevation of the heater borehole, represent the temperature distribution at the locations of the heater borehole wall, TC2, TC4, and TC8. Small deviations from the expected values in the temperature distributions were caused, in part, by fluctuations in the power levels at sites SB and NB. The power fluctuations at the Avery Island field site are caused by electrical load variations that depend on production activities in the mine.

Figure 14 Radial temperature distribution for site NB at the heater mid-elevation (-3.35 m). Heater power is 0.890 kW, and days of heating are $\square$, 0.02 ; $\circ$, 1 ; $\triangle$, 5 ; $+$, 10 ; $\times$, 50 ; and $\diamond$, 200 .

Heat-Transfer Analyses

Scope of the Analysis. To assess the amount of brine inflow into the heater boreholes in the experiments, we must measure the temperature and determine temperature gradients in the surrounding salt. To substantiate the temperature measurements, we conducted a heat-transfer analysis using the finite element (FEM) computer code SPECTROM-41 (Svalstad, 1981). The heat-transfer analysis assumed heat transfer by conduction from the heater to the surrounding salt. Convective heat transfer (cooling due to ventilation) was allowed at the mine floor. These modeling assumptions do not permit calculation of temperatures on the heater surface or within the heater borehole but do provide reasonable predictions of the salt temperatures. The calculated pseudo steady-state temperatures in the salt and related thermal gradients were used to estimate the brine inflow in the vicinity of the heater borehole wall.

Table 2 Material Properties for Heat-Transfer Analysis

Property	Value
Thermal conductivity (k)	5.94 W/(m · K)
Specific heat (C _p)	850.0 J/(kg · K)
Density (ρ)	2163.0 kg/m ³
Ambient mine air temperature (T _{amb})	26.7°C
Initial salt temperature (T ₀)	26.7°C

Thermal Material Properties.

The salt thermal properties used in the finite element thermal analysis are given in Table 2. For prediction of the temperature field around the heater, it was not considered essential to model thermal conductivity as temperature dependent because of the moderate level of induced temperatures. The heater was modeled to completely fill the borehole, and its material properties were assumed identical to those of salt. The heat generation per unit volume used in this simulation was 47.8 kW/m³. The convective heat-transfer coefficient applied at the floor surface was 7.1 W/(m² · °C).

Comparison of Measured and Calculated Temperatures. The results of the measurements and the FEM computations for several time increments are shown in Fig. 15. The FEM results and the experimental results compare quite favorably. For times exceeding 1 d, the maximum deviation between computed and measured temperatures in the salt is about 1°C. This deviation is within the expected precision of the temperature measurements in salt, which have a potential maximum error of about ±5°C. The maximum error considers calibration deviation, lead-wire inhomogeneity, thermal aging, signal processing error, and installation positioning errors. Since the use of

steady-state temperatures simplifies the calculation of expected brine inflow, we can observe from Fig. 15 that near steady-state conditions are obtained after 50 d. The temperature gradients shown in Fig. 16 were determined from the FEM solution, which gives specific values at selected radial positions.

Steady-State Temperature Field Approximation.

The salt temperatures (assuming steady-state at 150 d) used for the temperature profile of the heater borehole wall at site SB are based on the previously discussed FEM solution. These temperatures were approximated by a spline fit, which is shown in Fig. 17, together with the measured borehole wall temperatures. Near the heater mid-height, the spline approximation predicts slightly higher temperatures than those measured, but otherwise agreement is good. To predict the steady-state temperatures in the surrounding salt, we used a logarithmic temperature distribution:

$$T_i(r,z) = T_{w_i}(z) + C_1 [T_0 - T_w] \ln(r/r_w) \quad (1)$$

where $T_i(r,z)$ = temperature (°C) at any radius $r > r_w$ measured from the heater borehole center line

$T_w(z)$ = heater borehole wall temperatures (°C), based on the spline approximation shown in Fig. 17

T_0 = 26.7°C—ambient temperature of the salt

r_w = 0.0381 m

C_1 = 0.1887—a constant determined from approximating the outer radius of the hollow cylinder as $r_0 = 7.62$ m, where the gradient is very small

Figure 15 Comparison of the measured temperatures at site SB and the FEM computed temperatures at the heater mid-height (-3.35 m). Curves indicate finite element models; $\blacktriangleright$, heater borehole thermocouple; $\bullet$, borehole thermocouple. Conditions are $K = 5.94$ W/(m $\cdot$ $^{\circ}$ C), $\dot{q} = 0.93$ kW, $C_p = 0.85$ kJ/(kg $\cdot$ $^{\circ}$ C), and $\rho = 2163$ kg/m.

This expression applies at any elevation from the mine floor to the bottom of the heater borehole and gives a good approximation of the measured and FEM calculated temperatures.

Steady-State Thermal Gradient Approximation. The steady-state temperature gradient near the heater borehole wall is:

$$G_i(r,z) = C_2 \left[T_0 - T_w \right] \frac{1}{r} \quad (2)$$

where $G_i(r,z)$ is the temperature gradient ($^{\circ}$ C/cm) at any radius $r > r_w$ measured from the heater borehole center line and C_2 is 0.2113. Equation 2 is obtained by differen-

tiating Eq. 1 with respect to the radius r . To give a good approximation of the temperature gradient, based on the FEM solution, in the heater mid-height region, we adjusted the constant C_2 in Eq. 2 to produce the temperature gradient profile shown in Fig. 18.

Equations 1 and 2 are considered sufficiently accurate to represent the thermal conditions surrounding the heater borehole. Because thermal conditions are moderate and the inclusion migration velocities are, therefore, very low, only a narrow region of salt surrounding the heater borehole wall is considered in the brine inflow computation. Because of the limited region of significance, any minor deviations in thermal conditions would have a small influence on moisture inflow computations.

Figure 16 FEM representation of the salt temperature gradients at the heater mid-height (-3.35 m). Δ , finite element analysis. Heater power is 0.93 kW.

Assessment of the Moisture Collection Data

Moisture Collection at Sites AB, NB, and SB. Figure 19 compares the moisture collection data at sites AB, SB, and NB before cool down of site SB. During the initial 315 d of heating, the brine movement experiments showed moisture collection rates of 0.026 to 0.044 g/d. Site AB had the lowest collection rate, and site NB had the highest. Heating at sites NB and SB approximately doubled the collection rate in comparison with the unheated configuration at site AB. Site AB can be considered a background level of moisture related to moisture content in the initial air in the unheated borehole. Additionally, the nitrogen purging process would also dry the surfaces of the unheated borehole. The moisture collected at site AB can be subtracted (for similar

Figure 17 Heater borehole wall temperature profile at pseudo steady-state conditions. $\bullet$, spline fit, based on FEM. $\blacksquare$, measured temperature. Heater power is 0.925 kW.

collection periods) from the moisture collected at sites NB and SB to determine the moisture accumulation related specifically to heating. For example, with reference to Fig. 19, the actual moisture increase attributed to heating of site NB would be 7 g (instead of 19.5 g) at 310 d if the constant rate of collection is maintained at site AB. As shown in Fig. 19, the moisture collection data at all sites showed a significant initial collection rate; this can be related to removal of the residual moisture present in the air included in the heater boreholes and on the heater borehole walls and heater sleeve (at sites SB and NB).

Figure 19 also shows that the final pre-cool-down-moisture collection rate

Figure 18 Pseudo steady-state temperature gradient approximation at the heater borehole wall. ●, spline fit, based on FEM. Heater power is 0.925 kW.

at site SB was 0.037 g/d; whereas the collection rate at site NB appears to be 0.044 g/d. The constant steady-state collection rate at site NB was about 16% greater than the collection rate at site SB.

Figure 20 shows the moisture collection at site AB, which is considered the background unheated moisture collection baseline. To permit further analysis of the moisture collection data, the data at site AB was approximated by a power law fit, as shown in Fig. 20. To obtain the moisture gain caused by heating, we subtracted the moisture collected (power law approximation) at site AB (Fig. 20) from that collected at corresponding times at sites NB and SB (Fig. 19). The net result for both sites is the moisture gain caused by heating, which is shown in Fig. 21. Thus the total mois-

ture gain caused by heating at site SB before cool down was less than 5 g.

Moisture Collection and Post-Test Permeability Testing at Site SB During Cool Down. During the cool-down phase of the site SB experiment, the small desiccant cartridges on the moisture collection system were weighed once every 24 hr. The moisture collection during site SB cool down showed significant gains that corresponded with permeability changes, which were also measured during the cool-down period. The average apparent moisture collection rate at site SB before cool down was about 0.04 g/d for a 185-d moisture collection period before initiation of cool down on Aug. 25, 1980. As shown in Fig. 22, the moisture collection rates for the cool-down period at site SB are significantly greater than the pre-cool-down values. The increased collection rates can perhaps be attributed to microcracking and opening of the grain boundaries in the vicinity of the heater borehole wall. This explanation implies that the large amount of brine (moisture) release during cooling of the salt was caused by the change in tangential stresses created by thermal response of the salt during power reduction. These stresses were relieved during cooling, allowing the trapped water in the salt to break free and enter the heater borehole. This explanation is similar to that given for the Project Salt Vault experiments (Bradshaw and McClain, 1971).

Post-Test Permeability Testing at Site SB. Permeability testing of the brine boreholes at site SB was initiated before shutdown of the heater. The change in permeability corresponds to the increased rate of moisture collection. During the stepped power reduction schedule (shown in Fig. 22), the permeability testing and computations were performed as outlined by Stickney

Figure 19 Comparison of cumulative moisture collected during the initial 325 d of heating at site SB.

Figure 20 Moisture collection at site AB.

Figure 21 Collection of moisture caused by heating at sites SB and NB. Long-term steady-state moisture collection rates (m):
 $\dot{m}_{NB} = 0.0175 \text{ g/d}$
 $\dot{m}_{SB} = 0.0107 \text{ g/d}$

Figure 22 Heater power reduction schedule, measured moisture collection, and average salt permeability (ΔK) measured at the brine boreholes during the cool-down period at site SB.

(1980). Results of the permeability testing for site SB are also shown in Fig. 22, along with the total moisture collection data. We can easily observe a correlation between the moisture collection rate and the change in brine borehole permeability. The final permeability measurement shown in Fig. 22 indicates a decreasing trend after cooling to ambient temperature (26.7°C) in the salt. Although a slight amount of the pressure drop during permeability testing could be attributed to temperature decrease in the boreholes during site cool down, the majority of the rapid pressure decay, which is used to calculate permeability, is perhaps caused by microcracking in the vicinity of the brine boreholes.

The permeability tests conducted on Sept. 2 and 3, 1980, showed flow communication between the brine boreholes and the heater borehole, as indicated by a pressure rise in the heater borehole, which occurred simultaneously with the pressure drop in the brine boreholes. During the last permeability test (Sept. 10, 1980), brine boreholes B2 and B4 showed flow communication into thermocouple borehole TC2. Additionally, brine borehole B8 indicated a noticeable flow communication into thermocouple borehole TC8. These observations perhaps imply that cracking of the salt surrounding the heater borehole occurred during cool down. The over-coring at site SB may possibly indicate the locations of microcracking.

Comparison of Measured and Calculated Brine Migration Rates and Amounts

Discussion of Brine Inclusion Model. The single-crystal formulation of Anthony and Cline (1971a) gives the liquid inclusion velocity as

$$V = D \frac{C_d}{C_s} G_d \left(\frac{1}{C_d} \frac{\partial C_E}{\partial T} - \sigma \right) \quad (3)$$

where V = brine inclusion migration velocity (cm/s)

D = diffusivity of salt in brine (cm²/s)

C_d = concentration of salt in brine droplet (mol/l)

C_s = concentration of salt in solid salt (mol/l)

C_E = equilibrium concentration of salt in brine in contact with salt (mol/l)

G_d = $1.4 G_s$; G_s is the temperature gradient in the solid salt (°C/cm)

σ = Soret coefficient of salt in brine (°C⁻¹)

Additional terms relating to kinetic potential and grain boundary tension have been neglected. As originally shown by Anthony and Cline (1971a), the thermomigration of a brine droplet up a temperature gradient results from an increase in the solubility of the salt with increased temperature. Grain boundaries and droplet size can also influence the motion of brine inclusions within the salt. The diffusion enhanced model does not account for grain boundary influences on brine migration.

To facilitate a comparison of the measured moisture collection in the heater borehole with an inflow model, we must approximate the properties of salt (or related brine) required in Eq. 1. Because these properties are not precisely known for Avery Island salt, an approximate range of values was taken from the study by Jenks (1979). The values given by Jenks were for a 2.41M MgCl₂ solution in the temperature range from 25 to 200°C, as shown in Table 3. Porosity is assumed to be a constant for this analysis, and brine density is assumed to be the density of water.

Table 3 Salt (Brine) Properties Used in Eq. 3†

Approximations for properties used in Eq. 3:

$$D(T) = 7.8 \times 10^{-7} T - 0.8 \times 10^{-5}$$

$$C_r/C_s = 0.048 \exp(0.0028 T)$$

$$C_r^1 \partial C_E / \partial T = (2.863 \times 10^{-3}) \cdot 10^{7.449 \times 10^{-T}}$$

$$\rho = 1.000 \text{ (assumed constant over temperature range)}$$

Temperature (T), °C	D, cm ² /s	C _r /C _s	$\left[\frac{1}{C_r} \frac{\partial C_E}{\partial T} \right] / ^\circ\text{C}$	$\sigma / ^\circ\text{C}$
25	$1.15 \times 10^{-5} \ddagger$	0.0517	2.92×10^{-3}	-0.002
50	3.20×10^{-5}	0.0549	3.23×10^{-3}	-0.002
100	7.1×10^{-5}	0.0634	3.36×10^{-3}	-0.002

†Data from Jenks, 1979.

‡Extrapolated from the data of Jenks (1979).

Steady-State Inflow Model. To determine the steady-state moisture inflow (i.e., the moisture inflow at the steady-state temperature and temperature gradient) into the heater borehole, we used the temperature distributions previously discussed, along with the corresponding temperature gradients. Equation 3 was used to calculate the brine inclusion velocities near the heater borehole. Figure 23 shows the medium surrounding the heater borehole taken as a grid in radial coordinates (r,z). The inflow rate to the heater borehole is based on the average flow rates surrounding the heater borehole; this gives a simplified expression for mass flux:

$$M_i = \frac{\dot{m}_i}{A_{BH}} = \sum_n \phi \rho \frac{V_n}{n} \quad (4)$$

where i = number of vertical slices
n = number of steps in radial direction

ρ = brine density (g/cm³)

ϕ = formation porosity

$\Sigma V_n/n$ = average brine inclusion velocity (cm/s)

M_i = mass flux for each slice, ΔZ (g/s · cm²)

A_{BH} = surface area of the heater borehole (cm²)

$\dot{m}_i$ = mass flow rate (g/s)

To determine the total inflow for the heater borehole, we can divide the grid shown in Fig. 23 into small increments in the r and z directions. The total inflow can then be determined for the entire length of the heater borehole. The total mass accumulated within the borehole during the duration of the test can be determined by adding the flow rates for each slice (ΔZ) of the salt surrounding the heater borehole:

$$m = \Sigma M_i A_{BH} \Delta t \quad (5)$$

where Δt is the test duration (d) and m is the accumulated mass (g).

A brine inclusion can only travel a distance dictated by its rate of migration; therefore a "check-condition" must be used to determine how far a typical inclusion will travel in the radial direction toward the heated borehole. This distance is determined by

$$\Delta r_n = V_n \Delta t \quad (6)$$

where Δr_n is the radial distance an inclusion can travel (cm) and V_n is the brine inclusion migration velocity (cm/s).

During the test period (Δt), a brine inclusion can travel a distance of Δr_n , but, depending on where this inclusion

Figure 23 Representation of the rock salt medium surrounding the heater borehole. $T(r, z)$ and $G(r, z)$ are the temperature and the temperature gradient, respectively.

is positioned relative to the heater borehole wall, it may not reach the surface of the borehole during the test period. The radial distance measured from the heater borehole wall is given as

$$\Delta R_n = r_n - r_w \quad (7)$$

where ΔR_n is the radial distance measured from the heater borehole wall (cm), r_n is any radial position (cm), and r_w is the heater borehole radius (cm). Thus the check condition implies that if

$$\Delta r_n \leq \Delta R_n \quad (8)$$

the brine inclusion migration rate is too slow, and the inclusion will not be

able to reach the heater borehole surface. In a simulation of the inflow to the heater borehole, the check condition implies that the steady-state inflow rate, given by Eq. 3, is terminated according to Eq. 8, and the inflow simulation progresses to the next elevation, or slice.

This inflow simulation scheme also assumes that

- The porosity (ϕ) is a reasonable representation of the formation voidage and pore space occupied by the fluid (in this case brine inclusions).
- The brine inclusions within the salt surrounding the heater borehole will not be depleted during the test period. This condition implies that a source of inclusions is available for the duration of the test.
- Modeling of flow along or across the grain boundaries within the salt is not attempted.
- The inclusion velocity into the heater borehole is in the one-dimensional radial direction. The velocity of the brine inclusions toward the heater borehole is a function of temperature and temperature gradient, which are approximated by Eqs. 1 and 2, respectively.

Steady-State Zone of Brine Migration Influence. Because the temperatures and temperature gradients decrease in the increasing radial direction, measured from the heated borehole wall, the region of significance for brine migration surrounding the heated borehole is very small and can be defined as the zone in which inclusions will reach the heated borehole under the thermal conditions imposed for the experiments. Figure 24 shows that the magnitude of the zone of influence is only 5 mm after 1 yr of heating, with the steady-state thermal gradients shown in Fig. 18. Since the site SB experi-

Figure 24 Brine migration zone of inflow influence after 1 yr (365 d) of heating. Heater power is 0.925 kW.

ment operated for about 315 d of heating and 235 d of moisture collection before site cool down, the region of influence would be smaller than the 1-yr case shown in Fig. 24. For 315 d of heating, the brine migration zone of influence would be 4.5 mm.

Figure 25 shows the thermal conditions near the heater borehole wall at the heater mid-height (-3.35 m). Also represented in the figure is the brine inclusion velocity, which averages about 1.8×10^{-8} cm/s (0.57 cm/yr) in the region of brine migration influence. Figure 25 indicates that the mid-height maximum borehole wall temperature is about 52.6°C , with a

borehole wall temperature gradient of $1.44^{\circ}\text{C}/\text{cm}$. These thermal conditions are based on Eqs. 1 and 2, respectively.

Comparison of Measured and Calculated Steady-State Results.

The steady-state moisture collection rate was established during the test at sites SB and NB by purging the heater boreholes for extended periods. Table 4 compares the measured moisture collection rates and the measured moisture gain for sites NB and SB. In all cases, the measured moisture gain at site SB was slightly less than that at site NB; this indicates that the synthetic brine at site SB did not migrate into the heater borehole in large quantities. The total moisture gain and moisture collection rates shown in Table 4 are in good agreement with the collection rates and total moisture gain at site NB.

The analysis determined that the effective porosity of the region around the heated borehole is about 0.14%. The computed effective moisture content of the region of significance around the heated borehole is about 0.05% by weight. The effective porosity is based on the volume of brine available within the region of significance divided by the total volume of salt plus brine. The effective moisture content is based on the volume of salt and brine, with the component densities taken into account. Generally, the moisture content of Avery Island intact salt considered to be in the range of 0.02 to 0.1% by weight (Martinez et al., 1980). This analysis is compared with a previous preliminary estimate by Krause (1979) in Fig. 26; the figure also shows the brine inflow based on assumed moisture contents in intact Avery Island salt. The moisture collection for this experiment was very small, as originally predicted (Krause, 1979).

Figure 25 Brine inclusion velocity and thermal conditions at the heater mid-height (-3.35 m) after 315 d of heating. Heater power is 0.925 kW.

Table 4 Comparison of Measured and Calculated Moisture Collection Results

Site	Duration of heating, d	Duration of moisture collection, d	Measured steady-state moisture collection rate, g/d	Total moisture gain at steady-state rate		Measured moisture gain, g
				Days	Grams	
NB	315	205	0.0175	205	3.59	8.27*
SB	315	235	0.0107	315	5.51	5.10†
				235	2.51	
				315	3.37	
			Computed steady-state moisture collection rate, g/d	Computed moisture gain, g		
		Simulation time, d				
		315	0.0173‡	5.44		

*After 205 d of moisture collection.
†After 235 d of moisture collection.
‡Assumed porosity is 0.12%; assumed density is 1.00 g/cm³.

The measured moisture collection attributable to heating within the heated borehole at site SB consisted of about 5 g for a heating period of 315 d. Correspondingly, measured

moisture collection at site NB was about 8 g after 315 d of heating. In both cases, the heated borehole wall temperature was about 51°C, with a temperature gradient of about

Figure 26 Estimated brine inflow as a function of time after heater startup for a range of volumetric brine contents in domal salt. *b*, fractional volume of brine within salt. (Data from Krause, 1979.)

1.2°C/cm, measured at the heater borehole mid-height. The measured moisture inflow and that calculated from the brine migration theory showed reasonable agreement.

Summary of Preliminary Post-Test Evaluation Activities at Site SB

The cool down of site SB was conducted with simultaneous permeability measurements and moisture collection, as previously discussed. Before cool down the synthetic brine and glass beads were removed from site SB. During the post-test period the heater and associated instrumentation were also removed from the site. These items were saved for subsequent post-test examination.

The overcore of site SB was positioned as shown in Fig. 27. During the coring process the removed segments had exposed heater and accessory boreholes within the main overcore. These exposed boreholes were plugged at the top and bottom of the removed core segment by mechanical stoppers.

Figure 27 Planned overcore for post-test evaluation at site SB.

Borehole identity	Borehole diameter, mm	Borehole depth,* m
HBH	NX 76 (3.0 in.)	5.64 (18.5 ft)
B2	EX 38 (1.5 in.)	3.81 (12.5 ft)
B4	EX 38 (1.5 in.)	3.81 (12.5 ft)
TC2	EX 38 (1.5 in.)	5.64 (18.5 ft)
OC	406 (16.0 in.)	6.10 (20.0 ft)

*Tolerances are ± 0.03 m (0.1 ft).

Using this method preserves the interior surfaces of the boreholes from external sources of contamination. After removal from the site SB location, all cores were logged, packaged, and identified.

The overcore at site SB was held $\pm 0.5^\circ$ from the vertical, which was within the drilling capabilities at the Avery Island test facility. After being shipped to RE/SPEC's laboratory, the site SB core segments were subdivided into shorter segments in accordance with requests by interested research organizations as designated by the Office of Nuclear Waste Isolation.

Results of the post-test petrofabric examinations dealing with possible changes in deuterium oxide (D_2O) concentration in the salt surrounding the heater borehole are not currently

available. The U. S. Geological Survey has determined (Clynne et al., 1981) that D_2O was contained in the moisture collection desiccant cartridges removed from site SB during heating. The implication of their analysis is that D_2O migrated through the heated salt into the heater borehole at site SB. When overcoring is complete at site SB, it may be possible to determine if synthetic brine moved into the heater borehole through microcracks in the surrounding salt. This determination will undoubtedly require chemical analyses of salt sections surrounding the heater borehole.

Conclusion

The concept of the migration of brine inclusions surrounding a heater borehole can be studied on both a macroscopic and microscopic scale. The macroscopic scale considers the gross influences of thermal conditions (gradient and temperature) on the moisture moving toward the heater borehole. Microscopic studies consider the change in inclusion shape, possible movement of tagged synthetic brine through grain boundaries, and related petrographic examinations.

These brine migration experiments had three primary objectives. The first was to conduct scoping and exploratory experiments in domal salt to examine brine movement. This objective has been achieved. The second objective was to examine techniques for more sophisticated future follow-on experiments. A more sophisticated moisture collection system should include a "closed-loop cold-trap system" and dew-point sensing methods to determine the relative humidity in the heated borehole environment. The third objective was to determine the in situ permeability of salt at different temperatures; it was also achieved. The measurements indicate that permeability changes

significantly during rapid cool down of a heater borehole.

Because of the low moisture content of domal salt and the relatively moderate salt temperatures and thermal gradients in these experiments, we expected only a small inflow of moisture to the heater borehole. The moisture collection rates were indeed quite small, but they were still within a reasonable measurement range for the long-term test. The measured moisture inflow showed reasonable agreement with analytical predictions based on present brine inclusion migration theory.

Although the heater power levels at sites SB and NB were moderate, the heat fluxes produced by the heaters are significantly greater than those of certain types of nuclear fuel. This information was originally discussed by Krause (1979) in the experimental plan for the brine migration experiments at Avery Island. These comparisons are summarized in Table 5.

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Table 5 Comparison of Power Levels and Heat Flux for Various Types of Nuclear Fuels and Avery Island Heater Emplacements

Type of fuel	Canister size		Power level, kW	Heat flux, W/m^2
	Diameter, mm	Length, m		
10-yr spent fuel	356	4.3	1.189	215.6
10-yr spent fuel	356	4.3	2.378	431.2
10-yr high-level waste	356	4.3	1.003 (1 MTHM*)	180.2
10-yr high-level waste	356	4.3	3.006 (2 MTHM*)	360.3
Heaters for brine movement studies	76	4.3	0.985 (approximate)	954.7 (approximate)
Site B, heater installed at Avery Island	406	2.4	3	888.6

*Abbreviation MTHM is metric ton heavy metal.

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Radiation Damage Studies on Synthetic NaCl Crystals and Natural Rock Salt for Radioactive Waste Disposal Applications

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Radiation damage, particularly F-center and sodium metal colloid particle formation, was studied at 100 to 300°C in synthetic melt-grown NaCl crystals and natural rock salt from different geological localities. Optical absorption measurements were made at controlled temperatures during irradiation with 1.5-MeV electrons in a unique facility for making optical absorption and other measurements during irradiation. The electron irradiations produced the same damage as do gamma rays of similar energy. Phenomenologically, damage formation was similar in pristine natural and unstrained synthetic rock salt. At temperatures where colloids are formed readily, F-center concentration vs. dose curves increased monotonically at a decreasing rate to a well-defined plateau. Concomitantly, colloid formation was described by classical nucleation and growth curves, with the onset of rapid growth (i.e., the end of the induction period) occurring at doses of roughly 10^7 rads, where the F-centers reach a plateau. The F-center plateau levels were highest at 100°C, decreased monotonically with increasing temperature, and were negligible at 300°C. In contrast, the colloid formation rate was low or zero near 100°C, increased with increasing temperature to a broad maximum at 150 to 175°C, and decreased to a negligible level

at high temperatures (275 to 300°C). The high-dose part of the colloid growth curves was well approximated by (irradiation time)ⁿ or (dose)ⁿ relations. In natural rock salt not strained in the laboratory the average *n* value for 14 samples was 1.85 ± 0.18 at 150°C and at a dose rate of 1.2×10^8 rads/h. In unstrained synthetic NaCl, *n* values were in the 4 to 6 region below and in the 2 to 3 region above 190°C. At all temperatures the *n* values in both types of salt were reduced to 1.5 to 1.6 by plastic deformation before irradiation. In both natural and synthetic salt, the induction period was altered by straining before irradiation, diminishing as the strain increased to 10% and becoming negligible for larger strains. Preliminary measurements showed that, on a unit dose basis, the colloid formation rate increases as the dose rate decreases. The Jain-Lidiard theory for radiation-induced colloid formation in NaCl accounts for some but not all of the observations. Overall the theory appears to apply better to natural than to synthetic rock salt. The measurements made to date have been confined to total doses of 2 to 4×10^8 rads. Extrapolating the (irradiation time)ⁿ or (dose)ⁿ relations to doses expected at the surface of the waste form in a radioactive waste repository indicated that doses of 10^{10} rads will convert 0.1 to 10% and 2×10^{10} rads will convert 1 to 50% of the adjacent rock

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salt to sodium metal colloid particles. The salt adjacent to the canisters will reach these doses in 50 to 400 yr. Since this large variation in damage formation results from differences in the radiation-induced colloid formation rates between samples from different locations, radioactive waste repositories are best placed in localities and/or horizons where the damage rates are low. Also, the properties of rock salt subjected to doses of 10^9 to 10^{10} rads differ markedly from those of unirradiated salt. Irradiated salt is brittle and friable, contains chlorine, and reacts with water to form H_2 gas and other products. Thus waste form canisters, which will be subject to heat, radiation, and pressure, must be designed to withstand a variety of physical and chemical interactions with irradiated rock salt.

Introduction

The radiation emitted by radioactive waste canisters placed in underground repositories will deposit very large doses in the surrounding backfill and geological material. If the canisters remain intact, only gamma-ray irradiation will escape, and the material immediately adjacent to the canister will receive doses of 10^{10} to 5×10^{10} rads in the first 50 to 1000 yr. If the canisters are breached and the contents mix with the surrounding material, alpha and beta particle irradiation will increase the dose by a factor of 10^3 or more. These values are maximum radioactivity levels considered in 1981. Obviously the dose levels would be lower for canisters with less radioactive material. For repository site selection, site and canister engineering, safety assessment, environmental impact studies, etc., a reasonably complete understanding of radiation damage effects, including the kinetics of radiation damage formation, in all the applicable geological materials is essential.

Only three applications of radiation damage data to repository considerations are given here; many more could be included:

1. Site selection. To reduce radiation damage effects, most of which would certainly be unwanted, one would choose geological locations and/or horizons where the high dose and long irradiation time damage was minimal. Such damage can be classified as mechanical, chemical, thermal (e.g., stored energy), etc. As shown in this paper, radiation-induced colloid formation varies by a factor of 10 or more in natural rock salt from different localities. In other words, appreciably less radiation damage, particularly that appearing as colloid formation, will develop at certain sites than at others.

2. Canister design. A cost-effective canister that will provide a specified degree of containment must survive in an environment containing a number of hostile components. In the absence of water, these components include radiation, heat, radiation-damaged rock salt and/or backfill minerals, and, after an unspecified time, a confining pressure that is likely to enhance such interactions as stress-induced corrosion. Also, if chlorine gas is released from irradiated salt, it will react with the materials present, particularly steel and titanium. The introduction of water or brine would facilitate a large number of additional interactions, including the release of hydrogen gas from irradiated salt. Among other reactions, hydrogen will embrittle iron, steel, and titanium. A discussion of all possible interactions, which almost certainly include unknown radiation-related effects, is much too complicated to include here. However, in evaluating these interactions, it is essential to have fairly complete information on the characteristics of the radiation-damaged minerals that will surround the waste canisters.

3. Environmental impact. A reasonably complete environmental impact assessment of repositories in rock salt and other minerals should include enough radiation-damage information on all components present to span the total dose, dose rate, temperature and stress-strain dependencies, and any possible synergistic effects likely to be encountered during the first few thousand years.

When the study described here was initiated, very little was known about radiation damage in rock salt. It was known that irradiated material contains a certain amount of stored energy and, almost certainly, radiation-induced colloid particles. At present very little radiation damage information is available for granite, basalt, tuff, and other rocks of interest for radioactive waste disposal applications. Recent radiation damage studies on both synthetic melt-grown rock salt crystals and natural rock salt samples are summarized here. Natural rock salt samples from several geologic localities under consideration as radioactive waste repository sites and from different horizons at selected sites are included. The completed studies provide appreciable information on radiation damage formation, particularly colloid particle formation, as a function of temperature and total dose. Also included is preliminary information on the role of strain applied to samples before irradiation and damage formation as a function of dose rate. Additional studies are required to produce reasonably complete understanding of radiation damage in rock salt. The more important of these include studies to determine the dependence of damage on dose rate, the effects of strain applied during irradiation, and an unequivocal determination that chlorine gas is (or is not) released from rock salt before, during, or after irradiation at temperatures expected in repositories.

Preliminary reports on some of the material described here have been published previously (Swyler, Klaffky, and Levy, 1979, 1980; Klaffky, Swyler, and Levy, 1979; Levy, Swyler, and Klaffky, 1980). Additional details are included in a number of reports from the Office of Nuclear Waste Isolation (ONWI), either published or in preparation (Swyler, Klaffky, and Levy, 1982; Klaffky, Swyler, and Levy, 1982; Loman, Levy, and Swyler, 1982). Also being prepared are reports on heat-induced colloid formation in previously irradiated natural and synthetic rock salt (Elgort and Levy, 1982) and the thermoluminescence of irradiated natural and synthetic rock salt (Skinner, Levy, and Kierstead, 1982).

Previous Radiation Damage Studies on Natural and Synthetic Rock Salt

A very large fraction of the available information on radiation damage in rock salt (especially in melt-grown synthetic NaCl crystals), as well as general information on color centers, is contained in well-known books (Schulman and Compton, 1962; Fowler, 1968; Crawford and Slifkin, 1972; Markham, 1966; Stoneham, 1975). A concise summary of color center information has appeared recently (Levy, 1981). Considering the extensive literature available on color centers, it is surprising that the information on sodium chloride color centers above room temperature is limited. Specific information on radiation effects in sodium chloride relevant to the studies reported here falls into a number of different categories.

Jenks et al. (1975) described the chemical species formed when irradiated NaCl is dissolved in water. A number of papers and reports describe measurement of stored energy in natural and synthetic rock salt (Jenks, et al., 1975; Jenks and Bopp, 1977;

Dreschhoff and Zeller, 1977; Moss, 1980). Dreschhoff (1973) also described color center and related measurements on salt crystals irradiated with protons. Radiation damage studies in sodium chloride have been made with an electron microscope as both the irradiating device and the analyzing instrument (Hobbs, 1973, 1975; Hobbs, Hughes, and Pooley, 1973). The electron microscope studies are supplemented by color center measurements. The work of Hobbs and co-workers established a number of features of radiation damage formation in synthetic sodium chloride. The more important are:

- Colloid particles were observed at large doses.
- Colloid formation was accompanied by dislocation climb.
- Colloid formation appeared to depend on temperature, with the maximum colloid formation rate occurring at roughly 150°C.
- Dislocation climb occurring during colloid growth appeared to be accompanied by the incorporation of chlorine molecules in the dislocation debris.

Last, the work of Hobbs and co-workers prompted Jain and Lidiard (1977) to develop a theory for radiation-induced colloid formation in sodium chloride. As will be demonstrated, many aspects of this theory are in accord with the experimental results, but other aspects are at variance with the available measurements.

The information listed—even if many details are omitted or not understood—makes it possible to provide a qualitative description of the radiation damage processes occurring in NaCl above room temperature. In general, any gamma rays, in the MeV energy range, incident on solids produce electron recoils with somewhat less average energy. These recoils are entirely equivalent to electrons of similar energy produced in an accelerator. The energetic electrons create numer-

ous electrons and holes, i.e., ionization along the recoil trajectories. In NaCl the ionization causes Cl^- ions to be ejected from their normal lattice sites to form interstitial chlorine atoms and empty lattice sites. Usually the empty Cl^- lattice site traps an electron to become an F-center. This process, called ionization damage, is responsible for most of the radiation-induced vacancy-interstitial-pair formation in NaCl (Crawford and Slifkin, 1972). These defects, which separate immediately and are mobile, enter into many types of interactions. These include vacancy-interstitial recombination (which restores one lattice point to its original condition); the trapping of vacancies and/or interstitials by defects, dislocations, and colloid particles; and defect aggregation (e.g., to form vacancy-vacancy pairs). In the presence of ionization, some defects are converted to color centers by charge trapping, e.g., single vacancies to F-centers and side-by-side vacancies to M-centers. Most importantly, color centers and colloid particles give rise to distinctive absorption bands, and the corresponding defect concentrations can be measured by optical absorption techniques.

During irradiation the interstitial chlorine atoms in rock salt are quickly trapped by defects and enter into other processes, such as formation of Cl_2 molecules and the accretion of Cl atoms and Cl_2 molecules in climbing dislocation loops. The less mobile vacancies and/or F-centers enter into various interactions. The trapping of vacancies and/or F-centers on any existing colloid particle is the mechanism for colloid growth. Each vacancy arriving at the colloid surface allows one sodium atom in the NaCl crystal lattice to join the colloidal sodium metal lattice. The initial, or nucleation, step in the formation of colloid particles is one of several radiation-induced processes in NaCl not now understood.

Sodium atoms may diffuse from colloid particles. This process and vacancy and/or F-center diffusion are strongly temperature dependent. Thus radiation damage and particularly colloid formation should be strongly temperature dependent. At low temperatures the damage formation rate is low because the defect diffusion rate is low. At high temperatures colloids should grow very slowly, or not at all, because sodium atoms would readily diffuse from colloids. Thus the maximum damage formation rate would occur at an intermediate temperature. As is demonstrated in the following sections, the mechanisms sketched here provide a reasonably good qualitative description of what actually occurs.

Current Radiation Damage Studies of Natural and Synthetic Rock Salt

The kinetics of F-center and colloid particle formation have been studied in both natural rock salt and synthetic sodium chloride between 100 and 300°C. More specifically, F-center and colloid growth was recorded as a function of irradiation time for samples at controlled temperature while they were irradiated with electrons of specified energy and beam intensity. Making these measurements during irradiation enables one to examine transient radiation effects, i.e., to determine whether radiation-induced species are present during irradiation whose concentrations would change or whether species present might not be observed at all if the samples were measured after irradiation. Furthermore, by measuring during and after irradiation at different temperatures, we can determine if the radiation-induced defects are stable or if they increase or decrease after irradiation. The results will often appear as curves of F-center and/or colloid particle concentration vs. irradiation time,

or time after irradiation, at a given temperature and dose rate. The results will be used to determine which features are, or are not, in accord with the Jain-Lidiard theory. Also included are the data needed to make very rough estimates of the amount of radiation-induced sodium metal colloid formed in rock salt under repository conditions. Finally, additional research required to obtain a reasonably complete understanding of radiation effects in rock salt is outlined.

Experimental Details

Samples and Sample Preparation. All measurements of synthetic melt-grown NaCl were made on samples cleaved from a single large piece purchased from Harshaw Chemical Co. Individual samples were approximately 1 by 1 cm by 0.5 mm thick. Natural rock salt samples were obtained from a variety of geologic locations, usually as drill cores or hand specimens (see Table 1). Unfortunately, the information supplied with many of the samples was incomplete.

Approximately 80% of the natural samples received contained crystallites large enough to obtain 5- by 5- by 0.5-mm crystals; this is the smallest size that is useful for optical absorption measurements. Often 0.5 kg or more of sample had to be carefully separated before a crystallite large enough to study would be found. Some samples were not studied because they did not contain sufficiently large individual crystallites.

Certain samples were deformed before irradiation to determine how strain (i.e., plastic deformation) influenced the measurements. They were uniaxially compressed along the longest <100> direction in an Instron Corporation machine at a strain rate of approximately 0.01 mm/min. Stress-strain curves recorded during deformation indicated that the yield

Table 1 Natural Salt Samples

Name	Location	Depth, m	Formation	Minerals or impurities
AEC-8	Los Medanos, NM (WIPP site)	810		Br
Alt Ausee	Austria			Cr, Fe 6 ppm; Br, 84 ppm
Asse 1	Near Braunschweig, Federal Republic of Germany (FRG)	511	Leine series Liniensalz Na ₃ B	Halite, anhydrite (trace)
Asse 4	Near Braunschweig, FRG	775	Leine series Liniensalz Na ₃ B	Halite, 99%; anhydrite, 1%
Asse 6	Near Braunschweig, FRG	775	Stassfurt series, "Speissalz" Na ₂ SP	Halite, 99.3%; polyhalite, 0.5%; anhydrite, 0.2%
Asse 8	Near Braunschweig, FRG	800	Stassfurt series, Na ₂	Halite, anhydrite
Asse 9	Near Braunschweig, FRG	975	Stassfurt series, Na ₂	Halite
Avery Island	Louisiana	158.5		
ERDA-9	Los Medanos, NM (WIPP site)	812.5		Fe, 5 ppm; Br, 12 ppm
Lyons	Kansas			
Retsof	New York			
Rocanville	Saskatchewan, Canada		Above ore horizon	Br, 10 ppm
Rocanville	Saskatchewan, Canada		In potash ore horizon	Si, 0.2%; K, 0.1%; Br, 18 ppm; Ca, 0.05%; Fe, 9 ppm; Ni, 5 ppm
Rocanville	Saskatchewan, Canada		Recrystallized	

points for unirradiated synthetic crystals were in the 10 to 12 kg/cm² range and were quite reproducible. This indicates that the cleaving operation had not introduced detectable strain. In contrast, all the natural rock salt crystals appear to contain between 3 and 10% strain. Such strains are to be expected in both bedded and dome rock salt samples. During compression the samples almost always develop slip bands on the $\langle 110 \rangle$ planes that traverse the crystals in the shortest dimension. Heavily deformed samples exhibit lamellar banding, with numerous slip bands traversing the crystal perpendicular to the compression direction. Strains of

15% or less did not appear to affect the optical absorption measurements adversely.

Radiation Effect Measurements.

All radiation effect measurements discussed here were made with the equipment for making simultaneous optical absorption and luminescence measurements on samples while they are being irradiated with energetic electrons. This apparatus, usually referred to as the Optical Electron Radiation Facility, is shown in Fig. 1. It contains a computer-controlled 13-m-long double-beam spectrophotometer, with all radiation sensitive instrumentation outside the irradiation chamber. The spectrophotometer

Figure 1 Spectrophotometer used to make optical absorption and luminescence measurements on samples before, during, and after irradiation with 0.5- to 3.0-MeV electrons. The high-energy electrons are produced by a vertical accelerator located directly above the bending magnet that turns the electron beam horizontally into the irradiation chamber. The irradiation chamber temperature is electronically controlled. All radiation-sensitive equipment is located outside the target room. The entire apparatus is controlled by a computer, which is also used to record the data.

beam and the energetic electron beam intersect at right angles; the sample is placed at an angle of 45° to these beams. Both the sample and the reference beams are synchronously chopped in a way that makes it possible to determine both the absorption and radioluminescence spectra of the sample. In its present configuration, a

256-point absorption spectrum and a 256-point luminescence spectrum are recorded simultaneously, typically from 200 to 400 nm (6.2 to 3.1 eV) or 400 to 800 nm (3.1 to 1.5 eV), as often as every 40 s. Typical rock salt absorption and luminescence spectra recorded at various times after irradiation began are shown in Fig. 2.

Figure 2 Optical absorption and luminescence spectra of natural rock salt from Rocanville, Saskatchewan, recorded sequentially after irradiation began. Measurements of this type, typically at either 200 to 400 or 400 to 800 nm wavelengths, can be made as often as every 40 s. Because of the double-beam nature of the spectrophotometer, the "noise" in the luminescence spectra is eliminated from the absorption spectra. All natural and synthetic samples examined to date exhibit luminescence, but luminescence measurements are not discussed in this paper. The absorption spectra clearly show the F-center and colloid growth characteristics described in detail in the text.

For measurements above room temperature, the sample is placed in an irradiation chamber with electronic temperature control. The chamber has fused silica windows to transmit the spectrophotometer light beams and Havar windows to transmit the electron beam into and out of the chamber. Radiation-induced coloring of the fused silica windows and any fluorescence emitted by them is automatically corrected by the double-beam spectrophotometer.

The heated chamber is thermally insulated by a surrounding vacuum and filled with helium at approximately 5 torr to minimize thermal

gradients. The temperature-control sensing thermocouple is in the chamber gas, and the sample temperature is measured by a thermocouple in contact with it. Electron beam heating of the sample cannot be ignored. Consequently, before the start of irradiation the chamber is adjusted to a temperature approximately 3 to 5°C below that desired. Once irradiation begins the controller is set to the desired temperature, the sample temperature increases rapidly and, depending on the beam current, reaches that specified within 5 to 10 min. If the beam current is maintained constant to within $\pm 5\%$, the sample tempera-

ture does not vary by more than $\pm 1^\circ\text{C}$ during the remainder of the irradiation, which may continue for 4 hr or more.

For the measurements described, the electron energy was fixed at 1.5 MeV. A thin gold scattering foil was placed in the beam tube "upstream" from the irradiation chamber to insure that the sample was irradiated uniformly. Because of energy loss in the scattering foil and the irradiation chamber Havar window, the energy of the electrons incident on the sample was approximately 1.3 MeV. From calculations based on published dE/dx data, measurements made with aluminum foils, visual observations on the coloring of PVC film, and microscopic examination of irradiated crystals, it was established that the samples were uniformly irradiated. When examined after irradiation, crystals that do not contain colloids exhibited the golden brown color associated with F-center coloring. With rare exceptions, this coloring was quite uniform; it was very uniform in unstrained synthetic crystals. Unstrained crystals irradiated under conditions producing colloids exhibited the uniform blue, dark blue, or blue-black coloring characteristic of colloids. In some cases, particularly in strained natural crystals, the colloid coloring was nonuniform. The optical density may vary by as much as 1 or 2, and the darkly colored regions were often bounded by or banded along $\langle 110 \rangle$ planes. These observations are in accord with the well-known properties of natural blue rock salt and the demonstrated relation between F-center and colloid coloring with the $\langle 110 \rangle$ slip systems in plastically deformed synthetic NaCl (Agullo-Lopez and Levy, 1964). During irradiation the electron beam traversing the sample was continuously monitored by recording the current incident on a Faraday cup placed immediately behind the exit window of the irradiation chamber. The relation

between the current recorded by this cup and the current actually incident on the crystal being irradiated was determined by measuring with a Faraday cup located at the sample position inside the irradiation chamber. The beam current traversing the sample was recorded by the computer at the same time as the absorption measurements.

During almost all the measurements described, the beam current incident on the sample was $280 \times 10^{-9} \text{ A/cm}^2 (\pm 5\%)$. From published dE/dx data, it is readily computed that these radiation conditions impart a dose of 1.2×10^8 rads/h to NaCl crystals. Also, under these conditions the dose deposition is relatively uniform throughout the crystal, especially for crystals 0.75 mm or less in thickness.

It is well known that appreciable charge buildup can occur in insulators during electron irradiation, especially when the crystal dimensions exceed the electron range. Most electron irradiations were arranged so that the incident particles pass completely through the crystal to avoid charge buildup difficulties. Some charge buildup can still occur, however, primarily because electrons can be scattered into trajectories lying entirely within the crystal. Consequently, to determine whether charge buildup influenced the measurement of radiation effects in rock salt, we measured a number of crystals whose largest surfaces had been coated with a thin conducting layer. The results obtained for coated crystals were the same as those for the normal samples. Evidently, the high ionization density created in the crystal, conduction to the metal crystal holder, conduction through ionization in the exchange gas surrounding the crystal, and perhaps some other processes prevented charge buildup in these crystals from reaching detectable levels.

Before each series of irradiation measurements, the optical absorption of the unirradiated crystal was measured. The position of the crystal, the irradiation chamber, and other elements in the system were not changed during the subsequent measurements. Usually the absorption of the crystal before irradiation was subtracted from the numerous spectra recorded during irradiation. The resulting absorption spectra showed only the radiation-induced changes. This procedure is particularly useful; the data obtained are independent of minor variations in the position of the sample, the irradiation chamber, etc.

Measurements

The general features of the radiation-induced F-center and colloid formation in both synthetic NaCl crystals and natural rock salt samples, above approximately 100°C, are illustrated in Fig. 2. This figure shows both absorption and luminescence spectra from 350 to 750 nm recorded at various times after irradiation began. The luminescence has not been studied in detail and is not described here. The sample was at 150°C during irradiation, with 1.3 MeV electrons at a dose rate of approximately 1.2×10^8 rads/h. The absorption at the peak of the F-center band (roughly 2.6 eV) increases monotonically, but at a decreasing rate, until it reaches a "plateau" with a slight slope. Toward the end of the irradiation, however, the F-band growth again appears to increase rapidly. The F-band growth is markedly different from the growth at 2.1 eV. As will be demonstrated, the absorption at 2.1 eV includes an F-band component. During the initial part of the irradiation, the absorption at 2.1 eV is attributable to only the F-band component. At roughly the dose where the F-band absorption reaches the "plateau" region, the absorption at 2.1 eV begins

to increase at an ever increasing rate, and toward the end of the irradiation it is growing much more rapidly than the F-center absorption. Information from the color center literature and detailed studies on the absorption centered around 2.1 eV, which is contained in a separate paper (Klaaffky et al., 1982), indicates that the principal absorption near 2.1 eV is attributable to the presence of colloidal sodium metal particles. In a strict sense, the "absorption" arising from colloids should be referred to as "extinction," but here we refer to it as absorption.

Numerous spectra, such as those shown in Fig. 2, were recorded at various temperatures between roughly 100 and 300°C for one set of synthetic and one set of natural rock salt samples. The natural samples are from the 810-m level of drill hole AEC-8 at the waste isolation pilot plant (WIPP) site. Additional measurements were made on samples from various geological localities and different levels at certain sites, but only at 150°C. Phenomenologically, the radiation-induced F-center and colloid band absorption at various temperatures between 100 and 300°C is the same for both natural and synthetic samples. The F-band vs. irradiation time curves in the initial growth and plateau regions are most intense at 100°C and decrease with increasing irradiation temperature. At the high-dose end of the 2.6-eV growth curves, at temperatures where the colloid absorption is increasing very rapidly, the colloid band absorption causes the absorption to increase equally fast. The colloid band growth curves depend strongly on sample temperature during irradiation. There is little or no colloid formation at 100°C. As the radiation temperature is increased, the colloid formation rate increases rapidly until it reaches a maximum at the 150 to 175°C range; then it decreases rapidly. Colloid formation is low or negligible in the 250 to 275°C region.

The characteristics of the resolved F-center and colloid band growth curves are described in detail in the sections that follow. The F-center and colloid growth are shown to depend on irradiation temperature, dose rate, and strain applied before irradiation. The decay of F-center absorption, which occurs after the irradiation is terminated, is also described. Other factors, such as impurity content, the presence of voids, previous exposure to radiation, and temperature cycling and annealing, are known to influence the F-center and colloid growth. Except for the preliminary studies included in separate sections, these have not been studied.

Resolution of Recorded Absorption Spectra into Individual F-Center and Colloid Absorption Bands. As described, the F-center and colloid absorption bands overlap to the extent that the colloid band contributes to the measured absorption at the peak of the F-band and the F-band absorption underlies much of the colloid absorption. When precise F-center and colloid band growth curves and colloid band shapes are required, it is essential to resolve the recorded spectra into individual components. The following resolution procedure was developed: First, the shape of the F-center absorption band was determined from spectra recorded at low doses where the colloid band absorption was negligible. Second, a spectrum was chosen which contains F-center absorption near the saturation level and little or negligible colloid band absorption. This spectrum was subtracted from spectra recorded at later times. If this choice was satisfactory, the resulting spectrum contained only the colloid absorption induced by additional irradiation. If the resulting spectra contained F-band contributions, however, another spectrum was chosen, and the procedure was repeated until the F-band

contribution was negligible. The resolved colloid and F-center bands were then fitted to the measured spectra by a procedure that adjusted the F-center and colloid band intensities until a least-squares best fit was obtained. Although this procedure is laborious and time consuming, it provides an excellent separation of the F-center and colloid bands. If the intensity factors are not adjusted for each recorded spectrum, the procedure introduces small discontinuities in the growth curves. A typical spectrum resolved into individual bands is shown in Fig. 3.

The resulting colloid absorption bands can be fitted to small-particle versions of Mie theory (Klaaffky, Swyler, and Levy, 1979, 1982). This analysis provides useful information about the colloid particles. In fact, in most cases the average colloid particle diameter, the colloid particle concentration, and the total number of sodium atoms contained in colloid particles can be determined. A resolved colloid band fitted to small-particle Mie theory is shown in Fig. 4.

F-Center and Colloid Growth as a Function of Irradiation Temperature. From numerous data sets, such as those shown in Fig. 2, and the resolution procedure described in the previous section, we constructed F-center and colloid band growth curves (Figs. 5, 7, and 8) for selected irradiation temperatures for one set of natural (AEC-8) and one set of synthetic rock salt crystals. The resolved F-center growth plot (Fig. 5) illustrates a number of important features. First, as the irradiation temperature increases, the F-center saturation level decreases. Second, as the radiation temperature increases the rate at which the F-center coloring approaches saturation increases; at 303°C the F-center coloring curve has reached saturation at 1000 s; whereas the 132°C curve appears to be increas-

Figure 3 Absorption spectrum for synthetic NaCl resolved into bands. Uppermost data points correspond to a typical absorption spectrum, such as that shown in Fig. 2, recorded after the irradiation has reached a dose sufficient to produce an F-center band at approximately 2.6 eV and a colloid band near 2.1 eV. The measured spectrum was resolved into F-band and colloid-band components using the procedure described in the text. Lines through the data points are the sum (i.e., superposition) of the individual absorption bands. Almost all the F-center and colloid band growth curves shown were constructed from numerous spectra resolved into individual components.

ing at 6000 or 7000 s. Third, at intermediate temperatures the synthetic salt growth curves exhibit structure; e. g., the 174°C curve rises initially, levels off, and then rises again. In the color center literature such a curve is often said to exhibit first-, second-, and third-stage coloring. In contrast, as shown in Fig. 6, the natural salt samples do not exhibit this structure. The color center literature would describe them as exhibiting only a single coloring stage. Finally, in both natural and synthetic rock salt, the F-center saturation levels are strongly temperature dependent. Additional information on the temperature dependence is included in the discussion section.

Colloid band growth curves for synthetic NaCl at temperatures exhibiting significant colloid formation are shown in Fig. 7 on a log-log plot. Colloid formation at temperatures from 100 to 275°C in natural rock salt samples from the WIPP site is shown in Fig. 8. These figures illustrate a number of important characteristics of radiation-induced colloid formation in both types of rock salt. First, all the curves exhibit pronounced induction periods followed by a regime of rapid growth. (This may not be readily discernible for the lowest temperature curves.) In other words, colloid formation as a function of irradiation time or dose is described by a classical nucleation and growth curve.

Figure 4 Resolved colloid absorption band for synthetic NaCl. Points represent an absorption band similar to that shown in Fig. 3. Data were fitted to a small-particle version of Mie theory. Parameters obtained by this procedure are: 1.44 nm colloid particle radius, 7.19×10^{14} colloid particles/cm³, and 9.01×10^{-6} colloid particle volume fraction.

Figure 5 F-center growth curves for synthetic rock salt irradiated at various temperatures. Growth curves were constructed from spectra resolved into individual F-center and colloid bands by using the procedure illustrated in the previous figures. Saturation levels decreased monotonically with increasing temperature. Some of the growth curves, particularly at intermediate temperatures, exhibit structure often referred to in the color center literature as first-, second-, and third-stage coloring.

Figure 6 F-center growth curves for natural rock salt samples from drill hole AEC-8, 810-m level, at the WIPP site near Los Medanos, NM. In this case the F-center saturation level also decreases with increasing temperature. However, none of the growth curves exhibit the structure observed at the intermediate temperatures in synthetic rock salt samples. These data have not been corrected for F-center and colloid band overlap.

As is well known, for such curves the transition from the induction period to the rapid growth regime often is not accompanied by a discontinuity in the curve or in its first- or second-order derivatives. Consequently, in these cases the duration of the induction period and the onset of rapid growth cannot be defined in a nonarbitrary manner. Second, as mentioned previously, these curves exhibit a pronounced dependence on irradiation temperature. Although not shown in Fig. 7, colloid growth was not detected in synthetic samples irradiated at approximately 115°C. From the data shown in Fig. 7 and additional data that are not illustrated, we concluded that the colloid formation rate—at least in the dose range and dose rates covered by these measurements—is low or negligible in

the 100 to 115°C range, increases rapidly with increasing temperature to reach a broad maximum at 150 to 175°C, and decreases with increasing temperature until it is negligible in the 250 to 275°C range. Third, as illustrated by Figs. 7 and 10, at the high-dose end of the curves colloid band area vs. irradiation time is well approximated by $(\text{time})^n$ or $(\text{dose})^n$ dependence. Such t^n dependencies are often observed in nucleation and growth phenomena. On close inspection of Fig. 8 we see that the temperature dependence may not be completely regular; e.g., the colloid formation rate at 227°C appears to be greater than that at 200°C. Such deviations could be real or, as is quite likely, could be introduced by experimental error. Lastly, as illustrated in the following paragraph, colloid

Figure 7 Colloid band growth curves for synthetic rock salt samples used for Fig. 5 and irradiated at the indicated temperatures at 120 Mrads/h. At intermediate temperatures the curves contained the prominent low or zero growth regions followed by rapid growth regions, which are characteristic of classical nucleation and growth curves. The colloid formation rate is low in the 100°C region, increases with increasing temperature to a broad maximum at 150 to 175°C, and decreases as the temperature increases, reaching a negligible level at approximately 300°C. Colloid band growth data for synthetic rock salt are plotted on a log-log plot, which demonstrates that the colloid growth can be characterized by a t^n or dose n relation at the high-dose end of the rapid growth regime.

Figure 8 Radiation-induced colloid growth curves for natural rock salt from drill hole AEC-8, 810-m level, at the WIPP site, measured at various temperatures. Dose rate is 1.2×10^8 rads/h. These data are well described by a t^n relation at the high-dose end. The contour lines at constant irradiation time (solid lines) and separate contour lines at constant absorption coefficient (dashed lines) demonstrate that both the induction period and the colloid formation rate depend on irradiation temperature.

Figure 9 Temperature dependence of the power n in the Ct^n relation for colloid growth in both synthetic and natural salt. Dose rate is 120 Mrads/h. The power n is strongly temperature dependent in synthetic salt, with values between 1.5 and 6.2, but only weakly dependent in natural salt (values between 1.6 and 2.3).

growth is strongly influenced by a number of additional factors, e.g., strain applied to the samples before irradiation.

The $(\text{time})^n$ and $(\text{dose})^n$, or more concisely the Ct^n relations, are readily fitted to data curves (such as Figs. 7 and 10) by numerical best-fit procedures. A number of results are obtained. First, as shown in Fig. 9, the n values for synthetic NaCl are strongly temperature dependent; they vary from 1.5 to 6.2. In contrast, the n values for natural rock salt vary little over the same temperature range; they lie between 1.6 and 2.4. The n values for synthetic NaCl are reduced to 1.5 to 1.6 by severe plastic strain applied before irradiation. Additional details on colloid growth are described in the following section for several important situations.

Radiation-Induced Colloid Growth in Natural Rock Salt

from Different Localities. The measured colloid formation rate in natural rock salt from numerous geological locations and for different horizons at selected locations is summarized in Fig. 10. At the high-dose, or irradiation-time, end of the curves, the growth is very well described by the Ct^n relations. The best-fit values are tabulated in Table 2. The C values vary by a factor of 10^3 or more, but the n values cluster. The average value of n is 1.85 ± 0.18 .

The data in Table 2 can be used to estimate the sodium metal present in the salt, from the listed locations and for a given dose, if we assume that the effective salt temperature is 150°C and the Ct^n relation is valid up to the time, or dose, in question. For example, using the data in Table 2 to estimate the colloid metal present after an irradiation of 10^4 s (3.33×10^8 rads at a dose rate of 1.2×10^8 rads/hr), we find that the colloid metal in these samples varies by a factor of 80. These considerations have practical applications. A site, or certain horizons at a given site, should be selected to minimize colloid formation in a repository.

F-Center Decay After Termination of Radiation. For temperatures in the 100 to 300°C range, after the irradiations are terminated, the F-center absorption decays monotonically in both synthetic and natural rock salt. This is illustrated in Fig. 11, which shows the measured F-center absorption vs. time after irradiation for synthetic rock salt samples maintained at the indicated temperatures both during and after irradiation. As described elsewhere (Swyler, Klaffky, and Levy, 1982) plots of log absorption vs. time after irradiation are sensibly linear for most of the decay period. This indicates that the F-centers decay exponentially. From the usual Arrhenius plot (i.e., a plot of decay constant vs. $1/T$), we

Figure 10 Colloid formation in natural rock salt samples from numerous geological locations and different horizons at selected locations. All measurements were made at 150°C and at a dose rate of 1.2×10^8 rads/h. The average slope is 1.85, with a standard deviation of 0.18. When the colloid growth rate is described by the relation Ct^n or $(\text{constant}) \times t^n$, values of the constant differ by more than a factor of 10^3 . As described in the text, part of this variation can be attributed to impurities present in the samples; additional variations could result from sample-to-sample variations in strain, etc.

determined that the activation energy for the F-center decay, shown in Fig. 11, is approximately 1 eV. This is a reasonable value for several electronic and defect diffusion processes that could be invoked to explain the F-center decay.

The F-center decay data are a particularly good example of the special usefulness of the apparatus used for

this study of radiation effects in natural and synthetic rock salt. As explained previously, this apparatus records optical absorption spectra during irradiation. The data in Fig. 11 clearly demonstrate that the F-center concentration during irradiation is appreciably greater than that which would be recorded if the sample were measured some time after irradiation.

Table 2 Values of the Constants C and n in the Ct^n Relation*

Sample	n	C
AEC-8, New Mexico (WIPP site)	1.87	4.50×10^{-13}
Alt Aussee, Austria	1.98	3.60×10^{-13}
Asse 1, FRG	1.84	2.71×10^{-12}
Asse 4, FRG	1.77	1.34×10^{-12}
Asse 6, FRG	2.08	1.60×10^{-13}
Asse 8, FRG	2.17	1.86×10^{-14}
Asse 9, FRG	2.05	6.47×10^{-14}
Avery Island, Louisiana	1.66	8.80×10^{-12}
ERDA-9, New Mexico (WIPP site)	1.73	2.82×10^{-12}
Lyons, Kansas	1.87	7.43×10^{-13}
Retsof, New York	1.56	4.14×10^{-11}
Rocanville, Saskatchewan, Canada, above ore	1.57	2.72×10^{-11}
Rocanville, Saskatchewan, Canada, with ore	1.83	6.78×10^{-13}
Rocanville, Saskatchewan, Canada, recrystallized	2.41	6.14×10^{-15}

*Mole fraction NaCl converted to colloidal Na = Ct^n , where t is irradiation time (s). These values were obtained from the data used for Fig. 10. The validity of this relation has not been experimentally verified beyond the doses shown in Fig. 10.

This is especially true for samples measured at the highest temperatures. The measurements shown here are in accord with previous results showing that both synthetic NaCl and KCl F-centers decay when irradiated at room temperature (Mattern, Lengweiler, and Levy, 1971; Levy, Mattern, and Lengweiler, 1970). The ability to make measurements during irradiation is important for two reasons. First, it demonstrates that certain defect and/or color center levels are appreciably higher during irradiation in comparison with levels observed if measurements are made some time after irradiation. Second, in determining the kinetics of radiation-induced defect formation, it is clearly advantageous to know the defect levels present during irradiation rather than to surmise them from data obtained after irradiation. In fact, it is entirely possible that an adequate understanding of radiation effects in both natural and synthetic rock salt could not

be obtained if measurements could not be made during irradiation.

F-Center and Colloid Band Growth in Crystals Strained Before Irradiation.

It is well established that color center formation in alkali halide crystals can be strongly influenced by subjecting the crystals to strain before irradiation. Consequently, preliminary measurements were made to determine how preirradiation strain influences the F-center and colloid growth at the temperature corresponding to the most rapid colloid formation, namely, 150°C. The absorption that corresponds roughly to the peak of the colloid absorption band for unstrained crystals and for crystals strained before irradiation are shown in Figs. 12 and 13. These figures and additional data not included demonstrate clearly that the colloid growth induction period is shortened for strains between zero and roughly 10% and is

Figure 11 F-center decay occurring after irradiation in synthetic rock salt samples at different temperatures. Similar decay is observed in natural rock salt samples. This figure demonstrates the importance of making the measurements during irradiation. It would be difficult, if not impossible, to determine F-center concentrations during irradiation from F-center absorption present some time after irradiation, particularly at high irradiation temperatures. In most cases the colloid decay occurring after irradiation is appreciably smaller.

Figure 12 Radiation-induced colloid formation in synthetic rock salt samples strained by uniaxial compression to the indicated amounts before irradiation. As the preirradiated strain increases from 1 to roughly 10%, the induction period decreases. Strains greater than 10% do not induce additional induction period effects.

Figure 13 Radiation-induced colloid formation in natural rock salt samples from drill hole AEC-8 strained by uniaxial compression to the indicated amounts before irradiation. The dose rate was 120 Mrads/h, and the irradiation temperature was 150°C. Shortening of the induction period by preirradiation strain in both natural and synthetic rock salt samples is similar. Only samples strained 10% or more exhibit induction period free colloid growth.

effectively reduced to zero for strains of 10% or more. Since strains of this magnitude are known to introduce copious dislocations and slip systems, it is reasonable to assume that the colloid particle nucleation process is related to the dislocation density, e.g., see Hobbs, Hughes, and Pooley (1973). In crystals strained between 1 and 10%, the nucleation process depends on the dislocation and/or slip system density. At larger strains the dislocation density is high enough to obviate the induction process.

The corresponding F-center growth curves are also modified by preirradiation strain. The F-center saturation levels in the few samples measured do not appear to depend on strain in any regular manner. However, the rate at which the F-center concentration grows to saturation increases concomitantly with increasing preirradiation strain. These studies appear to show a strong connection between the colloid nucleation and growth processes and the dislocation content of the crystals. They clearly indicate that strain and dislocation related

processes should be studied in more detail.

Dependence of F-Center and Colloid Growth on Irradiation Dose Rate. To determine, at least in a preliminary way, how the F-center formation and colloid particle growth curves depend on dose rate, we irradiated unstrained samples at 150°C at different dose rates. The recorded colloid growth curves (Figs. 14 and 15) resemble closely those shown in Figs. 7, 8, and 10 and can be characterized in different ways. Inasmuch as there appears to be a close relation between the dose at which F-centers near saturation and the onset of rapid colloid growth, the F-center curves can be characterized by determining the dose at which the F-center concentration reaches 90% of the saturation concentration. As mentioned above, the colloid growth curves are more difficult to characterize since they do not have inflection points that provide a natural demarcation between the induction regime and the rapid growth regime. Consequently, the induction period has been defined as

Figure 14 Colloid formation in synthetic rock salt samples irradiated at different dose rates at 150°C.

the dose, or the irradiation time, required for the colloid absorption to reach an arbitrarily chosen value, usually 1.0 or 10.0 cm⁻¹. Saturation and induction period doses obtained in this way for synthetic rock-salt samples irradiated at different dose rates at 150°C are shown in Table 3. Similar results are obtained for natural rock salt.

The data shown in Figs. 14 and 15 and Table 3 could have important consequences for radioactive waste repositories. They indicate that the colloid formation is inversely dependent on dose rate. In other words, on a unit dose basis, low dose rates are more effective in producing colloids than high dose rates. The dose rates expected in the planned repositories are appreciably less, by factors of 10² to 10⁴ or greater, than those used in these studies. For this reason the dependence of colloid formation on dose rate must be investigated much more carefully.

Transient Dose-Rate-Dependent F-Center and Colloid Particle Interactions. An intimate interaction between the F-centers and colloid particles, which is dependent on both dose rate and the conditions applying when the irradiation is terminated, is

Figure 15 Colloid formation in natural rock salt samples from drill hole ERDA-9 irradiated at 150°C at different dose rates. Data for both the synthetic (see Fig. 14) and natural rock salt dose rates indicate that, on a unit dose basis, the lowest dose rate produces the largest colloid formation rate. These measurements were made at dose rates appreciably higher than those anticipated for actual repositories. If the suggested trend continues to very low dose rates, colloid formation in an actual repository can be expected to be quite large. For this reason, colloid formation dose rate dependencies should be carefully investigated.

shown in Fig. 16. This shows both the F-center and colloid particle absorption, recorded during irradiation, as the dose rate was changed. More explicitly, the F-center and colloid absorption was measured at a constant dose rate for the initial part of the measurement. Next, at the indicated points, the beam was decreased by the factors shown in the figure. Finally, the beam was restored to its initial level. A discontinuity appears in both the F-center and colloid band growth curves each time the beam current was changed. When the beam current is reduced, the F-center concentration drops abruptly and the col-

Table 3 F-Center and Colloid-Band Growth Parameters for Unstrained Synthetic Rock Salt Samples Irradiated at Different Dose Rates at 150°C

Dose rate, Mrad/h	F-center saturation absorption, cm^{-1}	F-center saturation dose,* Mrad	Colloid induction period dose,† Mrad
60	22	80	185
120	31	120	260
340	50	225	440

*Dose required to increase the F-center absorption to 90% of the saturation level.

†Dose required to increase the colloid band absorption to 10 cm^{-1}

Figure 16 Dose-rate-dependent transient interactions between F-centers and colloid particles for synthetic NaCl at 125°C. F-center and colloid absorption was recorded initially at a constant dose rate of approximately 10^8 rads/hr; then, at the indicated points, the dose rate was changed by the factors shown. Each decrease in dose rate is accompanied by a corresponding increase in colloid formation and a decrease in the F-center concentration. When the beam was restored to its original value, both the colloid particle and F-center absorption curves follow circuitous paths to levels that correspond roughly to extrapolations of the initial part of the growth curves. Finally, when the beam was turned off, the F-center and colloid absorption levels changed very little. These measurements indicate that at least one radiation-related species is present and/or is mobile only during irradiation.

loid growth rate changes discontinuously to a higher value. In each interval the F-centers tend to decay to a new plateau and the rate of colloid growth decreases. Finally, when the beam current was restored to the original level—an increase by a factor of 80—the changes induced by the previous decreases in beam current are abruptly reversed. The F-centers increase—first rapidly and then at a lower rate—and appear to approach a level corresponding roughly to that obtained by extrapolating the initial portion of the F-center growth curve. Concomitantly, the colloid particle concentration drops abruptly to a well-defined minimum corresponding to the point where the F-center increase changes from a fast to a slow rate; it then increases to a level that appears to lie on a reasonable extrapolation of the initial part of the colloid growth curve. Although it is not demonstrated by any of the figures, other than Fig. 16 (note that the beam was turned off near the end of the measurement), the changes occurring when the dose rate is changed are very much larger than those occurring when the beam is turned off.

The data in Fig. 16 lead to a number of conclusions that are scientifically very interesting and may have important practical consequences. First, the data indicate clearly that the salt contains a defect that is present and/or mobile only during irradiation. If this were not so, the effects observed when the beam was decreased would be qualitatively similar to those observed when the beam is turned off. Second, the observed changes can be attributed to a reversible F-center to defect conversion; evidence for such a process has been found in other studies (Mattern, Lengweiler, and Levy, 1971). Obviously the results sketched in this section must be investigated in appreciable detail.

Radiation-Induced Nonuniform Colloid Formation in Natural Crystals. Occasionally natural rock salt crystals do not color uniformly. Usually this is determined by visual or microscopic examination of irradiated samples. Nonuniform coloring can usually be correlated with less than normal radiation-induced colloid coloring. For example, one group of samples from Asse, in the Federal Republic of Germany, exhibits normal colloid formation, and a second group has lower than average colloid levels. The group with the lower colloid content contains samples with colloid-free regions. These samples exhibit a mottled appearance, with dark blue regions, indicative of colloids, interspersed among golden yellow regions where only F-centers are present.

Photomicrographs, such as that shown in Fig. 17, show that in many cases the lightly colored regions contain voids. In Fig. 17 they are arranged in a planar array. The presence of voids appears to suppress colloid formation in the surrounding region. The lightly colored region may extend over an appreciably larger area than that occupied by voids. In Fig. 17 the voids are $\sim 10\ \mu\text{m}$ wide; whereas the colloid-free region is $\sim 100\ \mu\text{m}$ wide. Most of the voids appear to be partially or completely filled with brine.

Occasionally a mottled pattern is observed that does not contain voids. Preliminary proton microprobe measurements (made in collaboration with C. P. Swann of the Bartol Research Foundation) show that impurities may suppress color formation. Lightly colored regions contain higher than average levels of calcium, sulfur, and iron and, on occasion, high levels of silicon, potassium, cobalt, and nickel impurities. Attempts are being made to determine if the suppression of colloid formation around voids is related to the presence of impurities.

Figure 17 Micrograph of an irradiated natural rock salt crystal. Dark areas contain both F-centers and colloid particles. The light area surrounding the line of voids contains only F-centers. Area shown is 0.79 by 0.94 mm.

Somewhat similar results were obtained with crystals from the potash mine at Rocanville, Saskatchewan, Canada. Rock salt samples from the horizon containing ore developed appreciably less radiation-induced colloid than samples from a horizon above the ore. Microprobe measurements showed that the salt from above the ore was appreciably purer than that from the ore level.

These observations on the relation between impurity content and radiation-induced colloids give rise to a novel suggestion. For numerous reasons it is desirable to locate radioactive waste in horizons that would be least likely to develop colloid particle radiation damage. In this case, one would choose the least pure, not the

most pure, rock salt horizons for the repository. Before this is done, however, it would be prudent to obtain a reasonably complete characterization of the radiation effects in numerous types of horizons.

Comparison of the Experimental Results with the Jain-Lidiard Theory for Radiation-Induced Colloid Formation

As explained previously, a theory describing radiation-induced F-center and colloid formation in sodium chloride was developed by Jain and Lidiard (1977). Numerous features of the Jain-Lidiard (J-L) theory can be compared with the data presented here, but only a brief comparison is

Table 4 Selected Comparisons with Jain-Lidiard Theory

Theory	Synthetic NaCl	Natural rock salt
F-centers increase monotonically to a "saturation level"	Observed	Observed
F-center saturation level independent of crystal source and strain	Observed	Observed
F-center growth described by $[1 - \exp(-2k_1t)]^{1/2}$	Not observed; crystals exhibit 1st, 2nd, and 3rd stage coloring	Observed
F-center saturation level varies as (dose rate) ^{1/2}	Observed	Observed
Activation energy obtained from F-center saturation single valued and ~ 0.8 eV	0.4 eV observed below $\sim 225^\circ\text{C}$; 1.8 eV above $\sim 250^\circ\text{C}$	0.66 eV observed below $\sim 250^\circ\text{C}$
Colloid formation in restricted temperature range	Observed	Observed
Colloid formation not observed at low dose rate	Not true; for a fixed dose, colloid formation increases as dose rate decreases	Not true; for a fixed dose, colloid formation increases as dose rate decreases
Colloid induction period depends on dislocation density	Observed; induction period reduced by prior strain	Observed; induction period reduced by prior strain
Colloid formation in the t to t^2 range	$t^{1.6}$ to $t^{6.2}$ in unstrained crystals, depending on temperature; $t^{1.2}$ to $t^{2.3}$ in highly strained crystals	$t^{1.6}$ to $t^{2.3}$ in unstrained crystals

made. (See Table 4 for a summary of similar features.) This comparison emphasizes differences between synthetic melt-grown and natural rock salt crystals. The J-L theory is based primarily on data that apply to only synthetic melt-grown crystals, which are described in the literature. However, the theory appears to describe measurements on natural rock salt better than those on synthetic rock salt.

Colloid Particle Nucleation. The J-L theory assumes that, in comparison with colloid particle growth, colloid particle nucleation occurs so rapidly that it can be ignored. The

data described, particularly that in Figs. 2, 7, and 8, clearly show that a pronounced nucleation stage precedes the rapid colloid growth stage. However, Figs. 12 and 13 demonstrate that the nucleation stage is negligibly short only in samples that have been plastically deformed 10% or more before irradiation.

F-Center Formation. The theory leads to three conclusions regarding F-center formation which can be readily compared with results. First, it predicts that the F-center concentration vs. irradiation-time curves at any given temperature will be given by the expression

$$C_F = C_F^{\text{SAT}} (1 - e^{-2K_1 t})^{1/2}$$

where C_F is the F-center concentration at time t , C_F^{SAT} is the F-center saturation value reached after long irradiation time, and K_1 is a constant that depends principally on the F-center diffusion constant and, to a smaller degree, the colloid particle characteristics. In a very broad sense the F-center growth curves (Figs. 5 and 6) are described by this expression. However, as explained previously, at certain temperatures the synthetic rock salt F-center growth curves contain structures usually referred to as first-, second-, and third-stage coloring. Such curves cannot be described by an equation in the form of Eq. 1. In contrast, the natural rock salt F-center growth curves do not exhibit comparable structure and, as a matter of fact, are quite accurately described by Eq. 1 (Levy, Swyler, and Klaffky, 1980; Loman, Levy, and Swyler, 1982). Thus the natural rock salt F-center growth curves are well described by Eq. 1; whereas the synthetic rock salt F-center growth curves are not.

Second, the theory indicates that C_F^{SAT} is given by the expression

$$C_F^{\text{SAT}} = \text{const } (\phi)^{1/2} e^{-E_F/2kT}$$

where ϕ is the dose rate, E_F is the activation energy for F-center diffusion, and k is Boltzmann's constant. The theory is based on the assumption that E_F is single valued. Thus an Arrhenius plot showing $\log C_F^{\text{SAT}}$ vs.

$1/T$ should exhibit two features: (1) It should contain a single straight line indicative of a single activation energy controlled process. (2) Based on data reported for synthetic rock salt, Jain and Lidiard concluded that 0.8 eV is the appropriate value of E_F . Figure 18 is such an Arrhenius plot constructed from the data in Figs. 5 and 6. The figure shows that the synthetic rock salt data are best described by two acti-

Figure 18 Arrhenius plot, to determine F-center diffusion activation energy (E_F), constructed from the F-center growth curve saturation levels (C_F^{SAT}) for both natural and synthetic rock salt. E_F is single valued for natural and double valued for synthetic rock salt. In a sense, colloid formation is controlled by F-center diffusion and, in turn, by E_F . Thus this plot indicates that colloid growth in synthetic salt should differ appreciably from that in natural salt, as is observed.

vation energies, with values of 0.4 and 1.8 eV. The natural rock salt data are best described by a single activation energy, with E_F equal to 0.66 eV, but the data do not rule out the possibility that there is a distribution of activation energies in natural rock salt. Thus the J-L theory describes the natural rock salt data better than it describes the synthetic salt data. Yet the experimentally obtained activation

energies do not compare well with the value anticipated by Jain and Lidiard.

Third, the theory makes the qualitative prediction that at any irradiation temperature the F-center formation will increase to a well-defined saturation value; whereas the colloid formation will continue to increase. This feature of the theory is clearly in accord with the measurements described.

Additional Comparisons with the Jain-Lidiard Theory. The data described here, as well as additional data not presented, can be used to test additional aspects of the J-L theory. These are summarized in Table 4.

The preceding discussion and the results summarized in Table 4 lead to a number of important conclusions regarding the J-L theory. First, many of the qualitative features of the theory are in accord with both the synthetic and natural rock salt data. A major qualitative disagreement is the appearance of well-defined induction periods in the colloid growth curves for all samples except those which had been strained 10% or more before irradiation. Second, there are numerous quantitative disagreements between data and theory. For example, the theory predicts that colloid formation will not be observed below a specified dose rate, but, in both natural and synthetic rock salt, colloid growth is observed at dose rates well below the predicted value. Third, as mentioned, the theory appears to describe results for natural rock salt better than those for synthetic rock salt. Finally, additional experimental data are being obtained which can be used to test other features of the theory, e.g., additional measurements on strained samples and measurements at dose rates lower than those presented here. Sometime in the future enough experimental data will have been accumulated to suggest the modifications required in the J-L

theory to provide an adequate description of the experimental results. Obviously, a completely satisfactory theory would be extremely useful for calculating the total colloid content of rock salt at the expected low dose rates, long irradiation times, and other conditions that apply to actual repositories.

Future Studies on Radiation Damage in Natural Rock Salt

We must strongly emphasize that the results described—although they outline the general features of radiation damage in rock salt—do not provide a reasonably complete characterization of radiation damage effects in natural rock salt. Data do not exist for a number of radiation effects in natural rock salt. A few rather obvious examples are listed here.

1. Important information on radiation damage formation, especially colloid formation, at various dose rates must be obtained. Except for the cursory dose rate studies described here, the data needed to accurately estimate colloid formation in actual repositories do not exist. Most of the existing information was obtained at dose rates 10^3 to 10^4 times higher than those expected in repositories, and, as emphasized previously, colloid formation increases as the dose rate decreases.

2. Additional data are needed on strain effects, especially on samples strained during irradiation. Data on natural and synthetic rock salt strained during irradiation do not exist. Results obtained by straining synthetic KCl during irradiation suggest that large effects may occur (Levy et al., 1971).

3. Measurements on samples exposed to a total dose of 10^{10} to 10^{11} rads, which are the highest doses expected in actual repositories, are needed. The measurements described

here did not exceed approximately 4×10^8 rads.

4. For both scientific and extremely practical purposes it will be necessary to demonstrate unequivocally that chlorine gas is—or is not—evolved from rock salt during irradiation at repository temperatures. Gas evolution studies have been started and results should be available soon.

Applications to Radioactive Waste Repositories in Natural Rock Salt

Even though the studies on radiation damage in rock salt are not complete, they do provide appreciable information. The phenomenology of radiation damage formation in rock salt is reasonably well established. At the temperatures at which radiation-induced colloid particles are formed, curves of F-center concentration vs. dose increase monotonically to a well-defined saturation level, which is highest at irradiation temperatures of 100°C and diminishes monotonically as the radiation temperature is increased. The F-center saturation levels are low or negligible above 300 to 350°C . The F-center measurements show that defects, particularly Cl^- ion vacancies, are formed as long as the radiation is present and at temperatures from 20 to at least 300°C . In addition, they show that the role of vacancies in the formation of colloidal sodium metal particles and other radiation-induced products is strongly influenced by temperature, strain, impurities, dose rate, etc.

At temperatures at which colloids are readily formed, curves of colloid concentration vs. irradiation time or dose resemble classical nucleation and growth curves that are well approximated by $(\text{dose})^n$ or $(\text{irradiation time})^n$ relations at the high-dose end. The colloid formation rate is low at approximately 100 or 115°C and

increases with increasing temperature to a broad maximum at 150 to 175°C . At higher temperatures it decreases monotonically to reach a negligible or low level in the 250 to 275°C range. The colloid growth induction period is greater than 10^4 s in the 100 to 115°C range, less than 3000 s at 150 to 175°C , and greater than 10^4 s at 275 to 300°C . The colloid growth curve induction period is diminished by straining samples before irradiation. As the preirradiation strain is changed from 1 to 10% , the induction period decreases monotonically to zero or a negligible value at roughly 10% strain. Larger strains do not further alter the induction period. The effect of preirradiation strain on the colloid formation rate has not been studied in detail. Preliminary dose rate data indicate that, on a unit dose basis, colloid formation increases as the dose rate decreases. As stated, additional dose rate studies are essential. The dose rates expected in repositories are much less than those used in this study, and it must be determined whether these low dose rates will produce unusually high colloid concentrations.

Estimated Radiation-Induced Sodium Metal Colloid Content of Repository Rock Salt. It is important to emphasize that the $(\text{dose})^n$ or $(\text{irradiation time})^n$ relations and the data in Table 2 make it possible to estimate the total amount of colloid sodium metal that will be formed in actual repositories. This is illustrated by Table 5, which shows the fraction of rock salt converted to colloid metal after receiving doses of 10^{10} and 2×10^{10} rads. If the dose rate is 2×10^4 rads/h at the waste form surface and if the attenuation in the canister is negligible, rock salt at the canister surface will acquire doses of this level in 50 to 400 yr, with the exact time depending on the radioactivity content of the canister,

Table 5 Sodium Metal Colloid Expected in Rock Salt at Canister Interfaces*

Sample	Percent colloid dose	
	10^{10} rads	2×10^{10} rads
AEC-8, 810-m level, New Mexico (WIPP site)	0.78	2.87
Alt Ausee, Austria	2.54	9.93
Asse 1, FRG	3.24	11.6
Asse 4, FRG	0.66	2.25
Asse 6, FRG	3.95	16.7
Asse 8, FRG	1.43	6.43
Asse 9, FRG	1.09	4.53
Avery Island, Louisiana	1.09	3.44
ERDA-9, New Mexico (WIPP site)	0.84	2.80
Lyons, Kansas	1.30	4.74
Retsof, New York	1.45	4.27
Rocanville, Saskatchewan, Canada, above potash ore	1.08	3.21
Rocanville, Saskatchewan, Canada, with potash ore	0.75	2.54
Rocanville, Saskatchewan, Canada, recrystallized	9.75	51.7

*Time period is approximately 50 to 400 yr, for a dose rate at waste form surface of 2×10^4 rad/h.

gamma-ray attenuation in the canister wall, etc. A number of comments on Table 5 are required. The constants in the $C(\text{dose})^n$ relations used to compute the colloid content were measured at 150°C . This is not an unreasonable temperature for rock salt in a repository. Also, a lower salt temperature may not reduce colloid formation. At lower temperatures the only effect may be a lengthening of the induction period. It is in the 3 to 6 month range at room temperature in strained salt. Impurities in the rock salt tend to reduce colloid formation. However, except for the Rocanville recrystallized salt, the estimates in Table 5 are for normally "impure" natural salt. Strain in the salt increases the colloid formation rate during irradiation. As stated previously, the salt used for these measurements was obtained from the largest

crystallites present in each sample, and efforts were made to use salt that was as free from strain as possible. Consequently, the results described here are biased toward low strain samples.

As emphasized, the colloid formation rate increases as the dose rate decreases. In other words, as the dose rate is decreased, the amount of colloid produced by a fixed dose is increased. Dose rate effects could cause the estimates in Table 5 to be low by a large factor. The measurements used in Table 5 were made at a dose rate roughly 10^4 times larger than the highest rates expected from the canisters currently planned. Finally, we must emphasize that the estimates described here were based on measurements that did not exceed 2 to 4×10^8 rads. Clearly, it is necessary to extend these studies to 10^{10} to

5×10^{10} rads, the range expected in repositories.

Physical and Chemical Properties of Irradiated Rock Salt.

Although they have not been studied in detail, some of the chemical and physical properties of highly irradiated rock salt can be described qualitatively. The most heavily damaged samples examined—recrystallized salt from Lyons, KS—were irradiated to a dose of roughly 5×10^9 rads at 150°C . Such salt contains between 0.1 and 1% colloidal sodium metal. It is friable and extremely easy to cleave, and both rock samples and individual crystallites are very brittle. During irradiation some samples broke apart along $\langle 100 \rangle$ cleavage planes. In other words, irradiation had altered the mechanical properties of the rock salt appreciably. When individual crystallites are dropped into water, numerous hydrogen gas bubbles form immediately and continue to form until the crystals are dissolved. Also, an odor of chlorine gas is often detected when highly irradiated salt is cleaved or broken.

Repository Site Selection. The information in Table 5 indicates that rock salt from certain sites or from selected horizons developed appreciably less radiation-induced colloidal sodium metal than salt from other locations. Clearly, repositories should be located in localities or horizons where the damage formation rates are a minimum to minimize radiation damage effects.

Waste Canister Design. Canister design and testing must take into account the chemical and physical properties of irradiated rock salt (and other minerals present, e.g., backfill). Under dry conditions one can expect corrosion and other interactions between the canister material(s) and radiation-damaged rock salt contain-

ing sodium metal and chlorine gas in an unknown form. In the presence of water or brine, hydrogen gas will almost certainly be formed and will interact with steel, iron, titanium, and other materials. In many situations hydrogen embrittlement can be expected. Numerous chemical and physical interactions can be expected in the system containing a waste form, canister material, backfill, irradiated rock salt, and subsidiary materials. Also, such systems will be "driven" by heat, radiation from the waste, and, eventually, the confining pressure of the overburden. It is essential to obtain reasonably complete radiation damage information on rock salt, other minerals, and all other materials that will be present to meaningfully evaluate and test the various interactions that will occur in underground radioactive waste repositories in rock salt.

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Part III Radionuclide Migration Through the Natural System

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Elemental Release from Glass and Spent Fuel

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In the past several years, emphasis on interactions between waste forms and aqueous solutions has shifted from data gathering to understanding, and numerous mechanistic investigations have been initiated. These rely heavily on surface analytical techniques and control of many of the variables. Out of these efforts has come new insight into interactions between waste forms and water. This paper concentrates on glass and spent-fuel waste forms.

Because of the fundamental differences in the interactions of simple silicate and complex borosilicate waste glasses with aqueous solutions, predictive models and/or results derived from simple silicate glasses generally cannot be used to predict the behavior of complex borosilicate glasses. In addition, it has been shown that realistic flow rates and groundwater differences do not alter elemental release from glass or spent fuel by amounts greater than one order of magnitude.

The solubility limits for actinides contained in glasses have been shown to be identical to those observed for crystalline actinide oxide states themselves. Therefore thermodynamic arguments can be used to predict the upper limits of actinide isotopes in solution.

Radiolysis effects in the absence of air have been shown to be important at lower temperatures but not significant at the elevated tempera-

tures expected in a repository. If air (or perhaps just nitrogen) is present, however, nitric acid is generated as a radiolysis product; this greatly enhances elemental removal at all temperatures.

Leaching of spent fuel is less sensitive to temperature change than is leaching of glass and, in some cases, shows a negative temperature dependence. As the oxygen content of the leachate decreases, actinide removal from both glass and spent fuel also decreases.

In general, existing release models for glass and spent fuel are not adequate to predict long-term behavior in a meaningful and believable manner. Enough understanding has been and is being generated, however, that the next version of predictive equations should be capable of defensible predictions. More detailed testing with site-specific groundwaters and package components under expected repository conditions are under way.

Introduction

For over two decades the major thrust of research and development on the permanent disposal of high-level nuclear waste has centered on the concept of deep geologic isolation. In this concept the waste, in some solid form, is buried in a stable geologic formation at a depth of several hundred to a thousand or so meters. A basic assumption is that a geologic formation that has been stable for many thousands of years will remain

so into the far distant future. A site with little or no groundwater flow would be chosen. In such a situation the nuclear waste is not expected to pose an unusual threat to the health and safety of the public. It is generally agreed that the principal mechanism by which waste isolated in this manner could reach the biosphere is by contact with groundwater, which will leach some radionuclides and subsequently transport them to the biosphere. Thus for many years research has been in progress to determine how and at what rate radionuclides are released from various potential waste forms in contact with groundwaters. The results of that research are the subject of this paper.

In the concept of deep geologic isolation the waste is a solid. A wide variety of possible waste forms have been suggested, and many of these have been investigated to some extent—mainly ceramics and glasses. Over the years glass has continued to be a primary candidate waste form because of its physical stability, chem-

ical inertness, ability to accommodate a wide variety of radioisotopes, and ease of fabrication. In the United States, the possible disposal of spent fuel is also being considered. In this paper we concentrate on the two types of materials on which the most research has been done, glass and spent fuel.

The waste form is only one part of the waste-package system that may eventually be emplaced in a deep geologic repository (see Fig. 1). The package as presently conceived is a multibarrier system consisting of the waste form, its container and possibly an overpack to the container, and/or a sleeve. The final barrier might be backfill placed between the host rock and the other package components. The reactions of each of these components with groundwaters are important to the overall performance of the package, and research on their interactions is presently under way. These interactions are not discussed in this paper except as they directly influence leaching of the waste form.

Figure 1 Components of the waste interaction system.

Background

Reporting Results. The term leaching, as used here, encompasses the many processes involved when a solid is placed in contact with an aqueous solution. Because nuclear wastes are complex solids, the interactions cannot be simply described, since undoubtedly several mechanisms are operating at the same time. These mechanisms include diffusion, ion exchange, dissolution of the waste-form matrix, surface resorption, and precipitation reactions. Leaching studies of a waste-package system must consider not only the waste form but also the other components, host rock, and the geochemistry of its associated groundwater.

A wide variety of reporting methods and units have been applied to results from leach testing; e.g., test results have been reported as:

- Leach or release rates [$\text{g}/(\text{m}^2\text{-d})$]
Based on weight loss of the solid
Based on element release measured in the liquid, corrected for losses (e.g., on container walls)
Based on element release normalized to element content in the sample
- Leach or release rates (g/d)
Based on weight loss
Based on element release
Based on element release normalized to element content in the sample
- Fractional loss (%)
Based on weight loss
Based on element release normalized to element content in the sample
- Penetration (m/s)
Based on weight loss
Based on element release
Based on element release normalized to element content in the sample
- Solution concentration ($\mu\text{g}/\text{ml}$)
Based on element release

It is important to realize that these methods were generated over long time periods by researchers throughout the world with many different objectives. Needless to say, the differences have contributed greatly to the confusion about "leaching" studies. Paramount among the needs of those involved in waste isolation programs aimed at licensing a repository is the ability to compare waste forms and provide input to source-term modeling efforts. The Materials Characterization Center (MCC) was established to standardize leaching procedures and reporting methods. A Materials Handbook of consistently taken and reported data is being prepared (Materials Characterization Center, 1981). The following units have been adopted as the most useful for this purpose (Bradley, McVay, and Coles, 1980; Mendel, 1980):

- For static tests having no solution flow
Release value ($\text{g waste form}/\text{m}^2$), based on a specific element normalized to element content in the sample
Solution concentration ($\mu\text{g}/\text{ml}$)
If a rate is to be expressed it should be derived by taking the slope (at a specified time) of the curve generated by release value vs. time
- For dynamic tests, where the solution is changed or where there is a flow of solution:
Release value ($\text{g waste form}/\text{m}^2\text{-d}$), based on a specific element normalized to element content in the sample
Solution concentration ($\mu\text{g}/\text{ml}$)

Thus both a solution concentration of the elements in the leachant and a normalized elemental weight-fraction value or rate would be reported. The latter must include values for element sorption on the walls of the test container. Therefore the leach or release data represent the total material

removed from the sample, and the solution concentration data represent only the material that remained in the solution. It should be stated whether or not the samples were filtered; if they were filtered, results should include the size of the filter paper, solution type, volume, surface area of the geometric sample, and temperature, time, and pressure, if applicable. All results must include pH values. Results reported in this manner will be useful to the entire waste isolation community.

Application of Leaching Studies. Leaching studies have been going on at numerous laboratories for some time. Let us look at how the results of these studies are used in the overall goal of performing safety assessments and eventually licensing a geologic repository.

The performance assessment of the package system, and the waste form as one of the elements of the package, is only one part of the performance assessment of the total waste isolation system (i.e., the package, the repository, and surrounding geologic formations). The release of radionuclides, via contact with an aqueous solution, from the package to the repository environment and hence to an aquifer discharging to the biosphere is the general process envisioned whereby humans could be exposed. Hence a leaching and/or release test is appropriate for determining the potential consequences of such contact.

A number of studies have shown that the major factors limiting release to the biosphere are retardation of radionuclide transport and other dispersive effects by the geologic environment through which the radionuclide moves, along with slow groundwater flow rates (Cloninger, Cole, and Washburn, 1980; Cloninger and Cole, 1981). If the leach rate from the waste form is low enough, how-

ever, it can become the rate-limiting step. We may envision situations (e.g., human intrusion into the repository) in which leach rates from the waste form and release from the package system become increasingly important.

The application of results from leaching studies has progressed significantly from the time when the first performance assessments of geologic disposal gave no credit for the waste form or canister; the integrity of the geologic formation was all that was deemed necessary. Either the waste form radionuclide inventory was considered to be all available for migration at the initiation of a repository breach, or, for salt, the waste form dissolved at the same rate as the geologic formation.

As a more conservative attitude became prevalent and as more data became available on waste forms, canister materials, and engineered barriers, a shift in the approach to isolation analysis gradually occurred. Emphasis was placed on the entire system, both man-made and natural (geologic) components, to do the job of containment.

At this point some specific elemental release rates were factored into preliminary safety assessments (Raymond et al., 1980), based on leaching data from studies of candidate waste form materials with simulated groundwaters.

Further improvements in the waste-form-solution-interactions database have led to the incorporation, under safety assessments, of categories of elemental release depending on whether or not the particular element is more likely to be a part of the matrix (solid-solution). Also included was a temperature dependence on release and an attempt to derive the surface area of the waste form to be exposed. The effects of flow rate were incorporated by adding solubility limit constraints on the

amounts of radionuclides released (Harwell et al., 1979).

At the present time investigators concerned with performance assessment are developing more detailed mathematical models of the package system to take a more realistic account of the degradation of barriers other than just the waste form (i.e., the canister and overpack, backfills, etc.). However, the leach rate of the waste form remains an important and perhaps rate-limiting factor in the release rate of radionuclides from the package. Therefore it remains an important factor in the source term for subsequent calculation of radionuclide transport to the biosphere and possible exposure to humans.

Leach Testing Methods. The concept of predicting the amount and rates of release of radionuclides from waste forms in a geologic storage environment is complex. In safety assessments a "source term" of radionuclides is incorporated into the concept. The source term is based on, first, the release from the waste form via contact with groundwater and subsequent interaction with surrounding engineered barriers and, second, the migration of the released radionuclide species to the biosphere via groundwater flow paths. In this paper we concentrate on only the first part of this source term.

How do components of the waste isolation system interact with each other to cause the release of radionuclides? A wide variety of possible interactions can be postulated, but only a small number are reasonably probable and need to be considered in detail when evaluating waste forms. Two cases that bound the responses of radionuclide release have been chosen for study.

Case 1. Groundwater contacts the waste form directly, short-circuiting the backfill-engineered-barrier sys-

tem, and then migrates through a fracture path in the host rock. As we will discuss later, in an effort to gain knowledge of fundamental waste-form-solution interactions, investigators have emphasized this case.

Case 2. In a more realistic situation, groundwater must penetrate or corrode the outer barriers before it contacts the waste form. Contact results in release of radionuclides, which then must traverse the barriers before entering a host-rock pathway to the environment. Because of the added barrier interactions, this case requires more attention to test design and to analytical detail to interpret the results. Although not the subject of this report, several studies are under way to assess waste-package system interactions (Shade and Bradley, 1980; Smith et al., 1980).

We can see that a single test will not cover the range of conditions presented in cases 1 and 2. Thus nuclear waste study programs have used a variety of procedures to gain data on radionuclide release and mechanistic understanding so that input can be provided for safety assessments in a timely fashion. On the premise that one should try to understand simple experiments first, we performed binary experiments (Case 1) using a combination of waste forms and solutions. The effects of temperature, solution composition, solution flow rate, radiation fields, and laboratory time are investigated to:

- Provide radionuclide release data
- Prioritize the effects of parameters
- Provide samples for surface analysis which will help us to understand the formation of protective layers and their compositions
- Provide solutions for use in sorption-migration studies
- Provide insight into the design of more complex tests.

Leaching data for all waste forms are obtained in essentially the same manner. There are numerous leach tests that fall under two broad categories, static and dynamic. In the static tests, the samples are immersed in the same leachate for the entire duration of the test, and, if time periods are long enough, solubility-limit data can also be obtained. These tests are conducted at temperatures both below and above the boiling temperature of the leachate. The higher temperature experiments, which must be pressurized, are conducted in an autoclave. Dynamic tests are those in which the original leachate does not stay in contact with the sample for the entire experiment; e.g., the solution flows past the sample continuously, or a series of static tests is conducted in which the leachate is renewed at intervals. If the renewal rates are short in comparison with the time required to reach saturation, these tests can be reasonable simulations of continuous flowing tests.

Most leaching results reported in the current literature used one of the following tests.

- Modified International Atomic Energy Agency (IAEA) test
- Static test
- Single-pass, continuous-flow test

Modified IAEA Leach Test. The major feature of the IAEA test is that the solution used is renewed on a preset schedule (Hespe, 1971). At the change times, the sample being studied is placed in a fresh volume of solution and the test is continued. Almost all investigators using this test have modified it to some extent, usually changing the schedule for solution renewal. In some cases the test has been modified by changing the longest leach time to 1 month to avoid the effects of sampling frequency on radionuclide release.

The various modified IAEA leach tests are simple to perform, require

little laboratory space, and are relatively easy to conduct in a hot-cell environment. Their disadvantages are that it requires more effort to conduct them than it does a static leach test because of the need to replenish the leach solution on a designated time schedule; because numerous leach solution samples are generated, the costs of analysis are higher; and probable groundwater flow conditions may not be correctly modeled, primarily because of periodic replacement of the leach solution during the test (solution changes cause cyclic pH and solution concentrations, which, in turn, affect leaching). Because of these problems, the data are difficult to interpret vis-à-vis the geologic environment.

Static Test. A static test investigates the effects of increasing radionuclide and matrix element concentration in the leachant, as well as reabsorption reactions on radionuclide release rates. As its name implies, this test involves no sample agitation, solution flow, or solution replenishment. To avoid potential difficulties with periodic removal of only a small leachate sample for analyses, the investigator usually designs the test so that a series of replicates, started at the same time, are leached, one replicate being sacrificed for each analysis.

The static leach test is the easiest test to conduct, and it simulates near-zero or very low groundwater flow in a repository. The static test also allows study of the approach to solubility limits for various radionuclides and matrix elements, which is important in determining thermodynamic solubility constraints. The test is also easily adapted to hot-cell environment operations and requires minimal work space. Some problems may occur when plastic leach containers are used, e.g., solution loss, interactions between the container

material and the leach solution, and container degradation when the tests run for long times (more than 1 yr) at temperatures near 100°C. These problems can be avoided by using welded gold or platinum capsules, but such test equipment is costly. Teflon containers or double containers can be used for long-term static tests.

For temperatures above 100°C, autoclaves are used for static tests. Autoclave tests can simulate worst-case repository temperature and pressure conditions, and, because of accelerated leaching at elevated temperatures, the tests are of shorter duration. Another advantage is that element solubility limits can be more rapidly reached at the higher temperatures. Autoclave tests have several disadvantages, however. They are the most expensive leach tests; large numbers of samples cannot be easily handled; they require more laboratory space than the other leach tests; and they are not easily used in a hot-cell environment. The tests also require experienced personnel for operation and maintenance and special safety precautions.

(For further details on static testing, see Materials Characterization Center, 1981; Bradley, McVay, and Coles, 1980; Deryagin et al., 1970; Scheetz et al., 1980).

Single-Pass, Continuous-Flow Test. As discussed in the previous section, an important part of testing is the ability to describe radionuclide release under conditions where the solution flow sweeps the accumulating reaction products from the surface of the waste form. Thus the complement to the static test is one that accurately meters a solution as it passes a waste-form sample.

One advantage of the flowing test is its close analogy to an actual flooded repository, where groundwater would flow slowly past the waste because of the natural hydraulic gra-

dient. Peristaltic pumps and tubing that will deliver volume flow rates typical of observed underground water velocities are available (Weed and Jackson, 1979).

Another advantage of this type of test is the ease of obtaining data regarding flow rate effects on leach rate. Flow rate is an important parameter because it is related to the total volume of water that contacts the waste form and it may control the rate at which radionuclides can be leached from the waste form. Because candidate repositories are likely to have the potential to experience a variety of groundwater velocity regimes, an understanding of the effect of flow rate on leach rate could become a key factor in evaluating repository performance (Weed et al., 1979).

The primary disadvantages of the flowing method are increased complexity and expense, in comparison with the modified IAEA and static leach tests. Pumps, hoses, and specially constructed cells are required. Assembling, monitoring, and maintaining the test requires experienced personnel. The test demands more laboratory space than the modified IAEA or static leach tests, and, like the autoclave test, it is not easily adaptable to a hot-cell environment.

Status of Glass and Spent-Fuel Leaching

Most interactions between waste forms and aqueous solutions involve both the removal of elements from and the introduction of elements into the sample by the contacting leachate solution. Therefore, to more fully understand the interactions occurring so that long-term predictive models can be developed, we must analyze both solution composition and solid-state surface. Solution analysis allows us to determine what has been removed from the sample but does not

yield much information about how elemental removal occurred. This information is obtained from analyses of the solid sample. Surface analyses can be used to determine the extent and type of layer development on sample surfaces. Also, surface analysis techniques, in combination with ion milling, yield valuable information about elemental depletion profiles from the sample.

One of the ever-present difficulties in leaching experiments is the container. The container material must be chemically inert and must not sorb elements into the leachate which might adversely affect the leaching results. The effects can be reduced by proper choice of container material and by exposing as little as possible of the container surface area to the leachate.

In leaching tests that result in significant reaction and elemental removal, precipitation must be considered. Elements can attach to precipitates, particularly silicates (precipitates can be colloidal in nature), and erroneous results for solubility limits and leaching characteristics may be obtained if the leachates are not properly filtered.

Numerous waste forms are being considered for containment of radioactive waste, e.g., several forms of crystalline ceramic materials, coatings of various types, glasses, and spent fuel itself. Since the largest body of data has been generated for glasses and spent fuel, these two waste forms are the focus of this paper.

Glass. The interactions of glass with aqueous solutions have been actively investigated for more than 20 yr. Until recently, the majority of experiments were conducted on relatively simple commercial or naturally occurring silicate glasses (Douglas and El-Shamy, 1967; Haldren and Berner, 1979; Hench, 1975; Sanders and Hench, 1973; Paul and Youssefi, 1978; Boksay

and Bouquet, 1975; Clark et al., 1976; Rimstidt and Barnes, 1980; Dibble and Tiller, 1981; El-Shamy, Ashmawy, and Ahmed, 1978; Imanov and Mamedova, 1975; Furnes, 1975). Consequently, most theories and models for glass-water interactions are based on simple silicate glasses (Douglas and El-Shamy, 1967; Haldren and Berner, 1979; Hench, 1975; Sanders and Hench, 1973; Doremus, 1979; Das, 1969). Currently, however, because borosilicate glass is a candidate material for containment of radioactive waste, many investigations are being conducted on the interactions of the more complex borosilicate waste glasses with aqueous solutions (Elliot and Auty, 1968; McVay and Buckwalter, 1980; Flynn, Jardine, and Steindler, 1980; Chapman and Savage, 1980; Wiley, 1979; Bradley, Harvey, and Turcotte, 1979; Westsik and Harvey, 1979; Weed et al., 1980; Boulton et al., 1978; Bradley, 1978). A typical waste containment glass has 30 or more elements (see Table 1) and can react with aqueous solutions in a manner quite different from simple silicate glasses. In addition, glasses containing fully radioactive waste must be handled in a hot cell; this is expensive and limits the type, quality, and quantity of analyses that can be performed on the samples. Therefore most investigations are performed on glasses containing simulated waste; i.e., non-radioactive elements are substituted for the radioactive elements where possible, and rare earths are substituted for actinides. In some cases actinides have been doped into the glass at expected levels. These experiments must be conducted in glove boxes, and surface analyses of the samples are somewhat restricted.

The elements removed from a glass exposed to an aqueous solution typically follow a time dependence similar to that shown in Fig. 2. In the initial time period, up to time t , the leach

rate begins rapidly and decreases with time (curve segment A). The data represented by this segment of the curve usually is linear when plotted

Table 1 Nominal Compositions of the Waste Glasses*

Component	Glass composition, wt. %		
	76-68 PW-8a-1	77-107 PW-9-1	77-260 PW-7c-1
Glass frit			
Al ₂ O ₃			2.0
B ₂ O ₃	9.5	13.0	9.0
CaO	2.0	2.0	1.0
CuO			3.0
K ₂ O		4.0	2.0
Na ₂ O	7.5	2.0	8.0
SiO ₂	40.0	38.0	36.0
TiO ₂	3.0	3.0	6.0
ZnO	5.0	5.0	
	67.0	67.0	67.0
Waste			
Ag ₂ O	0.03	0.05	0.02
BaO	0.56	1.13	0.55
CdO	0.03	0.08	0.03
CoO	0.11	0.20	0.10
Cr ₂ O ₃	0.41	0.21	0.02
Cs ₂ O	1.02	1.98	0.78
Fe ₂ O ₃	9.68	0.90	1.19
Gd ₂ O ₃			10.14
MnO ₂			0.11
MoO ₃	2.27	4.41	1.92
Na ₂ O	5.00	3.47	3.14
NiO	0.52	0.16	0.31
P ₂ O ₅	0.48	0.40	2.36
Rb ₂ O	0.13	0.25	0.11
RE [†]	4.76	9.24	3.84
RuO ₂	1.06	2.20	0.85
SrO	0.38	0.72	0.29
TeO ₂	0.26	0.50	0.22
U ₃ O ₈ [‡]	4.54	3.80	5.40
ZrO ₂	1.76	3.30	1.68
	33.00	33.00	33.00
	100.00	100.00	100.00

*Data from Marshall, 1980.

[†]A commercial rare earth mixture having the nominal composition (wt. %): Y₂O₃, 0.2; La₂O₃, 24.0; CeO₂, 48.0; Pr₆O₁₁, 5.0; Nd₂O₃, 17.0; Sm₂O₃, 3.0; Eu₂O₃, 0.8; and Gd₂O₃, 2.0.

[‡]U₃O₈ prepared from depleted uranium.

Figure 2 Schematic of the time dependencies of elemental concentrations in the leachate for a static leach test. Up to time t the leach rate is rapid and decreases with time (A). B, constant leach rates. C, elements with very low solubility limits. D, conditions that change during the course of the experiment.

vs. the square root of time. This has led numerous investigators to attribute this time period of leaching to diffusion-controlled processes (Douglas and El-Shamy, 1967; Hench, 1975; Sanders and Hench, 1973; Boksay and Bouquet, 1975; Clark et al., 1976; Doremus, 1979; Das, 1969). For times greater than t , elemental removal can have the time dependence described by either curve B, C, or D. Most elements in simple silicate glasses and many elements in more complex borosilicate waste glasses follow curve segment B. This is true partially because of the relatively short duration of typical leaching tests or the large volumes of water used. If leaching characteristics are described by curve B, elemental removal is linear with time (constant leach rate) and has generally been attributed to corrosion or dissolution of the glass matrix (Douglas and El-Shamy, 1967; Hench, 1975; Sanders and Hench, 1973; Clark et al., 1976; Doremus, 1979; Das, 1969).

If the glass is exposed to the same leachate for long periods of time or if an element has a very low solubility limit, then curve C may result. This represents a steady-state or apparent equilibrium value for the maximum concentration of a particular element that will stay in solution under the experimental conditions. When conditions change during the course of an experiment, as occurs in static tests, e.g. (changing pH and solution concentrations), then time dependence of elemental concentrations in the leachate can be described by curve D for certain elements. This decrease in solution concentration can be attributed to precipitation and/or sorption of elements on sample surfaces.

Any process that enhances leaching, such as increased temperature, less durable glass composition, or exposure to flowing conditions, results in a decreased contribution from segment A (smaller t). In addition, if a flowing test is sufficiently rapid, the

time dependence described by curves C and D will not exist for any of the elements.

The variation of leach rate with time (curve A, Fig. 2) for a natural glass has been shown to be the result of fines adhered to the leach sample surface (Haldren and Berner, 1979). When the fines were removed from the sample, only the time dependence described by curve B remained. The nonlinear portion of the curve (segment A) was caused by a more rapid reaction of the fine particles (large surface areas) with water. Therefore we should not automatically assume the process is diffusion controlled because the leaching data appear to have a square root of time dependence.

Solution data from a static leach test on a typical borosilicate waste glass (PNL-76-68) are presented in Fig. 3. As can be seen, the time dependence characteristics of curves A, B, and D in Fig. 2 exist for the dif-

Figure 3 Fraction of original elemental concentration per unit surface area of PNL-76-68 glass removed by leaching in distilled water at 89°C. Surface area to solution volume ratio, 10 m⁻¹.

ferent elements. The experiment was not conducted for long enough time periods to observe characteristics represented by curve C in Fig. 2. Leach tests conducted under normal laboratory flowing conditions typically have only linear time-dependent element removal, characterized by curve B in Fig. 2 (Coles, 1981; Heimerl, 1971).

Solution analyses of the leachate yield only part of the information about glass-water interactions. Analyses of the reaction layer that has developed on the solid sample will contribute to understanding of elemental release mechanisms. Elemental depth profiles have been obtained by progressive HF acid dissolution and analyses of the reaction layer (Boksay, Bouquet, and Dobos, 1967; White, 1979). This can lead to selective removal of alkali ions (McVay and Pederson, 1980b). A better approach is to use relatively new surface analytical techniques, such as electron spectroscopy for chemical analysis (ESCA), in combination with ion milling to obtain elemental concentration profiles in the reaction layer. McVay and Pederson (1980b) review surface analytical techniques and their limitations.

Elemental concentration profiles in the reaction layer that forms on the glass surface as a result of interactions with water can be described by one of the curves in Fig. 4. The solid curves (A and B) represent element concentration profiles that are more concentrated and the dashed curves (C and D), those that are less concentrated than in the bulk unreacted glass.

Curve A concentration profiles are obtained for elements that react less than do the glass matrix elements with water. Therefore, as the matrix elements are leached away, these less soluble elements build up concentrations larger than originally existed.

Figure 4 Schematic of elemental depth concentration profiles through a reaction layer resulting from leaching of a solid sample.

This concentration is enhanced to the depth where matrix elements have been removed. Concentration profiles of this type are seen quite frequently for heavy metals, rare earths, and actinides in borosilicate waste glasses but are seldom observed on simple silicate glasses. If elements precipitate or sorb on the glass surface (elements can be from some external source rather than from the glass), then the profile described by curve B can result. This profile is typically restricted to regions near the surface, although some diffusion into the reaction layer, which would broaden the profile, is possible.

Elements that are leached at rates comparable to or more rapid than those of the matrix elements typically have concentration profiles similar to either curve C or D in Fig. 4. Profiles similar to curve C are the result of ion exchange of elements in the glass with species from the water (e.g., H^+ or H_3O^+). It is in essence a diffusion profile. Matrix elements often have concentration profiles similar to curve C. This is the result of the previously mentioned ion exchange of elements in the glass with water species, which, in

turn, interact with and break up the glass matrix (Douglas and El-Shamy, 1967; Boksay and Bouquet, 1975; Doremus, 1979). Therefore the matrix elemental concentration profiles are similar in shape and closely related to elemental profiles that result from ion exchange with water species. As the glass-water interaction progresses, enough matrix breakup occurs to allow ionic species to move very rapidly through the highly reacted portion of the interaction zone. Thus curve D in Fig. 4 results. Curve C usually tends toward curve D with time. Diffusion of ionic species through the initial region of curve D occurs several orders of magnitude more rapidly than through the bulk glass (Boksay and Bouquet, 1975). For elements described by curve D, leaching is occurring as if the highly reacted region of the interaction zone were not there.

Elemental concentration profiles for a leached PNL-76-68 borosilicate waste glass are given in Fig. 5. These profiles were generated by combining ESCA surface analysis and ion milling. As can be seen, concentration profiles of the type described by curves A, B, and D in Fig. 4 are present. If the leached sample had been analyzed after a shorter exposure to water or had been leached at a lower temperature, concentration profiles like curve C in Fig. 4 would have been present.

Glass surfaces leached under more extreme conditions (i.e., at higher temperatures or for longer times) must be analyzed in other ways. If the reaction layer becomes very thick (many microns), sputter profiling is not practical and can lead to erroneous results caused by large-scale sputtering and by surface analyses at the bottom of a deep crater. These highly reacted glass surfaces are best analyzed by evaluating their cross sections with an ion microprobe or scanning electron microscope (SEM) in conjunction with energy dispersive X-

ray analysis (EDAX). These profiles are interpreted in basically the same manner as those previously described, but the reaction layers can become more complex with zone formations; this makes interpretation difficult.

The following discussions concentrate primarily on waste glasses but use data from the relatively simple silicate systems when it is beneficial or necessary for purposes of comparison or understanding. Although it is realized that when glass interacts with aqueous solutions, many effects occur simultaneously and are interrelated, these effects are discussed separately as much as possible in an attempt to describe what is known about each area.

Effects of pH and Eh. The effects of pH on elemental leach rates from glasses are well documented (Douglas and El-Shamy, 1967; Hench, 1975; Sanders and Hench, 1973; Ross et al., 1978; Boksay and Bouquet, 1980). An understanding of why these effects occur is lacking, however, particularly for the more complex borosilicate waste glasses.

The pH dependence of leach rates, based on silicon analyses or sample weight loss, can be described by the schematic curves in Fig. 6 (Douglas and El-Shamy, 1967; Ross et al., 1978). Curve A represents simple silicate glasses or fused silica, and curve B represents borosilicate waste glasses. As can be seen, there is a fundamental difference in the behavior of the two types of glass. The simple silicate glasses are durable in the acid region but suffer large-scale attack to the glass matrix in the basic pH region. The matrix attack on fused silica becomes significant at pH values above 8.5. The addition of alkali to the glass results in rapid attack of the matrix at lower pH values. Leach rates for alkali ions from simple silicate glasses have just the opposite pH dependence (Douglas and El-Shamy, 1967). They leach rapidly in acid pH

Figure 5 Elemental concentration profiles through the reaction layer of a PNL-76-68 glass sample exposed to 90°C distilled water for 14 d. Sample surface area to solution volume ratio, 10 m^{-1} .

solutions but slowly in basic solutions. This is because ion exchange between the alkali ions and a positively charged water species must occur for alkali ion removal.

The borosilicate waste glasses exhibit enhanced durability in basic

pH ranges but have poor acid resistance (curve B in Fig. 6). The pH-independent (high-durability) region is between pH 5 and 10 (Ross et al., 1978). Waste glasses contain many elements, most of which are more soluble in acids than in bases. Other waste-

Figure 6 Schematic of pH dependence of the leach rate for simple silicate (A) and complex borosilicate (B) glasses.

glass elements exhibit high leach rates in acids, but most of them have low leach rates in basic solutions (Buckwalter and McVay, 1981). Therefore it seems likely that in the acid pH range the silica portion of the matrix breaks up as a result of large-scale removal of most of the other elements. It has been demonstrated that rare earths make glasses more resistant to basic attack (Boksay and Bouquet, 1975). The fact that simulated waste glasses contain rare earths may be partially responsible for their increased durability in basic pH solutions.

The pH of natural waters ranges from 2 to 10; most groundwater, however, lies in a more restricted pH range, 5.5 to 8 (Wedepohl, 1967). Certain salt brines, when heated, can achieve a pH value of 3, which would not be desirable and would necessitate the use of buffers. In a static or slow-

flow situation, a glass will control its own pH by reactions with the water, unless the water is highly buffered or has a very large volume exposed to the glass.

The oxidation potential of groundwater, usually expressed as Eh, can decrease with depth in the earth, depending on geochemical conditions. Thus at proposed repository depths leaching may take place under reducing conditions. The leach rate of elements that exist in more than one valence state can be influenced by the Eh of the leaching solution. Important waste radionuclides that fall in this category are ^{99}Tc and most of the actinides. Essentially all of the leach test data on glass reported in the literature have been obtained in air-saturated solutions, however. One attempt has been made to leach actinide doped glasses in degassed water (approximately 1 ppm O_2) (Peters, 1981). A decrease in leach rate for the actinide elements investigated was generally observed.

Temperature Effects. The majority of leaching data have been generated at temperatures of 100°C or less. Much of these data are of the weight-loss type and give only gross indications of mechanisms. Many reactions occur simultaneously during glass-water interactions, and a temperature dependence exists for each reaction. It is possible that many of these processes have similar temperature dependencies, but there is no current method to isolate and measure each process separately. Therefore activation energies determined for leaching are a combination of several activation energies, one for each related process occurring. Plots of log leach rate vs. reciprocal temperature usually are linear over the experimental temperature span, however. In addition, leaching mechanisms may be changing with time, especially if conditions (e.g., pH) are varying with

time. Activation energies determined at different time periods for the same glass have yielded 7 kcal/mol initially and 14 kcal/mol for longer periods of time (Lanza, Jacquet-Francillon, and Marples, 1980). These results are presumably caused by changes in leaching mechanisms with time. The temperature dependencies of leaching should be determined with long-time leaching data.

Activation energies reported (Lanza, Jacquet-Francillon, and Marples, 1980; Elliot and Auty, 1976; Adams, 1979) vary from 7 to 22 kcal/mol for the glasses investigated. The temperature dependencies for leaching in various simulated groundwaters do not differ widely. Several of the elements from a borosilicate waste glass with leach rates equal to or faster than silicon have been found to have the same temperature dependence of leaching (Westsik and Peters, 1980). Presumably the mechanisms of release are similar or the same. It is important not to extrapolate accelerated high-temperature results to lower temperatures for predictive purposes until it is verified that a mechanism change does not occur.

Leachate Composition Effects.

Adding certain elements (e.g., aluminum or calcium) to distilled water has been shown to cause a reduction in the leaching of glass (Hench and Clark, 1978; Dilmore, 1977; Bacon and Raggon, 1959; Dilmore, Clark, and Hench, 1982). Many elements in an aqueous solution can react with the glass surface to alter its surface charge (Somasundaran, 1968; Tadros and Lyklema, 1968), and, therefore, affect the interactions occurring with water. Leachate compositions can modify the pH and, in turn, the leaching. Variations in compositions of aqueous solutions affect leaching differently for individual elements. Solutions of high ionic strength, such as salt water, typically enhance the

removal of alkali and alkaline earth ions from glass (McVay and Buckwalter, 1980); whereas leachates containing complexing anions can enhance actinide removal from glass (Bradley, Harvey, and Turcotte, 1979).

Many investigators have reported the effects of simulated groundwaters on elemental release from borosilicate waste glasses (Elliot and Auty, 1968; Chapman and Savage, 1980; Wiley, 1979; Bradley, Harvey, and Turcotte, 1979; Westsik and Harvey, 1979; Weed et al., 1980; Boulton et al., 1978; Bradley, 1978). The magnitude of the effect is somewhat element dependent, but the general conclusions are all the same; i.e., the various simulated groundwaters have a small effect in comparison with pH and temperature. The variation in leaching for all simulated groundwaters investigated fall within one order of magnitude. Typical results showing this effect are given in Fig. 7, which shows the results of an IAEA dynamic test at 22°C for ^{237}Np . As can be seen, the effect is small, with the largest release occurring in the sodium bicarbonate solution. This result is typical for all the actinides in waste glass.

Radiation Effects. A glass that contains radioactive waste is exposed to continual radiation from the waste itself. The greatest damage to the glass results from alpha decay, primarily from the recoil nucleus (Roberts, Turcotte, and Weber, 1981). Accelerated testing of this alpha-decay-related damage has been conducted by doping glasses with short-lived actinide isotopes (^{238}Pu or ^{244}Cm) and allowing damage to occur by self-radiation (Ross et al., 1978; Roberts, Turcotte, and Weber, 1981; Weber et al., 1979). Leaching these glasses as a function of accumulated dose has shown only a minor effect resulting from alpha-decay-related radiation damage (see Fig. 8 as an example). Alpha-recoil damage has also been simulated by charged-

Figure 7 Effect of various simulated groundwaters on the time dependence of cumulative fraction of ^{237}Np released from PNL-76-68 glass. IAEA leach test at 22°C. (Data from Bradley, Harvey, and Turcotte, 1979.)

Figure 8 Effect of radiation damage on leach rate; Soxhlet test leachability of ^{244}Cm -doped PNL-72-68, a high-level waste glass. (Data from Roberts, Turcotte, and Weber, 1981.)

particle irradiations (Dran, Maurette, and Petit, 1980). The premise is that low-energy lead ions simulate recoil nuclei generated by alpha decay. Leaching results on glasses damaged in this manner indicate a threshold

damage level above which rapid leaching occurs.

This is in contrast to the results obtained from self-irradiation experiments. It must be realized that low-energy ions only damage the glass to a depth of a few hundred ångströms, and therefore leaching results are based on extremely near-surface phenomena, which may not be representative. The effect of surface roughening caused by ion irradiation and its effect on leaching have not been addressed. Therefore it seems that self-radiation experiments are more realistic, but we cannot completely discount the charged-particle simulations. More research is needed to clarify the apparent discrepancies between these two acceleration techniques.

Another radiation-induced change that may affect leaching is the

Table 2 Comparison of Gamma-Irradiated* and Unirradiated Leaching of PNL-7668 Glass in Demineralized Air-Saturated Water‡

Element	50°C		90°C	
	γ irradiation (5 d)	No irradiation (5 d)	γ irradiation (13 d)	No irradiation (13 d)
Na	5.0	1.8	130.0	18.5
Cs		0.13		2.2
Ca	0.80	0.18	7.8	1.0
Ba	0.19	0.03	0.8	0.1
Sr	0.14	0.03	1.4	0.2
Si	6.5	1.44	177.1	21.0
B	1.1	0.26	31.3	4.5
Mo	0.1	0.13	7.2	2.6
Zn	2.0	0.17	37.6	0.09
pH	5.7-3.3	5.7-7.2	5.7-4.6	5.7-8.5

*Dose rate was 2.4×10^6 R/h

‡Sample surface area to solution volume ratio, 10 m

‡Parts per million by weight.

transmutation of the fission products. The two main sources of transmutations are the intermediate-lived fission products ^{137}Cs and ^{90}Sr , which transmute to ^{137}Ba and ^{90}Zr , respectively. Transmutations can involve valence changes and major changes in atomic radii. The question is, Do these transmutations affect elemental release from the glass? Experiments are currently under way to evaluate the effects of transmutation on leaching, but results are not yet available.

When a waste glass is in contact with an aqueous solution, radiation from the glass can cause changes in the chemistry of the solution, which can, in turn, have a significant effect on the leaching of the glass. Radiolysis of water can be caused by alpha, beta, or gamma radiation from the waste-containment material (McVay and Pederson, 1981a; Rai, Strickert, and Ryan, 1980; Jones, 1959; Burns and Moore, 1976).

If the leachate contains nitrogen, nitric acid is generated as a radiolysis product (McVay and Pederson, 1981a;

Rai, Strickert, and Ryan, 1980; Jones, 1959). This can cause rapid attack of the glass and result in greatly enhanced leaching (see Table 2). Experiments in which nitrogen is excluded show that leaching is still enhanced as a result of increased interactions by other radiolysis products in the aqueous solution (McVay and Pederson, 1981a). This enhancement is strongest at lower temperatures and is minimal above 90°C (McVay and Pederson, 1981b).

If real groundwaters contain nitrogen, radiolysis effects can be significant (an order of magnitude or larger increase in leaching). If nitrogen is not present, leaching of the glass matrix elements will not be enhanced at expected repository temperatures. However, the radiolysis of water can result in an oxidizing environment (Burns and Moore, 1976); this greatly enhances solubility and leaching of the actinide elements.

Solubility Effects. Amorphous materials are metastable and, therefore, cannot exhibit true thermo-

dynamic solubility limits. However, because the kinetics for transformation to more stable states are slow for most glasses at reasonable temperatures, apparent solubility limits exist. These are apparently constant elemental concentrations in solutions that are in contact with the glass. Investigations of solubilities of matrix elements (Fullam, 1981) and actinide elements (Rai and Strickert, 1980) have been conducted in demineralized water for borosilicate waste glasses. In addition, numerous literature sources exist for amorphous silicon solubility limits (Marshall, 1980; Fournier and Rowe, 1977; Marshall and Warakowski, 1980).

The apparent solubility limits determined from silicon concentrations in demineralized water for three borosilicate waste glasses (Fullam, 1981) do not reach the values reported for amorphous silica (Fournier and Rowe, 1977) even after a 1-yr exposure time. Furthermore, some elements, such as sodium and potassium, do not reach saturation levels in 1 yr. However, most elements in borosilicate waste glasses reach an apparent solubility limit within 3 months at 35°C, and somewhat shorter time periods are required at higher temperatures.

The actinide elements have very low solubility limits in comparison with glass matrix elements and, therefore, reach their limits rather quickly. At room temperature, plutonium and neptunium leached from PNL-76-68 glass reached saturation concentrations in approximately 5 d (Rai and Strickert, 1980). This concentration is identical to that observed for crystalline PuO_2 and NpO_2 ; this indicates that the solubility limits of these actinides in PNL-76-68 glass are the same as or are controlled by PuO_2 and NpO_2 . Since thermodynamic data are known for these oxides, if they are controlling the solubility, long-term predictions of actinide concentrations in solution can be made with

Figure 9 Solubility of crushed Pu-doped PNL-76-68 glass beads with and without the addition of $^{239}\text{PuO}_2(c)$, in 0.0015M CaCl_2 solutions containing quinuhydrone. (Data from McVay and Pederson, 1981a.)

confidence. The similarity of solubility limit data for PuO_2 and plutonium-doped glass is shown in Fig. 9.

Dynamic Leaching Effects. A dynamic leach test is one in which the leachate is renewed during the time the glass-water interactions are occurring. The major difference between leaching in dynamic and static tests is that saturation effects do not typically occur if the leachate renewal rate is frequent enough. Therefore solution concentration curves from flowing tests normally have only linear time dependencies (curve B, Fig. 2) (Coles, 1981; Heimerl et al., 1971). There is usually no square root of time dependency (curve A, Fig. 2) as in static tests. Increasing flow rate enhances elemental removal rates (Coles, 1981; Heimerl et al., 1977), particularly at temperatures above 25°C. The elements with the lowest solubility limits and/or leach rates seem to be affected most. Therefore as the flow rate increases the elemental leach rates all approach the same value and congruent dissolution (Heimerl et al., 1977).

Mechanisms and Models. When a glass interacts with an aqueous solution, many reactions occur simultaneously. Elements are being removed from the glass by ion exchange with positively charged water species (e.g.,

H^+ or H_3O^+) and by matrix breakup caused by hydroxyl ion attack. Therefore the glass is both losing and gaining ions in its interactions with water. Earlier work reported that ion exchange was occurring with the H^+ ion from water (Douglas and El-Shamy, 1967; Hench, 1975; Boksay and Bouquet, 1975; Das, 1969). Recent findings indicate that a more complex water species is involved, however, i.e., H_3O^+ (Doremus, 1979; Pederson, Baer, and McVay, 1981).

The removal of alkali ions from glass by aqueous solutions is several orders of magnitude more rapid than can be accounted for by their diffusion rates in the bulk unreacted glass. This has led some researchers to question the theory of diffusion-controlled processes because of an initial square root of time dependence (McVay and Buckwalter, 1980; Heimerl et al., 1971; Mularie, Furth, and Westwood, 1979). Both sodium diffusion coefficients and sodium leach rates in a series of simple silicate glasses have been measured (Heimerl et al., 1971). No correlation was found between them.

At least one calculation exists in the literature which attempts to explain the apparent enhanced diffusion observed for alkali ions in glass exposed to aqueous solutions (Mularie, Furth, and Westwood, 1979). The enhanced diffusion can be accounted for by a negative charge that develops on the glass surface as a result of initial reactions with the hydroxyl groups in the water. This surface charge then accelerates alkali ion diffusion in the near-surface region. A surface charge of approximately 200 mV is necessary to sufficiently enhance alkali ion diffusion. A surface charge of approximately this magnitude has been reported for a simple silicate glass (McVay and Pederson, 1980a).

As a result of the previous discussions of important effects on glass leaching, we can conclude that a

predictive model to be used for elemental release from a waste form under repository conditions must incorporate many effects, e.g., pH, temperature, leachate composition, radiolysis, solubility limits, and flow rates. Modeling of the glass-water interaction is, therefore, a difficult task.

Several models have been proposed to describe glass leaching in aqueous solutions (Douglas and El-Shamy, 1967; Hench, 1975; Sanders and Hench, 1973; Doremus, 1979; Das, 1969). A brief description is presented here, but a more thorough review is given by McVay and Buckwalter (1980). These models are all primarily applicable to relatively simple glasses containing only a few elements in contrast to the many elements in typical waste-containment glasses. Most of the models are similar in nature, with varying degrees of sophistication. Essentially all the models involve solid-state diffusion and predict a square root of time dependence for initial leaching; this suggests a diffusion-controlled process and a linear time dependence for longer leaching times, which indicates corrosion or congruent dissolution.

Two of the models warrant mention because of their special features. The model by Doremus (1979) incorporates the interdiffusion of alkali ions with hydronium ions in the water, and the model by Hench (1975) incorporates pH.

Waste-glass-water interactions are complex, and the models currently used to explain these interactions have been adapted from results with simpler silicate glasses. These results were normally obtained under limited conditions, with no intent to simulate or investigate behavior in a repository. Realistic predictive models for waste-glass leaching under repository conditions should incorporate the phenomena occurring during the glass-water interaction. The control-

ling parameters must be identified and characterized so that mathematical descriptions can be developed for them. As described in the previous sections, the controlling parameters—pH and Eh, temperature, leachate composition, radiation, solubility, and leachate flow effects—have been identified and quantified to varying degrees. Enough information currently exists to quantify all the controlling parameters reasonably well. Realistic models of the leaching characteristics of borosilicate waste glass are being developed, but significant results have not yet been published. These models will be the base from which alterations or interactions caused by other repository constituents can be determined.

Spent Fuel. Spent fuel is an inherently simpler material than borosilicate waste glass, but the properties of irradiated fuel depend on the irradiation history. As a result, irradiated fuel is not a single product but a range of products whose overall chemistry is dominated by the chemistry of UO_2 .

The chemistry of UO_2 fuel depends on such parameters as the oxygen-to-uranium ratio, the extent of burnup, and the power rating (Kleykamp, 1979). The physical changes that occur during irradiation include grain growth, fuel cracking, and the production of both closed and open porosity as a result of the formation of fission gas bubbles at grain boundaries. Chemical and physical factors combine to produce a high surface area material that is inhomogeneous on both the micro and macro scale. This inhomogeneity is reflected to a considerable extent in the results reported for spent fuel leach tests.

Unlike those of glass, most of the leaching investigations of spent fuel have been conducted recently (Johnson et al., 1980; Norris, 1979; Ekland and Forsyth, 1978; Vandergraaf, 1980;

Katayama, Bradley, and Harvey, 1980; Kayatama, 1976). Since spent fuel is highly radioactive, leaching experiments must be performed in a hot cell. Thus the number of facilities available for this type of work and the expense have limited the investigations to a few locations. In addition, relatively few surface analyses can be performed on such a highly radioactive material.

Most of the spent fuel leaching investigations are summarized in Table 3. The three laboratories represented are Battelle Pacific Northwest Laboratory (PNL), Los Alamos National Laboratory (LANL), and Whiteshell Nuclear Research Establishment (WNRE). The spent fuel source, burnup, and experimental descriptions, including leachate type, sample configuration, and time span of the experiments, are also given. As can be seen, many long-term tests have been conducted on the samples, which vary from chunks of spent fuel removed from the cladding to segments of fuel with the cladding intact.

Irradiated fuel experiences large temperature gradients from its axial center to the cladding. This results in a range of porosity, grain size, and elemental variations from the center to the edge of spent fuel (Kleykamp, 1979; Johnson et al., 1980). For example, ^{137}Cs concentrates at the fuel-cladding interface. Since spent fuel is highly cracked, removing the cladding leaves small chunks of fuel with wide size and property distribution. Therefore investigators can choose between spent fuel chunks or segments of spent fuel with the cladding intact for leaching samples.

If fuel segments including cladding are used, the entire range of spent fuel is exposed to the leachate. It is hoped that this allows the average leaching characteristics to be determined, but, because of the extensive cracking and the fuel-cladding interface, the surface area exposed to the

Table 3 Leach Test Parameters on Spent Fuel

Laboratory	Reactor	BU, GWD/MTU	Experiment description	Condition of fuels	Time span
PNL	Quad City BWR	9	25°C Paige Test	Chunks	Up to 1400 d for deionized water; up to 822 d for other
	H. B. Robinson PWR	28	Hanford groundwater		
	Zorita PWR	54	Synthetic seawater Deionized water		
PNL	H. B. Robinson	28	M—IAEA, 25°C Deionized water WIPP "B" brine 0.015M CaCl ₂ 0.03M NaHCO ₃ 0.03M NaCl	Chunks	Up to 769 d
PNL	H. B. Robinson	28	Static, 25 and 75°C Only 25°C completed All solutions listed above	Chunks	Up to 340 d
			Static, 150 and 250°C Deionized water 0.03M NaHCO ₃ WIPP "B" Brine		Under way
LANL	H. B. Robinson	28	IAEA, 25 and 70°C Reducing and oxidizing conditions Deionized water	Clad	Up to 78 d
WNRFF	Pickering-Canada	7.9	Static, 25 and 150°C Granite groundwater Carbonate groundwater Reducing and oxidizing conditions	Clad	Up to 500 d

leachate is not known; it can vary from sample to sample. Furthermore, relatively large amounts of ^{137}Cs are concentrated at the fuel-cladding interface and are preferentially leached. Thus leaching from the spent fuel alone is not being measured. Rather the combination of spent fuel and fuel-cladding interfacial leaching is being determined. Also the cladding can act as a sorptive surface for ions that have been removed from the sample. Thus leaching results are difficult to interpret with this sample type.

If spent fuel chunks without the cladding are used, leaching results are for only the spent fuel and do not include fuel-cladding interfacial leaching or sorptive effects of the cladding. In addition, a reasonable measure can be made of surface area exposed to the leachate. The chunks are very inhomogeneous, however, and, unless large numbers of them are used as a representative sample for spent fuel leaching results will not be obtained, and sample to sample variations will be large.

There is no one best representative sample type for spent fuel. Each one has its shortcomings. Each investigator has used sufficiently dissimilar leaching samples and experiments to make it impossible to compare results directly. General observations are that leaching is initially incongruent, however, with ^{137}Cs and ^{90}Sr being leached more rapidly from the fuel in the short term. At longer times congruent leaching is approached. Most researchers have incorporated UO_2 into their leaching programs as an aid to understanding the more complex and difficult to work with spent fuel. The following discussions attempt to describe what has been learned about some of the important effects on spent fuel leaching.

Temperature Effects. As can be seen from Table 3, only small amounts of temperature effect data are avail-

able. Experiments are in progress, however, which will add significantly to this data bank when they are completed and reported.

The temperature effects on spent fuel leaching are very small. Differences in leaching characteristics in demineralized water have been measured at 25 and 70°C at LANL (Norris, 1979) and at 25 and 150°C at WNRE (Johnson et al., 1980). An example of these results is shown in Fig. 10 for ^{137}Cs . As can be seen, the ^{137}Cs leach rate initially increased with a temperature increase from 25 to 70°C and then rapidly decreased again to essentially the original value. The rapid fluctuation in leach rate did not noticeably affect the cumulative fraction of ^{137}Cs removed from the sample. For most of the other ions leached from spent fuel, increasing the temperature from 25 to 70°C caused a decrease in the leach rate and in the cumulative fraction leached. Nearly identical results have been reported for temperature increases from 25 to 150°C (Johnson et al., 1980). Increases in temperature normally resulted in enhanced plateout of elements on container walls but only minor elemental changes in the leachate. The lower leach rates for most elements at enhanced temperatures may be related to a number of factors, e.g., oxide film growth or a lower U(VI) oxide solubility at higher temperatures (Holland and Brush, 1979).

Effects of Oxygen Level. The effects of oxygen on leaching of spent fuel are expected to be significant (Johnson et al., 1980; Grandstaff, 1976). Here again only limited data are available for consideration (Johnson et al., 1980; Norris, 1979). The work conducted at WNRE used 25°C distilled water at three oxygen partial pressures obtained with gaseous mixtures and a platinum gauze catalyst. The oxygen concentrations were 2.5×10^{-4} , 6.1×10^{-6} , and

Figure 10 Effects of temperature on leaching of ^{137}Cs from spent fuel. Cumulative fraction released under reducing ($\square$) and oxidizing ($\circ$) conditions and leach rates in reducing (Δ) and oxidizing ($+$) conditions. (Data from Vandergraaf, 1980.)

1×10^{-6} mol/kg. Oxidizing and reducing conditions were also used for spent fuel leaching in deionized water at 25°C at LANL. Again, these oxygen levels were obtained by using gaseous mixtures and had Eh values of $+0.55$ V for the oxidizing solution and -0.12 V for the reducing solution. Both laboratories found essentially the same results. Leach rates for ^{137}Cs are independent of oxygen concentration (see Fig. 10); this verifies that the initial release of cesium from leachable phases and that matrix breakdown is not required for this to occur. In general, dissolution rates for the other elements are decreased with decreasing oxygen in the leachate but not to the extent that would be expected if a first-order dependency of rate on oxygen concentration were to be obeyed (Grandstaff, 1976). This could possibly be attributed to the oxidation of the fuel surface during sample preparation. Once

the surface is partially oxidized, the dissolution process may become more facile, and the rate becomes somewhat insensitive to changes in oxygen concentration. An example of the effect of oxygen on leach rates of elements removed from spent fuel is given in Fig. 11 for $^{239,240}\text{Pu}$.

Leachate Composition Effects.

Spent fuel leaching experiments have been conducted in simulated groundwaters by several researchers (Johnson et al., 1980; Ekland and Forsyth, 1978; Vandergraaf, 1980; Katayama, Bradley, and Harvey, 1980; Katayama, 1976). The results are partially conflicting and difficult to explain. Johnson et al. (1980) found that the leach rates of ^{90}Sr , $^{239,240}\text{Pu}$, and rare earths in deionized granite and carbonate groundwaters are generally somewhat lower than in air-saturated distilled water. Uranium is the exception; it had a leach rate more than an order

Figure 11 Fractional release rates of $^{239,240}\text{Pu}$ from spent fuel at various oxygen concentrations at 25°C. (Data from Johnson et al., 1980.)

of magnitude higher in both simulated carbonate and granite groundwaters than in distilled water. This was presumably a result of carbonate complexing. Ekland and Forsyth (1978) from Karn-Bransla-Sakerhet in Sweden, using distilled water and a carbonate groundwater identical to that used at WNRE in their spent fuel leaching experiments, found that the final dissolution rate for uranium was the same for both leachants.

Mechanisms and Models. Similar mechanisms for the interactions of UO_2 with aqueous solutions was proposed by Johnson et al. (1980) and Wang (1981). In neutral or reducing conditions, dissolution of UO_2 involves only the U(IV) valence state, and the equilibrium solubility is very low. In solutions containing oxygen or oxidizing species, however, many reactions can occur, depending on temperature and pH. These reactions were

summarized by Wang (1981) and are illustrated in Fig. 12. Implied in this model is the fact that, even after the solubility limits have been reached, dissolution can still occur as long as precipitation is also occurring. If this applies to spent fuel, then elemental removal does not stop when the solubility limit for UO_2 has been reached. Rather dissolution and precipitation can continue to occur; this releases other elements whose solubility limit may not have been reached.

Since spent fuel contains grain boundaries, large inhomogeneities, and radiation damage, it is not clear whether it will react with aqueous solutions in a manner similar to UO_2 . The leaching mechanisms of spent fuel may be more complex and may require direct evaluation.

Comparison of Glass and Spent-Fuel Leaching. In general, spent fuel releases elements to aqueous solutions at a faster rate than borosilicate waste glass. This is illustrated in Fig. 13 for some elements common to both waste forms. The leachate was deionized water, and the leaching results were normalized by the weight fraction of the element in the sample. As can be seen, there is nearly two orders of magnitude difference in leach rates. These results represent the largest difference. If sodium bicarbonate leachate is used, the results are quite different (Fig. 14). With this leachate, borosilicate glass and spent fuel have similar leach rates after a few days. This represents the other extreme. Other generic groundwaters fall somewhere between deionized water and sodium bicarbonate solution. These solutions were all air saturated; different results might occur for the same solutions under reducing conditions.

Deionized water and four other generic groundwaters were used at PNL as leachates for spent fuel leaching tests (Katayama, Bradley, and

(1) Surface oxidation (several ångströms)

(2) Oxidation-dissolution

(3) Transport

(4) Hydrolysis-film formation, 25 to 75°C

(5) Hydrolysis-crystal growth, 150°C

Figure 12 Oxidation and dissolution mechanisms for UO_2 in deionized water. (Data from Wang, 1981.)

Figure 13 Comparison of elemental leach rates from spent fuel and PNL-76-68 glass in demineralized water at 25°C.

Harvey, 1980; Katayama, 1976). The generic groundwaters were 0.03M NaHCO_3 , WIPP "B" saturated salt brine, 0.03M NaCl , and 0.015M CaCl_2 . Essentially all elements (including uranium) leached more rapidly in air-saturated deionized water than in any of the groundwaters, which were also air saturated. These results are in

agreement with WNRE, except for uranium. At PNL uranium was found to leach in excess of an order of magnitude faster in deionized water than in the generic carbonate groundwater, with less difference than was observed for other groundwaters. Obviously carbonate complexation cannot be used to explain these results.

Figure 14 Comparison of elemental leach rates from spent fuel and PNL-76-68 glass in 0.03M NaHCO₃ solution at 25°C.

Results for the three different experiments comparing spent fuel leaching in groundwaters to that in deionized water are consistent for most elements; i.e., groundwaters reduce leach rate. There is total disagreement for uranium, however. More experiments are needed to resolve this discrepancy.

Solubility Effects. Solubilities have not been investigated to any extent for spent fuel, but several solubility studies have been conducted on UO₂ (Langmuir, 1978; Lemire and Tremaine, 1982; Gayer and Leider, 1975). The UO₂ is so insoluble in neu-

tral and alkaline solutions under reducing conditions that measuring its equilibrium solubility presents difficulties in analysis (Johnson et al., 1980). Under very reducing conditions, dissolution of UO₂ involves only the U(IV) valence state. The low solubility of UO₂ observed in slightly acidic and alkaline water increases sharply under even mildly oxidizing conditions because of the formation of the U(VI) species, UO₂⁺², and its hydrolysis products (Johnson et al., 1980). Many groundwater species complex with UO₂⁺², thereby increasing the UO₂ solubility. The solubilities of

UO₂ or spent fuel in groundwaters have not been adequately investigated. More thorough reviews of UO₂ solubility results are given elsewhere (Johnson et al., 1980; Langmuir, 1978; Lemire and Tremaine, 1982; Gayer and Leider, 1975).

Conclusions

A large body of information on the interactions of glass and spent fuel with aqueous solutions was reviewed, compared, and discussed. The following conclusions can be made:

- There is a fundamental difference in the pH dependence of leaching for simple silicate and borosilicate waste glasses. The waste glasses are more durable in the basic pH range; whereas the silicate glasses are more durable in the acidic pH range.
- Temperature dependencies for elemental leaching from borosilicate waste glasses have activation energies ranging from 7 to 22 kcal/mol and typically have linear log leach rates vs. reciprocal temperature dependencies over wide temperature ranges.
- Elemental leach rates from spent fuel have essentially no temperature dependency over the temperature range of 25 to 150°C. This conclusion is based on leachate concentrations alone and does not consider plateout on container walls.
- The variation in elemental leach rates from borosilicate glass between deionized water and four simulated groundwaters is one order of magnitude or less. The simulated carbonate groundwater typically resulted in the highest leach rates.
- The elemental leach rates from spent fuel are less in simulated groundwaters than in deionized water. The possible exception to this is the uranium leach rate, for which a large discrepancy exists in the literature.
- Lowering the oxygen content of the leachate decreases the leach rates of most elements in spent fuel. The notable exception is cesium, which is insensitive to the oxygen content of the leachate.
- Radiation damage in borosilicate waste glasses occurs because of radioactive waste contained in the glasses. The most damage is caused by alpha decay, primarily from the recoil nucleus. This damage caused by self-radiation results in only minor changes in the leaching characteristics of the glass.
- Radiolysis of the leachate results in enhanced leaching of borosilicate waste glasses. The enhancement is largest at lower temperatures and diminishes with increasing temperature. If nitrogen is present in the leachate, nitric acid is formed as a result of radiolysis. This greatly enhances leaching at all temperatures.
- The solubility limits of plutonium and neptunium from borosilicate waste glasses are identical to that found for PuO₂ and NpO₂; this indicates that these oxides may be controlling the solubility in the glass.
- Elemental release from spent fuel is typically higher than from borosilicate waste glasses. The only exception to this is in simulated sodium bicarbonate groundwater, where the rates are nearly the same.
- Models for both spent fuel and borosilicate glass leaching are currently not adequate to predict long-term leaching characteristics reliably. The new generation of models currently being developed should be adequate for predictive purposes, however.
- The effect of flow rate of leachate on elemental release is not large for reasonable simulated groundwater flow. The effect is somewhat temperature dependent, with a larger effect at high temperatures.

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The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program

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This paper focuses on interactions between dissolved radionuclides in groundwater and rocks and sediments away from the near-field repository. Two approaches were used to study the primary mechanism, adsorption-desorption. Empirical studies rely on distribution coefficient measurements, and mechanism studies strive to identify, differentiate, and quantify the processes that control nuclide retardation.

The empirical approach quantifies adsorption by use of a distribution coefficient (R_d), which is the ratio of the mass of a radionuclide present on the rock to the mass present in solution. Studies to standardize laboratory methods for measuring R_d are described. No one laboratory method best simulates all possible rock-groundwater-nuclide combinations, but two methods, batch and once-through-flow column, appear to complement each other and are recommended for further standardization. Their strengths and weaknesses are discussed. Results of generic empirical R_d work are summarized in tables of nuclide R_d values for five potential repository rock types. These data are ranked, and future improvements in the treatment of nuclide retardation in

existing computer safety assessment codes are suggested.

The status of sorption mechanism studies is discussed, with emphasis on delineating the usefulness of ideal ion-exchange, site-binding electrical double-layer, and redox-controlled sorption constructs. Since studies to date show greater potential for site-binding electrical double-layer models, future efforts will concentrate on this construct.

Laboratory studies are discussed which corroborate the importance of redox reactions in causing nuclide retardation for multivalent elements, such as Tc, Np, Pu, and U. Results suggest that both solution-mediated reduction, such as the Fe(II)-Fe(III) couple, and solid-solution heterogeneous reduction reactions, such as reduction of solution Pu(VI) at the mineral surface by structural Fe(II), occur.

Coupled microscopy, microprobe, and autoradiography studies have determined actual sorption sites for radionuclides on polymineralic rocks. The studies show that it is possible for minor phases to completely dominate the mass of radionuclides adsorbed. The most active minerals are typically alteration products (clays and zeolites).

Several exercises are discussed which rank radionuclides according to their potential dose hazards. In each of the analyses discussed, the top four radionuclides are I, Tc, Np, and Ra. Other elements that rank high in potential hazards are Pu, U, Am, Th, Pb, Sn, Pd, and Se.

A brief review of field nuclide migration and laboratory Rd comparisons shows general agreement between field observation and laboratory predictions of nuclide migration. The interplay between laboratory observations, field nuclide migration, and natural analog studies is discussed.

Introduction

Once a radioactive waste is emplaced in a deep geologic repository, few credible means exist for its return to the biosphere. The most likely is through dissolution of the waste and subsequent radionuclide transport by circulating groundwater (Interagency Review Group, 1978; Pines, 1978; de Marsily et al., 1977; and Arthur D. Little, Inc., 1980). Therefore safety and performance assessments in support of licensing nuclear waste repositories must be concerned with the physicochemical interactions between radionuclides in waste forms and groundwater, engineered barriers, and rocks and sediments since these processes can significantly delay or constrain the mass transport of radionuclides in comparison with groundwater movement (Hill, 1980; Kaszeta and Bond, 1980; de Marsily et al., 1977). For licensing purposes these physicochemical interactions must be described in quantitative terms to support assurances that, if radionuclides were released from a deep geologic repository, the magnitude of release and the ensuing migration rate to the biosphere would be sufficiently small

that wastes would not adversely affect the biosphere or accessible environment.

This paper focuses on interactions between dissolved radionuclides in groundwater and rocks and sediments away from the near-field repository influence of intense heat and radiation. It summarizes progress in the Waste/Rock Interactions Technology Program (WRIT) from 1976 through mid-1981. In support of preliminary site comparisons and safety assessment, empirical distribution coefficients for radionuclide adsorption are given for typical groundwaters in basalt, tuff, granite, bedded salt, and domed salt. Further, as an example of how these research efforts can focus current and future work on radionuclide migration and hazards potential, a prioritization exercise is described. Finally a brief discussion of the relationships among laboratory, field, and natural analog studies is presented.

Other germane studies conducted by WRIT, such as waste-form leaching and waste package systems performance testing, are the subject of another paper in this volume (McVay, Bradley, and Kircher).

Background

Among the processes that retard transport of radionuclides are hydrologic, geologic, and physicochemical processes. Hydrologic and geologic studies can supply the necessary data to quantitatively describe water velocities and probable path length to the accessible environment. These values provide an upper limit to the rate of radionuclide transport. Sorption-desorption studies are performed to estimate quantitatively the increase in effective travel time for nuclides to the accessible environment. Often the increase is significant, i.e., relative nuclide migration travel times are 10^3 to 10^6 yr longer than those of groundwater. Such long

travel times allow nuclides to decay to lower concentrations and less hazardous elements. Furthermore, some sorption processes irreversibly remove nuclides from groundwater, thus preventing their release to the biosphere.

In studying radionuclide retardation, WRIT has followed two approaches: empirical studies that rely on the measurement of distribution coefficients and mechanism studies that strive to identify, differentiate, and quantify the physicochemical processes controlling nuclide retardation (Relyea, Rai, and Serne, 1979; Serne, 1978a). The first approach allows the rapid determination of the relative affinity of nuclides for solid substrates without concern for the cause or controlling processes involved. An empirical parameter, the distribution coefficient (often called K_d or R_d), which is readily measured by laboratory experimentation, allows a quantitative estimate of nuclide migration relative to groundwater. Almost every existing computer code for safety assessment and site selection used in licensing support relies on the distribution coefficient concept. Other studies (Cloninger and Cole, 1980; Cloninger, Cole, and Washburn, 1980) have shown the importance of far-field nuclide retardation for guiding waste package design. Thus, to support preliminary site selection, performance assessment, and waste package design activities, WRIT has conducted empirical nuclide retardation studies.

During 1976 to 1978, WRIT performed generic screening sorption studies on a wide range of groundwater-rock-mineral-sediment combinations to develop bounding nuclide retardation values. During 1978 to 1981, empirical work shifted toward more comprehensive studies

with specific groundwater-rock-sediment combinations that are more representative of the media being considered for radioactive waste disposal. Results of these experiments can be used to identify probable sorption mechanisms for further study.

The mechanistic studies complement the empirical studies by providing fundamental data for understanding of physicochemical processes that control nuclide retardation. Plans are to interpret the available empirical data based on concepts identified in these more theoretically based studies and to develop predictive relationships that address the long-time extrapolations and allow interpolations or extrapolations based on knowledge of controlling physicochemical processes and laws. Mechanistic studies are not as rapidly completed and do not lead to useful results as readily as those of the empirical approach, but successful mechanism studies are valuable because their results are more general (i.e., site and methodology independent). Thus WRIT has attempted to meld theoretical and engineering approaches into a cohesive program to provide the necessary data for repository safety assessment, site selection, and waste package performance assessment and design.

Before we discuss the efforts to date, certain terms should be defined. Nuclide retardation encompasses all possible processes that hinder nuclide migration in solution, including ideal ion exchange, mineral precipitation, coprecipitation in amorphous* coatings, chemisorption or selective adsorption-complexation onto solid adsorbents,

**Amorphous coatings are amorphous-like but in practice are those that have minimal x-ray diffraction patterns (Jenne, 1972). The term is used for materials intermediate between totally crystalline and totally amorphous as determined by x-ray diffraction.*

redox or hydrolysis-mediated precipitation-sorption, and physical filtration of small particulates. Onishi et al. (1981) and Jenne (1977) describe the processes in more detail. In this paper adsorption or sorption refers to surface processes in which radionuclides in solution become incorporated onto the solid phase surface. The terms adsorption and sorption are more general and include more processes than ideal ion exchange but where possible exclude precipitation of identifiable mineral or amorphous compounds, such as oxides, hydroxides, or carbonates. One goal of WRIT has been to separate precipitation and adsorption studies and to differentiate the processes. At times this approach has been complicated by lack of knowledge of solubility limits for nuclides in groundwaters. In fact, some early adsorption studies were performed inadvertently at radionuclide concentrations that exceeded solubility limits. Future sorption work will incorporate recent advances in knowledge of nuclide solubilities.

To quantify adsorption, we typically measure the distribution of the adsorbate between the solid phase and the solution phase. Such a value or distribution coefficient is often called K_d , D , or R_d . Confusion arises because the term distribution coefficient has been used by other scientists much more selectively to refer to (1) the special case of ideal binary ion exchange where the element of interest is present in such trace concentrations that it does not appreciably affect concentration of the macroconstituent sorbed on the solid or the activity coefficient ratio of the mass action exchange (Meyer, 1979; Routson and Serne, 1972) or (2) a special case of a Freundlich empirical isotherm where sorption is linear

(Travis, 1978). Linear adsorption typically occurs only at trace adsorbate concentration in solution and trace loading onto the solid adsorbent surfaces. In both instances the adsorption refers to equilibrium conditions and, when used with mass transport theory, generally requires reversibility; i.e., desorption occurs at the same rate and leads to the same equilibrium ratio of adsorbate between solid and solution.

In this paper, when used to describe empirical studies, the distribution coefficient is called R_d and simply refers to the ratio of mass or activity of a radionuclide present in the solid phase (rock or sediment) to the mass or activity present in solution (groundwater). This empirical ratio does not require equilibrium conditions, quantitative reversibility, or ion exchange as the governing process. In this paper the term D is used to refer to a thermodynamic distribution coefficient that describes ideal ion exchange of radionuclides onto pure clays and oxide surfaces.

To date, when used by safety assessment modelers in extant computer codes, WRIT R_d or D data have been assumed to represent both equilibrium and reversible data, as required by model mathematical laws. The implications of these assumptions are discussed later in this paper.

The WRIT activities on far-field sorption fall in three general areas—development of laboratory adsorption-desorption methods, generation of empirical R_d values, and studies of the physicochemical sorption-desorption mechanism. Discussions of laboratory methods development focus on the strengths and weaknesses of the two most used methods, batch and once-through-flow column. The sensitivity of R_d to pro-

cedural steps, such as agitation rate, phase separation, and pore velocity, is discussed, along with results from an interlaboratory batch sorption comparison exercise and comparison of nuclide R_d values among methods. Results of generic empirical R_d experiments are distilled down to tables of R_d values for important nuclides contacting five potential repository rock types—bedded salt, dome salt, basalt, and granite. The quantity and quality of R_d data for these generic sites are ranked. Finally, the status of sorption mechanism studies is discussed. Results of scouting studies to identify more important variables among temperature, pH, Eh, and groundwater composition are given. Detailed descriptions of studies to identify the applicability of ideal ion-exchange, site-binding electrical double-layer, and redox-controlled sorption constructs are provided. The usefulness of these three constructs is also discussed.

Development of Laboratory Adsorption-Desorption Methods

Since data used in license applications will be critically reviewed, they should be obtained from formalized, standard, or commonly accepted methods. In 1976 several types of experimental methodologies were used with numerous variations on specific steps. The sorption values generated were perceived to be quite variable. Therefore the WRIT staff initiated studies with the goal of preparing a method or methods that could be recommended for certification. Various rocks and minerals in contact with radionuclide-laden solutions were used to assess the precision in R_d analysis; ease of method usage; time, equipment, and cost expenditures; method limitations; and R_d result comparisons. Laboratory methods investigated include batch, axial filtration, channel chromatography,

once-through-flow column on disaggregated or naturally permeable media, once-through-flow column on fractured or intact rock core, and recirculating-flow column. The batch and column methods are discussed in some detail since they are the most commonly used methods. The other methods are only briefly discussed. Each method's advantages, disadvantages, and applicability to providing credible long-term adsorption predictions for repository safety assessments are presented. References are provided for readers who wish further details on the methods and past uses. (See Serne, 1978b, 1979; Relyea, 1980, 1981; Daniels et al., 1981, for details on the methods and comparisons of the results. See Burkholder et al., 1979; Brandstetter et al., 1979, for annual summary reports.) Using information available through mid-1981, the WRIT staff concluded that no one laboratory method best simulates all possible rock-groundwater-nuclide combinations. Conceptually, a once-through-flow column on intact core best simulates expected long-term nuclide migration in the far field, but costs, time expenditures, and equipment malfunction have presented significant practical constraints. As a result, the WRIT staff currently recommends the use of at least two methods in concert to bound radionuclide migration for probable environmental conditions.

Batch Method. The most commonly chosen laboratory method to evaluate nuclide sorption is the batch test, which involves contacting the adsorbent (disaggregated rocks or sediments or rock tablets, shards, etc.) with a soluble adsorbate [nuclide(s)] in groundwater within a container. In most instances the system is continually agitated to facilitate mixing and contact. At specified times the solid and solution are separated, and the resultant distribution of adsorbate is determined. Because the equipment,

space, cost, and time requirements are low and the methodology is quite simple, the batch method is popular. However, the seemingly elementary operations mask numerous subtleties that WRIT studies have identified as the probable cause for much of the past variability in reported results.

In 1978 nine participants conducted a round-robin exercise on batch sorption to gather data on interlaboratory precision and identify procedural details that may cause variability. Large quantities of three rocks were homogenized and characterized (Ames, 1978). General guidelines on groundwater compositions, radionuclides, and procedural details were given to participants. Although the concentrations of radionuclides and the exact methodology instructions were not specified, details on actual procedures used by each participant were requested. The results are listed in Table 1. (See Relyea and Serne, 1979, for more details.)

It was anticipated that close agreement would be found for cesium and strontium adsorption results and that plutonium would possibly behave erratically. There was agreement between $R_d(\text{Cs})$ and $R_d(\text{Sr})$ on both basalt and limestone contacting brine solution and on basalt in a basalt groundwater. Adsorption results for cesium in dilute limestone groundwaters were more widely scattered than anticipated. The $R_d(\text{Sr})$ values generally appeared to depend on the pH of the final solution but not on the tracer concentration. The $R_d(\text{Cs})$ values did not appear to depend on final pH. The data reported are insufficient to determine why $R_d(\text{Cs})$ had a range of three orders of magnitude in the limestone rock groundwater system, but other studies (e.g., Seitz et al., 1980) suggest that the variability was caused by a nonlinear cesium adsorption isotherm (see Fig. 1) or incomplete removal of fine particles from solution.

Figure 1 Dependence of cesium adsorption by basalt on cesium concentration.

Batch adsorption determinations of $R_d(\text{Pu})$ were not satisfactory (two to three orders of magnitude differences) because of adsorption of plutonium on container walls and formation of and plutonium adsorption on filterable particles. The effects of other variables (e.g., pH, plutonium concentration, and spiking method) which can significantly affect adsorption also must be considered. Direct determination of plutonium adsorbed by the rock and plutonium in effluent solution reduced the variability in $R_d(\text{Pu})$ in a prescribed rock-solution system by only one order of magnitude.

Results indicated that several uncontrolled parameters may have affected results. These were (1) method of tracer addition to solution, (2) solution-to-rock ratio, (3) initial tracer concentration in influent solution, (4) particle size distribution, (5) solid-solution separation method, (6) sample containers, and (7) temperature. Their effects are discussed in the following paragraphs.

Table 1 Interlaboratory Comparison of Rd (ml/g) Values for Limestone and Basalt for Cesium, Strontium, and Plutonium*

Cesium				Strontium				Plutonium				Participating laboratories
Limestone		Basalt		Limestone		Basalt		Limestone		Basalt		
pH	Rd	pH	Rd	pH	Rd	pH	Rd	pH	Rd†	pH	Rd†	
7.9	880 ± 160	8.7	380 ± 70	7.9	14.9 ± 4.6	8.7	92 ± 3	7.9	1090 ± 120(a) 690 ± 320(b)	8.6	200 ± 170(a) 15 ± 2(b)	Pacific Northwest Laboratory
7.9	65 ± 2	7.8	401 ± 21	8.0	5.4 ± 0.3	8.1	68 ± 17	7.6	1027 ± 41(a) 2134 ± 77(c)	7.5	8.8 ± 3.4(a) 67 ± 14(c)	Argonne National Laboratory
8.5	88 ± 1	8.4	265 ± 4	8.5	1.4 ± 0.2	8.4	81 ± 1	8.1	4745 ± 4931(a) 3198 ± 512(c)	8.0	1078 ± 716(a) 843 ± 658(c)	Los Alamos National Laboratory
ND	60 ± 30	ND	290 ± 70	ND	2.7 ± 0.5	ND	43 ± 1	ND	70 ± 36(b)	ND	580 ± 12(b)	Lawrence Livermore National Laboratory
8.2	227 ± 14	8.3	380 ± 5	8.3	5.9 ± 0.2	8.4	89 ± 5	8.2	198 ± 50(a)	8.2	592 ± 134(a)	Oak Ridge National Laboratory, Study 1
ND	663 ± 61	ND	453 ± 12	ND	9.3 ± 2.4	ND	93 ± 6	ND	63000 ± 19000	ND	312 ± 66(a)	Oak Ridge National Laboratory, Study 2
ND	6.8 ± 0.6	ND	255 ± 7	ND	13.4 ± 0.6	ND	73 ± 4	ND	2616 ± 1135(b)		89 ± 17(b)	Rockwell Hanford Operations
7.8	13 ± 0.4	7.4	31 ± 2	7.6	1.8 ± 0.5	7.4	41 ± 6	7.5	547 ± 356(b)	7.5	1000 ± 590(b)	Atomic Energy of Canada
ND	48.9 ± 5	ND	296 ± 10	ND	2.4 ± 0.1	ND	55 ± 2	ND	1009 ± 162(d)	ND	221 ± 147(d)	Lawrence Berkeley Laboratory

*The limestone and basalt samples were crushed to 297 to 840 μm in size. All Rd's are for a 7-d equilibration period except those for Oak Ridge National Laboratory, Study 2, which are for a 29-d equilibration period. The abbreviation ND means not determined.
 †Equilibration solution treatment a, centrifuged at ~4000 g and filtered through 0.2- to 0.45-μm filter; b, centrifuged at ~4000 g, c, adsorbed activity was determined directly from the geomeedia sample instead of calculating from the change in concentration of the radionuclide in solution, and d, based on original influent, which was not corrected for the loss of activity from the solution not containing geomeedia (blank correction).

A strong system agitation rate is suspected to cause sample abrasion, which exposes new surfaces (increases surface area) and increases the chances that fine suspended particulates may be present in solution (Barney and Brown, 1980; Ames and McGarrah, 1980). These fine particles generally have adsorbed nuclides on their surfaces, and often they remain in the solution phase during solid-solution separation steps. Calculating the R_d ratio yields results that are biased low and introduces large variability in observed solution nuclide concentration (Rai, Serne, and Moore, 1980a). Apparently disaggregated glassy Columbia Plateau basalt may be particularly susceptible to particle abrasion. Thus, for all readily weatherable rocks, the WRIT staff recommends that a very gentle agitation rate (a few oscillations per minute) be used to minimize surface grinding.

The method chosen to separate the solid and liquid phases can seriously affect R_d determination. Two approaches are typically used—centrifugation or filtration. Results to date show that centrifugation often leads to greater variability and lower R_d values than equivalent experiments that use membrane filtration. The WRIT staff recommends filtration with polycarbonate membranes (0.0018 to 0.015 μm) rather than cellulosic filters because polycarbonate appears to adsorb minimal amounts of tested radionuclides. Studies performed at Los Alamos showed that filtration may yield values biased high because radionuclides in solution are adsorbed by the membrane filter (Erdal et al., 1980). This membrane adsorption phenomenon needs further study because results have not been duplicated and appear to be most evident for the highly insoluble actinide americium, and perhaps plutonium. The

potential filter adsorption impact can be minimized by using a small diameter filter, filtering a larger volume of solution, and discarding the first portion of filtrate.

Another source of variability is the amount and method by which radionuclide tracer is added to the groundwater. In the past a small aliquot of the radionuclide was added to the groundwater or rock-groundwater slurry from a concentrated stock (typically strong acid) solution. The pH of the system was then adjusted to the desired value with strong base or acid. The chances for system supersaturation or for formation of radionuclide polymers, such as Pu(IV), were great (Cleveland, 1979; Rai and Swanson, 1981). Since it is a goal of WRIT to separate nuclide adsorption onto surfaces from nuclide precipitation, this tracer addition technique is not adequate. Therefore the WRIT staff endorses an alternative tracer addition method in which the aliquot of concentrated nuclide is dried at sub-boiling temperatures in a container. Groundwater is then added, and the container is shaken or stirred for several days, with pH adjustment if needed. The traced groundwater is then filtered just before use in sorption tests. Some comparisons of tracer addition techniques for americium and plutonium in representative solutions in contact with tuff are shown in Table 2 (Erdal et al., 1980). Although the differences are not thoroughly understood, the potential for the presence of different species is suspected. Differences in measured solution nuclide concentrations may not be the only cause for the variability since R_d sensitivity to plutonium concentration (10^{-7} to $10^{-15}M$) is not great for batch experiments on granite and argillite (Daniels et al., 1981). Data are not currently available on the effect on R_d values of varying plutonium and americium concentrations on tuff.

Table 2 Average Rd Values for Tuff as a Function of Tracer Addition Method

Element and tuff sample	T, °C	Tracer dried then water added	Tracer added as liquid, pH adjusted
Americium			
1	22	180 ± 30	440 ± 5
	70	230 ± 30	
2	22	130 ± 30	1,100 ± 120
	70	110 ± 30	
3	22	670 ± 210	8,800 ± 1,100
	70	970 ± 240	34,000 ± 6,000
Plutonium			
1	22	140 ± 30	
2	22	110	1,200 ± 210
3	22	280 ± 100	3,300 ± 1,200

Thus, at present, the cause of the observed (Table 2) Rd variation with tracer addition method is not thoroughly understood.

Methods for correcting container adsorption and for calculating Rd have been important sources of variability. Because it is most convenient to analyze only the solution phase (both before and after contact with the rock) in a batch test, the Rd calculation scheme assumes that the difference in solution activities represents the amount adsorbed on the rock or sediment. No container appears to be totally inert to interaction with trace constituents in solution. To increase the chance of producing conservative Rd values, the WRIT staff has normally run blank containers (nuclide-laden solutions with no rock or sediment) alongside the batch tests. The loss of activity from solution in these blanks was monitored, and corrections were made to the amount of nuclide presumed to be adsorbed on the rocks. This method also corrects for inadvertent supersaturation and subsequent precipitation if the blanks are maintained at the same pH and Eh as the rock slurries.

More detailed studies in which the solids were also counted have shown that, for elements such as americium, plutonium, and lanthanides, blank corrections are in fact biasing results low (Relyea and Serne, 1979). In the containers with rock present, the greater available surface area of the rocks tends to outcompete the container for nuclide adsorption. Thus much smaller percentages of the radionuclide are actually adsorbed on container walls than the blank tubes would lead us to believe. The WRIT staff now recommends that, for Rd measurements in which accuracy is the major goal (as opposed to scouting and bounding studies), the actual radioactivity on the solid phase should be determined. A novel approach that used a container fabricated of the rock itself was also tested but was not pursued further because of its limitations for several porous rock types (Seitz et al., 1979). The effect of choosing different values for the original nuclide solution concentration and deciding whether to use a blank correction is dramatically shown in Table 3 (Coles, Weed, and Tewhey, 1980).

The round-robin results and interpretations lead to the first detailed recommendation for a proposed batch method (Relyea, Serne, and Rai, 1980). Further findings have identified steps in the batch methodology which should be specified. Further we wish to emphasize the need to develop adsorption isotherms (Rd as a function of nuclide concentration). Results of isotherm studies are proving that distribution coefficients for rocks are exceptionally sensitive to nuclide concentration down to extremely low values. Results for cesium adsorption onto such rocks as basalt and limestone (Seitz et al., 1980) show Rd dependence on cesium concentrations, even as low as $10^{-12}M$ (see Figs. 1 and 2). Clay minerals and soils appear to be less sensitive and exhibit the linear isotherm (constant

Rd) vs. nuclide concentration at higher concentrations. An example is shown in Fig. 3 (Meyer, 1979).

The WRIT batch adsorption studies to date show that Rd results with a precision of 5 to 25% around the mean value are typical if experimental details (e.g., agitation rate, solution-solid phase separation techniques, tracer addition technique, and calculational scheme) are standardized and if the resultant rock surface composition, nuclide concentration, and groundwater composition, including Eh and pH, are controlled within a narrow range.

The batch sorption test, because of such strengths as simplicity and cost efficiency (Brandstetter et al., 1979), remains the most frequently used test to obtain empirical Rd values. The WRIT staff endorses its use for

Table 3 Plutonium Rd Values on Shales, Climax Stock Shear Zone Material, and Thirsty Canyon Tuff

Sample	Groundwater	K _d for ²³⁷ Pu*	
		Method of calculation†	Method of calculation‡
Thirsty canyon tuff	Granite	190 ± 20%	8,000 ± 18%
Green argillaceous shale (20-50 mesh)	Limestone	≥10,000	≥20,000
Conasauga shale (20-50 mesh)	Limestone	≥6,000	≥72,000
Climax stock			
Shear zone 1 (100-325 mesh)	Granite	400 ± 83%	20,000 ± 80%
Shear zone 2 (100-325 mesh)	Granite	470 ± 18%	19,000 ± 17%
Shear zone 2 (50-100 mesh)	Granite	500 ± 58%	20,000 ± 56%
Shear zone 3 (<325 mesh)	Granite	80 ± 30%	3,700 ± 25%
Shear zone 3 (100-325 mesh)	Granite	30 ± 65%	1,700 ± 43%
Shear zone 3 (50-100 mesh)	Granite	8 ± 72%	900 ± 24%

*Mean + 1σ SD of three replicates. All experiments ran for 7 d.

†With a blank as "influent" solution.

‡With filtered stock solution as "influent" solution.

Figure 2 Dependence of cesium adsorption by limestone on cesium concentration.

screening purposes and recommends that, when site-specific Rd values are necessary, adsorption-desorption isotherms, such as the empirical Freundlich isotherm (Travis, 1978), be determined over a realistic range of nuclide concentrations and groundwater compositions as opposed to single Rd determinations. Such empirical relationships could be used for overall safety assessment sensitivity studies and could offer insight into probable mechanisms, such as precipitation (Barney and Brown, 1981).

Further work is necessary to evaluate the observed Rd dependency on solution-to-solids ratio (Daniels et al., 1981; Dosch and Lynch, 1980; Ames and McGarrah, 1980) and to quantify the surface area relationship between disaggregated and intact material.

One significant limitation is inherent in the batch methodology.

Figure 3 Dependence of cesium adsorption by montmorillonite on amount of cesium loaded on the clay [amount of cesium in solution (M) = loading $\div$ Rd].

The typical analytical procedure of counting total radioactivity in solution, and perhaps in the solid, does not differentiate multiple species if they are present. The calculational scheme to generate a distribution coefficient from total activities represents a gross average value and cannot separate the distinct sorption values for different species. For instance, if a radionuclide happened to be equally distributed in deep groundwater between two species that do not rapidly interconvert [one that did not sorb ($R_d = 0$) and one that exhibited strong sorption ($R_d = 1000$)], the laboratory batch method would yield an intermediate R_d of about 30 ml/g in an experiment with a solution-to-solid ratio of 30. Using the R_d value 30 ml/g in subsequent mass transport calculations would not be conservative since 50% of the radionuclide would move at the speed of the carrier solution. For this reason, when there is any suspicion that multiple species with significantly differing distribution coefficients may be present, a second sorption methodology, such as a once-through-flow column sorption experiment, should be run to search for early breakthrough. A second batch experiment could also be performed with the effluent from the first experiment to verify whether sorption continues.

Column Methods. Once-through-flow column sorption experiments are the second most-used laboratory method. The classical use of once-through-flow column sorption testing has been on permeable sediments and soils. The method has been used for many years to verify R_d values determined by batch methods (Routson and Serne, 1972). WRIT funded the development of procedures and high-pressure apparatus to modify the flow-through method to allow experimentation on intact and fissured rock with low permeability.

Once-through-flow column experiments are appealing in that they allow observation of nuclide migration rates without significant rock alteration (e.g., crushing). Hydrodynamic effects (dispersion, colloidal transport, etc.), as well as chemical phenomena (multiple species, reversibility, etc.), can be studied. Ideally once-through-flow column experiments would be used exclusively, but equipment costs, time constraints, experimental complications, and data reduction uncertainties often discourage potential users.

Typical equipment used in column experiments includes a cylindrical holder for the rock or sediment, a pump to control the solution flow rate, an automatic fraction collector to collect effluent aliquots, and connecting tubing and end caps to constrain and support the rock or sediment. For very slow flow situations typical of deep geologic repositories, a controlled atmosphere-humidity chamber is necessary to simulate redox conditions and minimize effluent evaporation. The experimental methodology for disaggregated or porous materials, such as soils, is well developed (Serne, Routson, and Cochran, 1974; Nielsen and Biggar, 1961; Passioura and Rose, 1971; Van Genuchten, Wierenga, and O'Conner, 1977). For low permeability material, such as crystalline rock, special high-pressure confining jackets and pumps are needed to promote reasonable water flow rates. Costs for such equipment are often \$15,000 to \$25,000. Furthermore, the high-pressure apparatus used for sorption studies is generally small scale, accepting cores of only a few centimeters in diameter by a few centimeters in length. Homogeneity problems can become quite serious for such small samples, especially for fractured or fissured rock, which requires samples of several meters to accurately simulate field hydrologic conditions. The greatest experimental problem in per-

forming core sorption tests on low permeability samples has been that the solution escapes along the interface of the rock and the confining jacket or column. Solution traveling down the interface does not interact appreciably with the rock and yields premature breakthrough of radionuclides (Daniels et al., 1981). Since it is often difficult to judge whether short-circuiting is occurring, applicability of results is often indeterminable.

Two other practical constraints are the amount of time available for experimentation and the frequency of equipment failure. The flow of water through low permeability rock is extremely slow unless large hydraulic gradients are imposed. This slow flow, coupled with the retardation most radionuclides encounter, creates breakthrough times often exceeding a few years for column lengths of centimeters. Few experimenters will accept these long periods; they usually resort to small columns (millimeters in length), high-pressure-induced increased pore velocities, or both. Short columns and increased water velocity significantly reduce water and nuclide residence times within the rock. This reduced residence time increases the likelihood that kinetic effects will become significant.

Furthermore, failure of equipment, especially pumps and fraction collectors, put practical constraints on laboratory experimentation. Experience at Pacific Northwest Laboratory shows that we can expect some sort of equipment failure about every 3 or 4 months. To minimize downtime, we found it advantageous to have an extra complete setup so that a second pump or fraction collector can be exchanged for use while the broken one is being serviced.

Seitz et al. (1979, 1980) discussed several column experiments where kinetics appears to be creating more rapid breakthrough because the short

residence times do not allow nuclide interactions to reach equilibrium. Kuhn and Peters (1981) presented mathematical arguments concluding that the repository setting includes groundwater velocities and path lengths sufficiently low and long, respectively, to allow nuclide sorption equilibrium to occur. Pickens et al. (1981) remarked that for some near-surface aquifers (coarse-grained sediments) pore velocities are such that nuclide adsorption equilibria do not occur. Results of Pickens et al. and Seitz et al. represent the opposite end of the spectrum from deep geologic repositories. More evaluation of the kinetic aspects of nuclide adsorption under plausible repository conditions is warranted, and kinetics definitely must be considered in evaluating laboratory sorption studies. Otherwise the results obtained at less than realistic residence times can bias nuclide retardation results.

A final complication in using column data has been the interpretation of asymmetric or peakless breakthrough curves. When ideal chromatographic peaks are observed in column tests of porous or fractured rock, R_d can be calculated or R_f , a nuclide retardation factor (ratio of the travel time of the radionuclide to the travel time of the carrier groundwater), can be directly evaluated by use of well-established equations (Burkholder et al., 1979; Inoue and Kaufman, 1963; Harada et al., 1980). Several solutions also exist which can describe slightly asymmetric breakthrough peaks, e.g., those discussed by Van Genuchten, Davidson, and Wierenga (1974), Pigford et al. (1981), Gee and Campbell (1980), and Gee et al. (1981). Peakless breakthroughs of solution have been observed in several WRIT-sponsored column nuclide adsorption experiments (Rickert, 1981; Vine et al., 1981; Daniels et al., 1981). The frequent occurrence of these peakless curves

warrants attention to ascertain whether experimental artifacts, such as core-holder interface leakage or selective channeling over the small core lengths, is occurring. If the peakless breakthrough curves prove to be accurate reflections of expected deep geologic nuclide transport, we will need methods to calculate a distribution coefficient (R_d) or nuclide retardation factor (R_f) or to predict radionuclide solution concentrations.

Further work is needed to advance the state of the art for column experimentation on low permeability rock. The observable short-circuit leaking malfunction rate still exceeds 30% of the experiments attempted, and other peakless results occur which are presently suspect.

Column methods on disaggregated or porous rock are available but are of limited usefulness because of residence time constraints for nuclides with appreciable adsorption. Current techniques that force rapid flow under high-pressure gradients may be biasing results low because of nonequilibrium kinetic effects.

At present the WRIT staff recommends that once-through-flow column experiments be used in concert with batch sorption experiments to produce the most credible bounding values for nuclide retardation. Replicated batch tests should be performed over a range of nuclide concentrations and groundwater compositions on several samples of rock to delineate the probable range of R_d values for each nuclide. In addition, such batch tests would delineate the concentration of nuclides at which confounding reactions, such as precipitation or polymerization, might occur. The R_d studies vs. time should allow estimates of the importance of kinetics on sorption. Once-through-flow column experiments at nuclide concentrations below solubility constraints and at realistic residence times should be performed to support the batch R_d values.

Effluent breakthrough curves should be monitored for low sorbing elements and for "leakage" of highly sorbing elements. Attempts should be made to verify whether the leakage is caused by actual mobile species, colloid transport, or column short-circuiting. After a reasonable period of time (3 to 6 months), the column should be sectioned, and the distribution vs. distance of strongly adsorbing nuclides should be determined to qualitatively verify batch R_d values.

Other Methods. Two laboratory methods under study in 1976 through 1978, axial filtration and channel chromatography, have been dropped from further consideration because the first requires specialized equipment and the second, complex data reduction. Meyer et al. (1978, 1981), Meyer (1979), Triolo, Harrison, and Kraus (1979), Francis and Reeves (1978), Francis et al. (1979), and Brandstetter et al. (1979) describe these methods and discuss their strengths and weaknesses.

Recently a recirculating-column technique (Daniels et al., 1981) was used to investigate whether self-grinding in batch systems is the cause of slow increases in R_d with time and larger R_d values than comparable column experiments. The recirculating column is a hybrid technique that is a closed system like the batch test and relies on recirculating flow to provide solution-rock contact. The porous rock, disaggregated or intact, is fixed so that particle abrasion is minimized. A reservoir of solution is present to adjust the system solution-to-solid ratio equal to that used in comparable batch tests. Contact time can also be adjusted to equal that in a batch test. At present too few results are available to determine whether the recirculating-column method offers advantages over the batch and once-through-flow methods or complements these commonly used methods.

Rd Value Comparisons by Different Laboratory Sorption Techniques. Ideally the distribution coefficient obtained by experimentation for a particular radionuclide for any given rock-groundwater system at equilibrium should not vary or depend on the experimental technique used. The previous discussions of the laboratory methods indicated the subtleties and difficulties encountered in insuring that the actual rock-groundwater radionuclide system being studied by one experimental technique can be reproduced by a second technique. Although the large number of variables present make it nearly impossible to duplicate all conditions, studies have been performed on the sensitivity of R_d to changes in individual parameters. It is still difficult, however, to provide sweeping and general conclusions about the sensitivity of R_d to any one parameter while allowing other parameters to vary over plausible deep geologic environmental ranges. As more variables are fixed or allowed only small changes, it becomes more sensible to describe the effects of perturbations of a few select parameters on the R_d value; i.e., empirical R_d values are unique only when site-specific conditions are chosen and set.

In following R_d value comparisons, experimenters applied different test methods but carefully held constant many variables among the rock-groundwater-nuclide parameters. Table 4 compares R_d values of two or more methodologies from studies in which care was taken to maximize the experimental variables that remained similar between tests. Results do not cover a large number of nuclides but concentrate on the "well-behaved" elements, e.g., strontium, cesium, and barium. Thus a definitive and comprehensive comparison is not possible at present. The comparison shows that for most of the cases cited

batch R_d values are greater than R_d values from once-through disaggregated or intact cores by a factor of three to six and, in one instance, a factor of ten. One exception is the sandstone sorption of strontium from brine; in this case the intact core data yield a larger R_d value. At present this observation is not explainable. For other isotopes that exhibit large R_d values, (> 500 ml/g), such as those typically found for lanthanides and americium and plutonium, column experiments will need to run for very long times or at significantly increased velocities to produce breakthrough. Because of the kinetic and potential short-circuit effects mentioned previously, it is not too surprising that available comparisons that rely on small columns and shortened residence times yield lower R_d results than batch tests do.

Until more definitive work is available (e.g., studies using both batch and once-through-flow column methods), the WRIT staff suggests that batch R_d values for elements exhibiting moderate sorption ($R_d < 50$ ml/g) could be reduced by a factor of three and batch R_d values between 50 and 300 ml/g could be reduced by a factor of five when used in conservative safety assessments. For elements that exhibit batch R_d values greater than 300 ml/g, batch values could be reduced by a factor of ten to increase conservatism. For elements with a batch R_d less than 20 ml/g, the WRIT staff recommends that actual column experiments be performed at realistic residence times to gather more data to evaluate methodology dependence. Finally, National Waste Terminal Storage (NWTS) systems modelers should perform sensitivity calculations to ascertain whether differences in R_d factors of a factor of three to ten are, in fact, significant in preliminary safety assessment and site selection exercises.

Table 4 Comparisons of Rd Values by Methods

Rock-groundwater (GW) type	Axial filter	Channel chromatography	Batch	Crushed column	Intact core	Recirculating column
Shale-0.1M Ca(NO ₃) ₂ GW						
Rd(Ni)		5-9	6.5			
Rd(Sr)		2-4	2.4			
Montmorillonite-0.6M NaCl GW						
Rd(Sr)	3.8		4	4.2		
Kazenta, Berea						
St. Peter sandstone-						
WIPP brine B GW			-0.11-		0.012-0.019	
Rd(Sr)			-0.13			
San Felipe sandstone-						
WIPP brine B GW						
Rd(Sr)			0.01		0.098	
Yucca Mountain tuff-tuff GW						
Rd(Sr)			50, 84*	30, 44	20	23, 45
Rd(Cs)			290, 250	120, 100		410, 120
Rd(Ba)			900, 620	360, 120		105, 130
Jackass Flats tuff						
tuff GW						
Rd(Sr)			300	110		390
Rd(Cs)			740	>600		1770
Rd(Ba)			835			860
Climax stock granite-						
granite GW						
Rd(Sr)			14-18	10-25		
Rd(Cs)			330-350	>600		
Rd(Ba)			150-180	32-44		
Eleana argillite-						
argillite GW						
Rd(Sr)			140-160	40-50		
Rd(Cs)			1500-1800	7600		
Columbia Plateau basalt						
basalt GW						
Rf(Cs) at $<10^{-8} M$			1000-1100	170-190		
Rf(Cs) at $>10^{-7} M$			170-300	25-125		
Oolitic limestone						
limestone GW						
Rd(Cs)			80	120		

Availability of Empirical Rd Values

Thousands of Rd values have been generated in the past decade in efforts to support shallow land and deep geologic nuclear waste disposal. In addition, WRIT has generated Rd values while evaluating laboratory methodology and investigating sorption mechanisms. In the latter instance, a wealth of characterization data on the rocks, sediments, minerals, macro and trace constituents (including the radionuclides), and experimental details have been generated. Experiments have been performed to ascertain the sensitivity of Rd to such parameters as temperature (up to $\sim 80^\circ\text{C}$); equilibration time (up to approximately 8 months); changes in groundwater pH, Eh, and dissolved solids content (up to 5M NaCl); and changes in nuclide concentration. These parametric studies were performed with the intent of focusing more detailed mechanism studies on only the more important parameters. In addition, these well-characterized studies yield valuable empirical data that can be statistically analyzed to produce Rd relationships that are functions of important independent variables (rock, groundwater, and nuclide characteristics). Although the calculated relationships do not prove cause and effect, they do allow predictions. Thus, from finite generic Rd data, estimates of Rd values can be made for environmental conditions not directly studied.

A statistical analysis of seven radionuclides, four synthetic groundwaters, 12 minerals, and four rocks was performed on a selected Rd data base developed at Pacific Northwest Laboratory (Relyea et al., 1978, 1979). The analysis showed that Rd empirical models are feasible and lead to valuable predictor capabilities. Table 5 shows empirical model predictions vs.

Table 5 Comparison of Actual and Predicted Rd for Strontium and Americium Adsorption for Data Not Used in Model Synthesis

Observation number	Rd(Sr)*	
	Actual	Predicted
1	2.0	1.7
2	3.2	2.8
3	43.7	44.4
4	293.0	246.7
5	2.7	1.6
6	2.6	2.7
7	51.0	43.7
8	123.0	192.5
9	5.6	6.3
10	3.9	3.8
11	69.1	61.0
12	635.0	653.7
Rd(Am)†		
	Actual	Predicted
13	18,170	14,312
14	1,593	2,957
15	7,162	12,198
16	450	822
17	250	159
18	71,455	22,157
19	105	103
20	1,815	1,770
21	153	150
22	4,469	2,248
23	14,258	18,996
24	213	182
25	246	387
26	4,473	2,267
27	16,430	10,016

*Correlation coefficient between actual and predicted strontium Rd is 0.991.

†Correlation coefficient between actual and predicted americium Rd is 0.804.

actual experimental values for studies not included in the data base used to create the model. The nonlinear statistical technique, adaptive learning networks (ALN), was used (Mucciardi et al., 1979; Mucciardi, Johnson, and Saunier, 1980). The analysis of the

minerals suggested that better predictive models can be developed when mineral groups (phyllosilicates, tectosilicates, inosilicates, etc.) are treated separately. The data analyzed also suggested that groundwaters of extremely high ionic strength (salt brine) should be treated separately from typical freshwaters. The large gap in solution concentrations between freshwaters ($\leq 0.3M$) and brine ($5M$) and the nonlinear mathematical relationships made intermediate interpolations difficult.

It is important to realize that empirical R_d relationships are more powerful tools than R_d values themselves; R_d values represent sorption for only a unique set of rock, groundwater, and nuclide conditions, whereas empirical relationships, such as ALN models, can be created to describe R_d as a function of important rock and groundwater characteristics. Safety assessment codes based on numerical approximation techniques rather than closed-form analytical solutions can accommodate R_d relationships, however complicated, and can accept single R_d values. Statistical relationships, such as ALN models, allow predictions of the sorption distribution coefficients with changes in the environmental parameters.

The WRIT generic R_d data bank presently includes data on many long-lived nuclides for rocks, sediments, and minerals common to six potential repository rock types (domed salt, bedded salt, granite, shale, basalt, and tuff), with a wide range of plausible groundwater compositions. The R_d data from other NWTS programs [tuff data from Nevada Nuclear Waste Storage Investigations (NNWSI) and basalt data from the Basalt Waste Isolation Program (BWIP)], the Waste Isolation Pilot Program (WIPP) (sedimentary rocks in contact with brines), and international programs (granite data from

Sweden and granite and metamorphic rock data from Canada) supplement the WRIT data. These data and others will be critically reviewed and selected for installation into a computer data management system fashioned after the Sorption Information Retrieval System (Hostetler, Serne, and Brandstetter, 1979; Hostetler et al., 1980). The computerized information retrieval system will (1) greatly increase efficiency in managing the mass of available data, (2) provide an auditable method for choosing sorption distribution coefficients for safety assessments, site selection, and licensing pursuits, and (3) aid research on mechanism and statistical studies to identify controlling parameters.

To aid preliminary safety, siting, and licensing activities, the WRIT staff has reviewed available sorption data (Tables 6 and 7). The tables present empirical sorption distribution coefficients for redox insensitive and sensitive elements. The R_d values were selected from actual experimental data whenever possible. Conservative (low) values were selected from the range available because, since the quantity and quality of available data vary, it is difficult to select most probable values without more specific information. Many available R_d values were found to be invalid because radionuclide concentrations used in the experiments were too high and resulted in precipitation as well as sorption. Other values were discarded because of lack of control or improper control of redox conditions. Nearly all available data were determined on disaggregated material.

For nuclides for which no experimental data were found, estimates were made based on the known chemical behavior of the radionuclide or the behavior of similar elements. As mentioned, Table 6 lists R_d values for radionuclides that are not expected to be directly affected by redox reac-

Table 6 Rd Values for Radionuclides Not Affected by Redox

Isotope	Rd, ml/g*				
	Bedded salt†	Dome salt†	Basalt	Tuff	Granite
³ H	0	0	0	0	0
¹⁴ C	0	0	0	0	0
³⁶ Cl	0	0	0	0	0
^{59 63} Ni	1	10	50	50	10
⁸⁵ Kr	0	0	0	0	0
⁹⁰ Sr	0.5	8	100	100	12
⁹³ Zr	500	500	500	500	500
⁹³ Nb	50	50	100	100	100
¹⁰⁷ Pd	1	5	50	50	10
¹²⁹ I	0	0	0	0	0
^{135,137} Cs	1	800	300	100	300
¹⁵⁴ Eu	50	50	50	50	100
¹⁵¹ Sm	50	50	50	50	100
²¹⁰ Pb	0.5	5	25	25	5
²²⁶ Ra	0.5	8	50	200	50
²²⁷ Ac	50	50	50	50	200
²³⁰ Th	50	100	500	500	500
²³¹ Pa	50	50	100	100	100
^{241 243} Am	300	300	50	50	200
^{242 244} Cm	300	300	50	50	200

*Rd in milliliters per gram is used for porous flow, for fracture flow the values must be normalized to available surface area, not mass

†Sorption values are for typical sedimentary rocks associated with salt, not for the salt per se

tions; i.e., they are expected to exist in the same oxidation state under both oxidizing and reducing conditions. Elements in Table 6 may be affected indirectly by redox conditions because of changes in groundwater chemistry and mineral stability, and thus the term redox insensitive should not be taken literally. Table 7 gives Rd values for elements that are expected to exhibit different behavior under differing oxidation-reduction conditions.

The concept of Rd for radionuclides that are affected by redox potential may be only marginally applicable (e.g., Pu, Se, Np, Tc, and Mo). Under reducing conditions, removal of these radionuclides from solution appears to be caused primarily by the precipitation of an in-

soluble compound with a lower oxidation state (Bondietti and Francis, 1979). Solubilities of the precipitated compounds are poorly known but are believed to be extremely low; thus there may be no need to invoke sorption to explain the low solution concentrations observed. This behavior is similar to that of phosphate in soils, which is more likely controlled by the precipitation of its solid compounds.

Of the five media considered in these two tables, fewer Rd data are available for rocks associated with domed salt, and more data are available for basalt, tuff, and granite. In general, we need more and better laboratory data for sorption under reducing conditions.

For preliminary assessments, we need adequate laboratory values of

Table 7 Rd Values for Redox Sensitive Elements

Element	Rd, ml/g*†									
	Bedded salt‡		Dome salt‡		Basalt		Tuff		Granite	
	Red	OX	Red	OX	Red	OX	Red	OX	Red	OX
⁷⁹ Se	20	10	100	20	20	5	3	1	3	1
⁹³ Mo	0	0	5	1	10	4	10	4	5	1
⁹⁹ Tc	1.5	0	5	0	20	0	10	0	4	0
¹²⁶ Sn	1	50	10	100	50	500	50	500	10	500
²³³ ²³⁴										
²³⁵ ²³⁸ U	2	1	3	15	10	3	5	1	5	1
²³⁷ ²³⁹ Np	50	10	25	5	150	10	50	3	50	1
²³⁸ , ²³⁹										
²⁴⁰ ²⁴¹ Pu	500	50	500	50	500	40	200	100	500	100

*Rd in milliliters per gram is used for porous flow, for fracture flow the values must be normalized to available surface area, not mass

†Abbreviations are Red, reducing conditions sufficient for the radionuclide to be more stable in lower valence state, OX, oxidizing conditions sufficient to oxidize the radionuclide from lower to upper valence state

‡Sorpton values are for typical sedimentary rocks associated with salt, not for the salt per se

Rd (typified by data presented in Tables 6 and 7). If these Rd values (which most likely are lower than values to be expected over very long time periods) are large enough to reduce the environmental effects of radionuclides to acceptable levels, more comprehensive studies at longer contact times may not be necessary. Long-term processes, such as weathering of rock to secondary minerals (e.g., clays, zeolites, and amorphous hydrous oxides) should increase the sorption of nuclides by increasing available surface area and exchange sites. In addition, nuclide diffusion into the bulk matrix over long time periods should also increase retardation in low permeability rocks. Studies discussed later show that nuclides tend to desorb off rocks, sediments, and minerals more slowly and reach larger steady-state Rd values than those measured during adsorption. Presently WRIT cannot explain thoroughly why the desorption process differs from adsorption, but several plausible

hypotheses are discussed later in this paper. Even without an understanding of the controlling mechanisms, we might incorporate at a minimum a two-valued Rd variable (Rd adsorption and desorption) into second-generation safety assessment models. An even more defensible empirical approach would be to incorporate adsorption and desorption isotherms that would describe the distribution coefficient dependency on total elemental concentration.

Adsorption-Desorption Mechanism Studies

Results from the empirical approach to describing adsorption-desorption, although useful in assessing the migration potential of radionuclides, are very specific to the particular host rock and groundwater studied. Thus the empirical approach in itself does not lead to a general understanding of the physicochemical processes controlling the interactions among rocks, groundwaters, and trace

concentrations of radionuclides. Nor do the empirical results lend themselves to extrapolation to other conditions not studied. Therefore mechanism studies are used to investigate the factors and interactions that control the adsorption-desorption behavior of actinides, long-lived fission products, and activation products in rocks. A knowledge of nuclide retardation mechanisms allows us to predict migration rate for any proposed storage environment more defensibly. Theoretical constructs and fundamental data enhance the credibility of long-term predictions and should reduce the costs of quantifying the migration rates of nuclides at specific sites.

For a full understanding of radionuclide behavior, we must understand radionuclide chemistry as it affects various retardation mechanisms. Figure 4 identifies two processes (formation-dissolution of minerals and precipitates and exchange and surface adsorption) which largely determine radionuclide concentrations in solutions available for groundwater transport. The figure also lists the types of data required to understand these processes: (1) Accurate thermodynamic data on solid phases and solution species that may be present or may form; (2) adsorption-desorption isotherms; (3) equations that quantify effects of different factors as they influence exchange, adsorption, precipitation and dissolution, and solution species; and (4) mineralogical and physicochemical properties of rocks and sediments. The figure emphasizes far-field interactions away from the near-field thermal and radiation zone neighboring the waste container.

Although WRIT performs studies to determine solubility products and solution complex stability constants (see Rai, Serne, and Moore, 1980; Rai, Serne, and Swanson, 1980; Wood and Rai, 1981), these important studies are

not discussed to focus the discussion on adsorption-desorption. The reader should consider that solubility and solution complexation processes act in conjunction with adsorption to control the overall nuclide behavior.

The following five sections of this paper discuss details on specific mechanism studies that are under way. The first section, Scouting Studies, describes WRIT's first efforts, which were similar to a parametric study, to identify the most important groundwater and rock characteristics that control adsorption. When these characteristics were identified, specific mechanism studies were developed. The second section briefly describes efforts to identify the applicability of ideal ion-exchange theory to nuclide adsorption on rocks and minerals. The theory of ion exchange is well developed for industrial purposes and, if applicable to radionuclide adsorption onto rocks, would provide a well-understood prediction capability. The third section discusses the status of work to assess the applicability of a more generalized adsorption theory, the site-binding electrical double-layer model. This model considers ion exchange and surface adsorption as the formation of a complex between the solid substrate and a solution species. The fourth section presents findings on redox-mediated nuclide retardation. The scouting studies identified redox potential as a key parameter affecting the retardation of radionuclides, especially multivalent elements. For redox-mediated reactions the actual mechanism of nuclide retardation appears to be a precipitation process. Results reinforce the fact that surface adsorption and precipitation processes work in concert to restrict nuclide migration. The final section discusses detailed rock and sediment studies to identify actual sites within the solid substrate where nuclides are bound. In the past, most studies concentrated on detailed solu-

Figure 4 Conceptualization of important nuclide retardation processes, data needed, and interactions with system components for the far field.

tion characterization. To better identify adsorption mechanisms, WRIT has instituted detailed characterization of both the solid and solution. Recent advancements in surface science instrumentation should greatly improve the scientists' ability to study solids and to identify adsorption sites.

Scouting Studies. Many of the empirical sorption studies were performed with a dual purpose: (1) To generate generic Rd values to support safety assessment, waste package

design, and site selection activities, and (2) to select the important parameters (temperature, pH, Eh, groundwater composition, etc.) for subsequent mechanism studies. The Rd sensitivity to such parameters gives indications of which processes might be controlling nuclide retardation. For instance, when Rd is sensitive to groundwater macro-cation concentrations (Na^+ , Ca^{2+} , Mg^{2+} , and K^+), the retardation mechanism is likely to be a cation exchange process if other variables are held constant.

When R_d is sensitive to changes in Eh and the solution chemistry of the nuclide is known to exhibit multivalent species, the change in predominant solution species (Eh mediated) is probably the process causing different R_d values.

Variables that have been systematically studied include temperature, particle size of rock or sediment used, pH, atmospheric gas composition (an attempt at Eh control), groundwater ionic strength, nuclide concentration or exchange site loading, equilibration time, and reversibility between adsorption and desorption. (See Serne, 1978b, 1979; Relyea, 1980, 1981, for details).

Studies of temperature effects have shown that sorption of most radionuclides is not significantly affected by temperature variations within the range from 20 to 80°C. Thus, for expected far-field environments, the effects of temperature variations on radionuclide sorption need not be a concern, and laboratory or field studies performed near room temperature should be applicable.

The particle size of disaggregated rocks used in laboratory experiments has been varied from about 50 μm up to cubic-centimeter-sized tablets. In general, R_d values reported on a weight basis show that R_d increases as the particle size decreases or as available surface area increases. Measurements of surface area by either the BET (Branauer, Emmet, Teller, 1938) or the ethylene glycol method (Bower and Goertzen, 1959; Rai and Franklin, 1978) do not correlate consistently with observed R_d values. The increase in R_d with decrease in particle size (over the range studied) is seldom as large as two orders of magnitude and often a factor of 3 to 10 or less. Thus, in comparison with other variables, the particle size is of moderate importance. An important and as yet unresolved

problem is that of obtaining scaling factors to convert laboratory sorption data on freshly disaggregated material to equivalent sorption values on in situ fractured rock with low matrix porosity. The use of measured surface areas for disaggregated material has yielded inconclusive results.

Groundwaters are typically well buffered by the geologic setting through which they flow. Thus large pH changes are not expected for far-field studies. The few studies performed by WRIT show that actinide, rare earth, and transition metal adsorption is sensitive to pH changes. The most dramatic changes (e.g., see Fig. 5) occur between pH 4 and 6, which is below the range of pH values expected for deep groundwater. The WRIT studies typically show increased nuclide adsorption as the pH increases. For pH 6 to 10, the pH effects on apparent americium sorption (shown in Fig. 5) appear to be explained by a solubility constraint (Rai et al., 1981). The WRIT staff concluded that, over the pH range of interest (6 to 10), surface adsorption reactions on layer-type clays are not significantly affected but that overall nuclide solution concentrations can be very dependent on hydrolysis reactions that limit solubility and change nuclide speciation. Further, adsorption by hydrous oxides that exhibit variable capacity and surface charge with pH is significantly affected by changes in pH (Shiao, Egozy, and Meyer, 1981). Thus the overall nuclide retardation potential (adsorption plus precipitation) can be significantly affected by changes in pH.

Several WRIT studies have shown that the oxidation-reduction potential present in the rock-groundwater system can significantly affect the observed nuclide retardation properties for multivalent elements such as technetium and neptunium (Bondietti

Figure 5 Effect of groundwater pH on the adsorption of americium on various rock-forming minerals. (Data from Allard and Beall, 1979.)

and Francis, 1979; Daniels et al., 1981). The increased technetium and neptunium apparent sorption at lower-than-atmospheric oxygen fugacities (assumed to be equivalent to reducing conditions) appears to be explained by the large solubility decrease predicted thermodynamically for these elements when conditions change from oxidizing to reducing. The experiments to date, which used controlled atmosphere chambers, are too limited by atmospheric leaks to readily reach the low oxygen levels projected for some deep geologic environments, e.g., basalt (Smith et al., 1980). Therefore development of acceptable methods for creating and controlling reducing (low Eh) conditions in the laboratory to allow nuclide solubility and studies of adsorption and solution complexation

should be high priority endeavors within the NWTS program.

The effect on nuclide adsorption of ionic strength changes in groundwater has been studied with emphasis on variations in sodium and calcium (Meyer et al., 1978; Meyer, 1979, 1980; Silva et al., 1980, 1981; Relyea et al., 1978). In general, nuclide adsorption for alkali and alkaline earth elements shows consistent decreases in Rd values as the concentrations of Na^+ or Ca^{2+} in groundwater increase. Theoretical predictions based on ideal ion-exchange relationships model the data adequately. For lanthanide elements (e.g., Eu) and for the actinides, the Rd values at neutral pH are much less sensitive to ionic strength. Uranium and neptunium actually show increased adsorption in brines. It appears that, except for strontium,

cesium, radium, and a few other long-lived nuclides, ideal ion-exchange processes are of limited utility in explaining nuclide retardation.

On the other hand, work by Shiao, Egozy, and Meyer (1981) and Shiao and Meyer (1981) on adsorption of trace Cs, Sr, Eu, Co, and Cd onto aluminum oxide (Al_2O_3) vs. salt concentration appears to be explainable from general ion-exchange theory, in which constancy in exchange capacity and activity coefficient ratios is not required. For pH values between 5 and 9, adsorption of Cs, Sr, Eu, Co, and Cd onto alumina increases strongly with pH, and varying the ionic strength of the solution generally has little observable effect. At pH values above 9, strontium and cesium appear to be salt dependent (adsorption decreases with increasing ionic strength but at a rate less than that predicted by ideal exchange theory). Europium sorption was so large at high pH values that experimental scatter in remaining solution concentrations precluded determination of solution ionic strength effects. For cobalt and cadmium, no ionic strength effects on sorption at high pH values were observed if complexation effects (cadmium chloride solution species) were considered.

As previously mentioned, the traditional derivation and use of R_d assumes that the nuclide adsorption isotherm is linear, i.e., that R_d is constant with changes in nuclide concentration. The WRIT studies found that adsorption of most nuclides, including cesium, exhibit nonlinear sorption isotherms for rock material even at extremely low nuclide concentration ranges ($10^{-9}M$ and lower). For clay minerals and weathered rocks with high clay contents, more nuclides approach linear isotherms, but the majority continue to exhibit nonlinearity (Barney, 1981). In most cases the R_d value increases as the nuclide concentration decreases, and the

empirical Freundlich isotherm equation is useful for describing results:

$$S = aC^N \quad (1)$$

where S is the mass of nuclides adsorbed on the solid per gram, C is the mass of nuclides in solution per liter, and a and N are empirical constants. When N is 1, the isotherm is linear, and, if equilibrium conditions prevail, a is equivalent to K_d . Two examples of the dependence of R_d on nuclide concentration are shown in Figs. 1 and 2, taken from Seitz et al. (1980). Thus we must develop the adsorption isotherm over the plausible range of total elemental concentration for nuclide and stable natural isotopes to collect necessary empirical adsorption data for radionuclides.

The time of contact between rock and solution has been varied from a period of hours to about 8 months. In general, surface adsorption of radionuclides that appear to be controlled by ion exchange (Sr, Cs, Ba, and Rb) occurs rapidly (in hours to at most a few days). Meyer et al. (1978) found that on clay materials these elements reached steady-state solution concentrations within 10 hr, but americium took 21 d. This suggests that the controlling mechanism for americium adsorption differs from that for such elements as strontium and cesium. Investigators at Los Alamos (Erdal et al., 1979; Daniels et al., 1981) performed batch R_d experiments on granite, argillite (shale), and tuff and measured R_d values at 1, 2, 3, 4, and 8 weeks. In general, R_d values for most elements increased with time. Europium and cerium, which are hydrolyzable, often showed an R_d increase over 8 weeks of up to one order of magnitude. Data for americium, uranium, and plutonium showed no sorption trends vs. time.

Sorption of actinides onto rock tablets was followed for 32 d (Silva,

Benson, and Apps, 1979). For the elements plutonium, americium, and curium, adsorption was essentially complete after 10 to 15 d, with only a few percent of activity left in solution. The decrease in solution activity was quite rapid, with less than 10% of the initial activity left in solution after 5 d. Uranium and neptunium sorption was much smaller and, except for neptunium sorption on shale and uranium sorption on basalt, did not show any trends vs. time. For the two exceptions, adsorption increased slowly over the observation period.

Long-term (> 200-d) experiments on nuclide adsorption are under way at Rockwell Hanford Operations (Barney and Anderson, 1979; Barney, 1981). After 110 d, the sorption of cesium was still increasing on granite and had possibly leveled off on basalt and argillite. Strontium adsorption onto granite was increasing and onto basalt and shale appeared to be decreasing. Neptunium sorption onto basalt was increasing and onto granite and shale was perhaps increasing very slowly. Americium sorption on granite and shale became constant after 30 d but appeared to be decreasing on basalt. Plutonium adsorption appeared to be increasing for granite and shale and decreasing for basalt. The major cations and anions and selected trace metals were also monitored over these times. Apparently slow groundwater-rock reactions were occurring. The systems continued to be dynamic, and thus the variation in sorption is not surprising. The apparent decrease in sorption with time for some of the nuclides contacting basalt was found to be caused by formation of colloidal particles, which remained suspended in solution (Barney and Anderson, 1979; Ames and McGarrah, 1980). The unstable glassy matrix of the basalt appears to generate fine siliceous particles into solution. These particles are not easily removed by centrifugation

but are retained on submicron filters. Altered basalt and basalt secondary minerals show fewer long-term changes in nuclide concentrations with time; this suggests that, once the rock material has weathered and approaches equilibrium with the groundwater, surface adsorption reactions will approach steady state in a matter of days.

Desorption studies have been performed to evaluate the reversibility of nuclide adsorption. Ion-exchange and other selected surface adsorption processes are expected to be reversible. All existing computer codes that rely on the distribution-coefficient approach assume reversibility. This assumption, coupled with mass transport analyses, makes the sorption process a delay function only. That is, after the waste form is totally dissolved, the mass of radionuclides that have not decayed radioactively will eventually reach the biosphere if groundwater continues to flow through the contaminated rock. Assuming reversible sorption and relying on the delay function only is conservative because some sorption and precipitation reactions may be considered irreversible. In general, WRIT has found that R_d values calculated from desorption of contaminated rocks and sediments are significantly larger than or equal to R_d values calculated from adsorption studies, even when the period of desorption is greater than the adsorption time. The increase in R_d desorption over R_d adsorption often reaches an order of magnitude for elements such as Am, Pu, Ce, and Eu and a factor of two for elements such as Cs, Ba, and Sr.

We can speculate that the differences in R_d values are caused by some of the following processes: (1) Collapse of interlayers of 2:1 lattice clays, such as illite, when such nuclides as cesium diffuse into the clay (Frink, 1971); (2) precipitation of insoluble minerals

or coprecipitation and entrapment in amorphous coatings; (3) reduction to more insoluble species or solid complexes by crystal lattice elements, such as Fe^{2+} (Rai, Serne, and Moore, 1980b); (4) nonlinear isotherms where R_d increases as total mass of nuclide in a system is reduced; (5) diffusion of nuclides deep into the rock matrix (Neretnieks, 1980); and (6) presence of multiple sorption sites a few of which have extremely high affinity for the particular nuclide (often referred to in the literature as specific adsorption).

The parametric studies described in this section have identified several variables to which nuclide distribution coefficients are quite sensitive and have suggested areas for further detailed mechanism activities. As mentioned, the empirical approach based on nuclide distribution coefficients does not provide a physical understanding of controlling processes. Furthermore, R_d values themselves are very specific to the rock-groundwater-nuclide conditions present during the determination. More general relationships that describe the sensitivity of sorption to important rock-groundwater-nuclide parameters, especially those based on established laws of physics and chemistry, are being sought. The WRIT approach has been to assess the applicability of theoretical constructs and models for describing laboratory results. On the basis of the parametric studies and the desire to incorporate models, WRIT has focused its sorption mechanism efforts on (1) delineating the utility of classical ion-exchange and site-binding layer mathematical constructs and theories, (2) redox-mediated adsorption processes, and (3) mineralogical sorption site identification by autoradiography.

The constructs and models presently considered include thermodynamic (equilibrium) geochemical models of solution species and crystalline and amorphous compounds, which

describe complexation in solution and dissolution-precipitation of solid phases, and ion-exchange and site-binding electrical double-layer models for adsorption. A detailed discussion of the thermodynamic equilibrium models and their use by WRIT is beyond the scope of this paper.

Deutsch (1980), Jenne (1981), Wolery (1980, 1981), and Deutsch, Jenne, and Krupka (1981) discuss the topic in some depth, however.

Ideal Ion-Exchange Studies.

The use of ideal ion-exchange constructs has been explored by Meyer et al. (1978, 1981), and Meyer (1979, 1980). Results of laboratory studies of nuclide adsorption onto solid adsorbents from one-metal-component salt solutions were compared with mathematical descriptions based on the following ideal ion-exchange equation:

where a = valence of the radionuclide ion

b = valence of the macro ion

M_1 = macro component in the salt solution

M_2 = trace radionuclide

$-X$ = solid adsorbent

A mass action equilibrium expression yielding a thermodynamic equilibrium constant (K) is

$$K = \frac{[M_1 - X]^a [M_2]^b}{[M_1]^a [M_2 - X]^b} \quad (3)$$

where the brackets, $[\]$, indicate thermodynamic activities of the species (valence states on the metals M_1 and M_2 have been deleted for clarity). The activities can be further broken down into concentrations and activity coefficients.

If we assume that the exchange capacity (C) of the solid adsorbent is constant (equivalents per unit weight) and that M_2 is present in the system at trace concentrations, then $[M_2 - X]$ is much less than C ; thus the distribution of macro ions on the exchange sites is approximated by

$$[M_1 - X] \approx \frac{C}{b} \quad (4)$$

Furthermore, $(M_2 - X)/M_2$ defines the equilibrium distribution coefficient (D) for the radionuclide. If we substitute Eq. 4 and the definition of D into Eq. 3 and assume that the ratio of activity coefficients (Γ) is constant (a condition likely in a system where a trace constituent is being adsorbed onto a solid medium with constant exchange capacity), D becomes a function of only the solution concentration of the macro ion solution (M_1). Taking the logarithm of the resultant equation yields

$$\begin{aligned} \log D &= \frac{a}{b} \log \frac{(C/b)}{M_1} \\ &+ \frac{1}{b} \log \frac{\Gamma}{K} = \frac{a}{b} \log \frac{C}{b} \\ &- \frac{a}{b} \log M_1 + \frac{1}{b} \log \frac{\Gamma}{K} \end{aligned}$$

which can be differentiated with respect to M_1 to yield Eq. 5 (C , Γ , and K are constant; thus the other terms drop out):

$$\frac{d \log D}{d \log M_1} \approx -\frac{a}{b} \quad (5)$$

Thus, if the trace element constituent is cesium and the macro element is sodium, plotting the logarithm of the cesium distribution coefficient vs. that of the sodium solution concentration yields -1 . For strontium exchange with sodium, the slope would be -2 , and, for americium exchange, the

slope would be -3 . If ideal ion-exchange laws describe the adsorption of a radionuclide, we can measure D or laboratory R_d (assuming equilibrium was attained) for a nuclide and predict the distribution coefficient at other concentrations of the electrolyte. These relationships would be quite useful for such groundwaters as NaCl brines of various strengths, which might be found around bedded salt and domed salt sites. Mathematical equations in which the trace loadings, $[M_2 - X]$, are not readily approximated by zero and equations for mixtures of solid adsorbates are also available (Triolo and Lietzke, 1980; Meyer et al., 1981).

Comparisons of theory and experiment have progressed from the study of strontium and cesium exchange on purified clays as a function of Na^+ and Ca^{2+} electrolyte concentrations to the exchange of Eu(III) , U(VI) , Cs(I) , Sr(II) , and Tc(VII) onto clay mixtures, oxide surfaces, and oxide mixtures. Results show good predictive abilities for only a few elements (e.g., strontium and cesium) onto pure clays and clay mixtures. The adsorption of other ions (e.g., actinides) onto clays or oxides, and even strontium and cesium adsorption onto oxides (aluminum and silicon), is not readily modeled by these ideal equations. Reasons why use of ideal ion-exchange constructs is not successful include the nonconstancy of the exchange capacity and activity coefficients of the adsorbents; release of other competing ions, such as Al^{3+} (under acidic conditions), from solution interactions with the solid; and probable changes in radionuclide speciation distribution via hydrolysis and complexation (e.g., europium, plutonium, etc.) as pH and groundwater ionic strengths are changed. All these complications require separate exchange equations for each nuclide species and for each type of exchange site on the solid. As

previously mentioned, Shiao, Egozy, and Meyer (1981) and Shiao and Meyer (1981) have had some success using the general ion-exchange equation (Eq. 3) without the subsequent simplifying assumptions to model sorption on aluminum oxide.

Site-Binding Electrical Double-Layer Model Studies.

A site-binding electrical double-layer model is another general sorption model that, when coupled with solution thermodynamic equilibrium models, allows a complete description of nuclide chemical interactions. (See Silva et al., 1980, and Davis, James, and Leckie, 1978, for a detailed description of the model.) Briefly, the model assumes that most solid materials acquire a surface charge when placed in contact with a polar solvent, such as water. The net charge may be positive, negative, or neutral (point of zero charge) depending on the nature of the solid and the composition of the solution, particularly the pH. The most common way for a surface to obtain a net electrical charge is through uptake or release of potential-determining ions on the surface (e.g., H^+ or OH^-). Charged surfaces tend to adsorb ions of opposite charge to maintain electrical neutrality and, thus, develop an electrical double layer. Permanent charges are also present on solid surfaces because of isomorphous substitution in the crystal structure (e.g., when Al^{3+} substitutes for Si^{4+} or Mg^{2+} for Al^{3+}). These permanent charges are treated as ionizable sites in the site binding model. If a surface is assumed to have only one kind of ionizable site, two reactions determine the surface charge:

where S refers to the surface to which the oxygen is bonded, the subscript s refers to an ion at the surface (but not adsorbed) and differs from the ion in bulk solution by the amount of energy needed to move the charged ion across the difference in electrical potential between the surface and bulk solution, and K_{a1} and K_{a2} are the surface ionization constants for these two dissociation reactions.

Normally, when a supporting electrolyte is present, ions other than H^+ balance the surface charge. If the solution contains only NaCl, the reactions describing the cation-anion charge balance are

The electrical work needed to bring an ion from bulk solution to the charged surface results in a difference in activity for that ion at the two different positions. The model makes this correction so that the reaction constants can be related to quantities measured in solution. In normal groundwater numerous other cations and anions are found. These may be treated by writing equations similar to Eqs. 8 and 9.

Exchange reactions, such as Na^+ for H^+ , can then be written as

The constant $K_{Na/H}$ is frequently referred to as the selectivity coefficient. If more than one kind of exchange site exists on the surface,

another set of equations similar to Eqs. 6 through 10 can be added to the model.

The resulting set of equations can then be solved algebraically to predict both solution and surface concentrations for a particular element. If a distribution coefficient is needed, it can be calculated in a straightforward manner from the predicted surface and solution concentrations.

Estimates of the surface ionization constants (K_{a1} and K_{a2}) are made from acid and/or base titrations of the adsorbing solids over a suitable range of electrolyte concentrations. Naturally, care must be taken that the pH range during titration does not extend outside the range in which the solid phase is stable. The selectivity coefficients that describe the exchange of one cation (or anion) for another (e.g., Cs^+ exchange with Na^+) must also be determined experimentally or calculated from existing data for the system of solids and solutions being studied.

Perhaps the most important aspect of this sorption model is that it is compatible with thermodynamic-based geochemical models. The surface ionization and exchange equations (Eqs. 6 through 10) are written in the form of chemical reactions with their respective equilibrium constants, as are the solubility and complexation reactions present in thermodynamic models. At Lawrence Berkeley National Laboratory, this adsorption submodel has been included in MINEQL [a computerized thermodynamic code developed by Westfall, Zachary, and Morel (1976)] so that precipitation, dissolution, complex-ion formation, oxidation-reduction, and adsorption reactions can be considered simultaneously in a single geochemical model. If the initial surface and solution ion concentrations are known, a radionuclide can be added to the system and

its distribution between the solid and solution phases can be predicted.

Figure 6 compares Cs^+ Rd values determined experimentally (data points) with those predicted (lines) by MINEQL for Belle Fourche clay (a montmorillonite) over a wide range of pH and NaCl solution concentrations. The activity correction for the difference between bulk solution and surface potentials was used to calculate the dashed lines, and the solid line was calculated without the correction. The predicted Rd values for Cs^+ exchange with Na^+ show a good correlation with the experimental data. It can be seen that including the activity correction term (dashed line) did little to improve the fit.

Figure 7 shows the adsorption of Cs^+ on SiO_2 powder in two sodium

Figure 6 Rd(Cs) values for adsorption on montmorillonite vs. pH at several brine concentrations. ●, 0.002M NaCl; △, 0.01M NaCl; ▲, 0.1M NaCl; ■, 1M NaCl. Symbols are experimental data points; solid lines are computer model predictions; and dashed lines are activity corrections for the model predictions.

Figure 7 $R_d(\text{Cs})$ values for adsorption on colloidal silica vs. pH at designated brine concentration and initial solution Cs concentration of 10^{-9}M . Symbols are experimental data points; vertical bars are experimental uncertainties ($\pm 1\sigma$); solid lines are computer model predictions; and dashed lines are computer model predictions that consider electrical double-layer activity corrections.

chloride solutions. Again, the activity correction (dashed lines) did little to improve the fit of experimental and predicted results. Below pH 7 the observed and predicted data for cesium sorption on SiO_2 deviate, but fair agreement is found in the

environmentally important range, pH 7 to 10.

Further work is in progress (Silva, White, and Yee, 1981) to model the adsorption of U(VI) solution species onto SiO_2 and montmorillonite. The described cesium predictions compare adequately with experimental results. In addition to other studies of transition element adsorption onto oxide surfaces (Davis and Leckie, 1978; James and Healy, 1972, 1975; and Schindler et al., 1976), WRIT has decided to focus adsorption modeling efforts on the site-binding electrolyte double-layer model.

Oxidation-Reduction-Mediated Nuclide Retardation Studies.

The oxidation-reduction potential has been identified as a key variable in controlling radionuclide retardation (Ames and Rai, 1978; Rai and Serne, 1978) for several long-lived isotopes, e.g., ^{239}Pu , ^{238}U , ^{237}Np , ^{79}Se , and ^{99}Tc . Most studies of nuclide adsorption performed before 1978 did not measure or consider the oxidation-reduction potential during characterization or reporting of results. Thus empirical data for background information were virtually nonexistent, but thermodynamic constructs were available. The range of oxidation-reduction potentials expected in deep geologic environments is open to wide speculation since very few measurements of Eh are available. Baas-Becking, Kaplan, and Moore (1960) presented ranges for near-surface groundwaters and aquatic environments which can be used as a guide. The perceived importance and dearth of knowledge led the WRIT staff to embark on studies of oxidation-reduction processes and their effects on nuclide adsorption. In studies performed at Oak Ridge National Laboratory (Francis et al., 1979; Francis and Bondietti, 1980; Bondietti and Francis, 1979; Bondietti,

Lee, and Hall, 1981), experiments were conducted to see if redox measurements of igneous rock suspensions and nuclide solution valence states in anoxic stirred cells agreed with thermodynamic aqueous stability diagram predictions. Thermodynamic predictions show that the species TcO_4^- and NpO_2^+ would not be the stable forms of these elements under the reducing conditions probable in deep repositories. When TcO_4^- and NpO_2^+ in solution were added to anoxic rock suspensions, their solution concentration did decrease and they were perhaps reduced in part to less soluble species. The rocks used included Sentinel Gap basalt, Westerly granite, Climax Stock granite, Conasauga shale, and a green argillaceous shale. In the presence of an N_2 atmosphere, the granites and basalt readily removed TcO_4^- from solution by a reduction process as evidenced by the inability to remove adsorbed technetium by ion exchange but the ability to remove it by adding oxidants. Neither shale exhibited this reduction-sorption capability, but some (10%) of the TcO_4^- was removed by weathered Conasauga shale; this suggests anion sorption by positively charged sesquioxides. Thermodynamic predictions suggested that NpO_2^+ would be even more unstable than TcO_4^- in solution as the redox potential is decreased. Rock sorption studies of Np(V) showed that all these rocks except the argillaceous shale rapidly removed more than 90% of the Np(V) in solution. Column verification of the TcO_4^- rapid reduction by basalt was attempted, but only at a residence time of 5 d was there any indication of reduction. Thus loss of TcO_4^- was much slower in columns than in the stirred anoxic cell.

Later technetium studies, which included variation of Eh, pH, solution Fe^{2+} and S^{2-} concentrations and time, led to the following conclusions. The

loss of TcO_4^- anion from solutions in contact with rocks under reduced oxygen fugacities is not caused by sorption of the anion onto the rock but rather by the reduction of TcO_4^- to a lower valence state and precipitation, most likely as Tc(OH)_4 . Adding Fe^{2+} and S^{2-} to solutions containing TcO_4^- also reduced the solution concentrations of technetium; Fe^{2+} was more effective than S^{2-} when added singly, but the largest decreases in TcO_4^- concentration occur when both are added. Experiments suggest that precipitates of amorphous iron hydroxides, technetium sulfides, and iron-technetium sulfides are formed. Adding Fe^{2+} and S^{2-} to rock suspensions in contact with TcO_4^- solutions enhances the removal of technetium. The reactions continue, with technetium removal increasing slowly over the 10-d observation period. In nature it appears plausible that the $\text{Fe(II)}\text{-Fe(III)}$ solution system may mediate reduction of technetium and removal from solution. The investigators showed a few data and speculated that plutonium and uranium may also be reduced and removed from solution. The "adsorbed" technetium was found to be slowly released back into solution as oxygen or oxidizing agents were allowed to enter the system. Thus the kinetics of the redox process should be considered further before quantitative retardation estimates are made.

Rai, Serne, and Moore (1980b) studied the adsorption of plutonium from aerated $5 \times 10^{-3} M$ CaCl_2 solutions containing $7.3 \times 10^{-9} M$ $^{239}\text{Pu(VI)}$. The adsorption of plutonium from this solution by several minerals and a basalt (see Table 8) was determined for pH values from 4 to 9.5. At pH ~ 4 and a solution-to-rock ratio of 34:1, adsorption depended on mineral type and increased from approximately 10 to nearly 100% in the following order: gibbsite < kaolinite <

Table 8 Exchangeable Plutonium and Selected Properties of Minerals and Rocks

Sample*	CEC, meq/100 g	Surface area, m ² /g	Iron content, weight %			Desorbed or exchangeable plutonium‡
			Fe(II)	Fe(III)†	Fe (total)	
Kaolinite	5.0 ± 0.9	37 ± 3	0.03 ± 0.02	0.28	0.31 ± 0.10	17.2
Montmorillonite	87.4 ± 2.7	767 ± 30	0.02 ± 0.0	2.40	2.42 ± 0.35	32.2
Nontronite	95.0 ± 3.0	888 ± 45	0.05 ± 0.05	23.48	23.53 ± 0.91	1.4
Vermiculite	77.0 ± 4.8	317 ± 8	1.29 ± 0.12	5.22	6.51 ± 0.11	9.0
Biotite	15.3 ± 1.1	71 ± 3	11.44 ± 0.22	2.46	13.90 ± 0.28	4.8
Hematite	§	§	1.19 ± 0.08	61.21	62.4	1
Gibbsite	§	§	<0.01	0.69	0.7 ± 0.16	§
Vesicular basalt	4.0 ± 1.4	72 ± 4	1.24 ± 0.01	4.08	5.32 ± 0.23	28.1

*The particle sizes used were <2 μ m for kaolinite, montmorillonite, nontronite, vermiculite, and biotite and <105 μ m for hematite, gibbsite, and basalt. X-ray diffraction patterns showed the montmorillonite, nontronite, and biotite to be free of detectable amounts of crystalline impurities. The kaolinite sample contained a small amount of mica. The vermiculite sample was found to contain a small amount of interstratified vermiculite-mica. Hematite and gibbsite were found to contain small amounts of quartz.

†Fe(III) was calculated by subtracting Fe(II) from Fe(total)

‡At the end of sorption (the pH 4 period noted in Fig. 8), the exchangeable plutonium at pH 4 was determined with 1M NaCl (except in vesicular basalt, where 0.005M CaCl₂ was used). The results are presented as a percentage of the total plutonium originally adsorbed.

§Not determined.

vesicular basalt < montmorillonite < nontronite < hematite < vermiculite < biotite. At pH values from 6.4 to 9.5, the minerals did not differ significantly from each other in their adsorption properties, and adsorption of plutonium exceeded 93% for the four minerals studied—kaolinite, gibbsite, montmorillonite, and vermiculite.

At pH values of approximately 4, the exchangeable plutonium in all the minerals studied ranged from 1 to 32% of the total adsorbed. The adsorbed plutonium did not correlate with either the cation exchange capacity or the surface area of the samples. Therefore ion exchange did not appear to be the dominant mechanism for the adsorption of plutonium. The montmorillonite, nontronite, and vermiculite had nearly the same cation exchange capacity but differed significantly in plutonium adsorption affinity (Fig. 8) and exchangeable plutonium. The biotite, which had a much lower cation exchange capacity than montmorillonite,

nontronite, or vermiculite, was similar in its percentage of plutonium adsorption and exchangeable plutonium to vermiculite. In general the 2:1 type clays (montmorillonite, nontronite, vermiculite, and biotite) showed higher adsorption than the 1:1 type clay (kaolinite), but no such pattern was obvious in the amount of exchangeable plutonium.

The oxidation state of plutonium in solutions in equilibrium with different minerals was also studied. The results showed that essentially all solution plutonium was in an oxidized state [Pu(V) and/or Pu(VI)], but the presence of oxidized plutonium is no guarantee that the adsorbed plutonium is also oxidized.

Ozone-treated vermiculite and biotite at pH ~4 showed considerably less adsorption of plutonium (< 50%) when the adsorption experiment was carried out in the presence of ozone (Fig. 9). Ozone had little effect on the adsorption of plutonium by kaolinite.

Figure 8 Adsorption of $^{239}\text{Pu(VI)}$ by aerated mineral suspensions (34 ml/g) at pH 4. Averages of duplicate samples are plotted. $\circ$, <7%; $\square$, 7 to 15%; $\triangle$, 15 to 30% difference between the duplicates.

Figure 9 Adsorption of Pu(VI) in the presence of ozone at approximately pH 4 and 34:1 solution-to-solid ratio by mineral samples also pretreated with ozone. Averages of duplicate samples are plotted. $\circ$, <4%, and $\square$, 9 to 15% difference between the duplicates.

These results suggest that a large amount of plutonium adsorption by vermiculite and biotite is caused by reduction of plutonyl ions, whereas the adsorption of plutonium by kaolinite is not predominantly caused by the reduction of plutonyl.

Vermiculite and biotite are known to contain Fe(II), which, when in solution, is a rapid reductant for plutonyl ions (Cleveland, 1979). All the minerals were analyzed for Fe(II) and Fe(III) to determine whether the amount of Fe(II) in the minerals could explain their reducing nature and the differences in their adsorption behavior (Fig. 8). The results show that the concentration of Fe(II) in the minerals varied from less than 0.01 to 11.4 wt. % (Table 8). All the minerals that had high concentrations of Fe(II) (vermiculite, biotite, and hematite) also showed very high adsorption of the plutonium originally present in solution as Pu(VI). Vesicular basalt, however, although it contained a high concentration of Fe(II), did not show high adsorption. The reasons for its anomalous behavior are not known. Kaolinite and gibbsite had relatively low concentrations of Fe(II) and also showed low adsorption. Montmorillonite and nontronite are similar in structure and chemical properties except that the octahedral layer in montmorillonite consists predominantly of aluminum and the octahedral layer in nontronite consists mainly of iron. No significant amounts of Fe(II) were found in montmorillonite, nontronite, and kaolinite. Therefore the differences in plutonium adsorption and desorption by these minerals may be specifically related to their structure and chemical composition. The results indicate that Pu(VI) may be reduced at the mineral surface interface by crystalline lattice iron so that an enhanced adsorption or precipitation reaction occurs even though the bulk solution exhibits high oxygen

fugacities. Detailed mechanistic studies of redox-mediated nuclide retardation will continue to receive high priority within WRIT.

Studies of Specific Adsorption Sites.

Laboratory sorption studies, such as empirical R_d measurements, delineate data on the gross sorption affinity of rocks, minerals, and sediments. Much more detailed studies of the solid phase are needed to identify the actual sorption sites active in polymineralic rocks. Studies identifying the specific minerals or amorphous phases that are the active adsorbents on the rock surfaces would aid greatly in acquiring a basic understanding of sorption mechanisms. Autoradiography, coupled with optical and electron microscopy studies, is being performed by WRIT on thin sections of rock to identify specific sorption sites.

Hinkebein and Hlava (1978, 1979) contacted flat rock chips with solutions containing high concentrations ($\geq 0.0006M$) of either Cs, Sr, Gd, or U. They then rinsed the rock surfaces and measured adsorbed Cs, Sr, Gd, or U by electron microprobe X-ray fluorescence. By matching the qualitative information given in the photomicrograph with known mineral analyses, they could identify many mineral phases and determine the location of the adsorbed test elements. Four rocks were studied—Eleana argillite, Bell Canyon sandstone, Magenta dolomite, and Salado Formation halite. The latter three are of interest to the WIPP site. Cesium was detectable only on Eleana argillite and was possibly associated with illite or vermiculite minerals. The strontium predominately precipitated as carbonates and sulfates on the dolomite, sandstone, and clay partings in the halite. The uranium was detectable in the dolomite and clay partings of the halite, probably as a carbonate precipitate. Gadolinium was detectable on all four rocks, partly because of

hydrolysis and precipitation and possibly because of adsorption onto chlorite.

This scouting study supported the concept that selected minerals within the bulk rock matrix could be the predominant sorption sites. The microprobe work, although qualitatively useful, suffered from a lack of adequate sensitivity for the adsorbed elements; thus unrealistically high solution concentrations were used. The high solution concentrations led to the adsorption process's being confounded by precipitation reactions; this might not have occurred at the trace solution concentrations expected under repository conditions.

Smyth, Thompson, and Wolfsberg (1980) and Thompson and Wolfsberg (1979) performed microautoradiographic studies on Eleana argillite, Climax Stock granite, Jackass Flat tuff, and tuffaceous alluvium, all obtained from the Nevada Test Site. Polished thin sections were spotted with several drops of radioactive groundwater (uranium or americium) in a 100% humidity chamber. After several hours to days of contact, the thin sections were rinsed with distilled water and prepared for autoradiography. The alpha tracks from uranium or americium were counted and photographed through a microscope. The concentration of adsorbed nuclide was indicated by the track density. Sites of particularly high sorption gave rise to "stars," with many tracks radiating from a single point.

For the granite, more than 90% of the adsorbed uranium was confined to a clay-rich alteration band in the plagioclase, even though this phase makes up only 1% of the bulk rock. The zonation bands in plagioclase in situ would not likely be readily accessible to groundwater; thus laboratory studies on crushed rock or thin sections that expose these bands may give unrealistic sorption values.

The uranium adsorbed onto argillite surfaces was associated with clay phases and not with detrital quartz. The uranium adsorbed onto the tuff sample was associated with the zeolite clinoptilolite, which comprised 65% of the sample. The primary minerals quartz, feldspar, and biotite adsorbed very little uranium. The alluvium sample also showed that the uranium was adsorbed onto zeolites in preference to quartz and feldspar sand.

The americium autoradiographs for all rocks did not correlate to specific minerals in the thin sections. It is believed that the track patterns originate from randomly precipitated americium. The original americium solution concentrations (6×10^{-7} to $6 \times 10^{-6}M$) do, in fact, exceed the solubility values that Rai et al. (1981) found in simulated groundwater in equilibrium with an unknown americium solid.

Two other non-WRIT-funded autoradiography studies (Beall et al., 1980; Vandergraaf, Abry, and Belanger, 1981) also corroborate the finding that alteration minerals (smectite clays, illite clays, and zeolites) adsorbed radionuclides greater than mafic minerals, such as pyroxenes, micas, and hornblende, and that quartz and feldspars exhibit the least adsorption. Such elements as americium and promethium exhibit random autoradiographs; this suggests that precipitation can greatly influence laboratory adsorption experiments for the very slightly soluble actinides and lanthanides.

These studies illustrate that it is possible for minor phases to dominate completely the mass of radionuclides adsorbed. That these minor phases may not be identified or quantified in even detailed rock characterization efforts may explain why two seemingly similar rock samples can yield very different *Rd* values. The identification of sorption sites and adsorbing

phases will increase our understanding of adsorption mechanisms.

Prioritization of Nuclides and Recommendations for Future Nuclide Retardation Work

Preliminary nuclide priorities were offered at the conclusion of the first WRIT workshop (Serne, 1978b). Although the prioritization process was not quantified or discussed in detail, such attributes as element solubility, adsorption affinity, radionuclide half-life, and results of past safety assessments were considered. The prioritization included three general categories—first, second, and lower. The prioritized elements are

First priority: Tc, Pu, Np, I, U, Cs, Ra, Sr, C

Second priority: Am, Sm, Ni, Se, Cm

Lower priority: Zr, Sm, Mo, Eu, Pd, Th, Pb, Pa, Nb

Since this prioritization, WRIT staff and BWIP staff (Barney and Wood, 1980) have performed several quantitative nuclide prioritizations; the study of Barney and Wood concerns itself with the Columbia Plateau basalt environs only. Both studies rely on quantitative estimates of waste-form nuclide inventories as a function of decay time, the biological toxicity of each radionuclide, and, finally, the propensity of the radionuclide to retardation. A combination of these factors was used by both studies to generate hazard indexes.

The index for hazard selected for this WRIT study is the Hazards Available (HA) Index, which is given by

$$HA = \log \left[\frac{(Q)(TF)}{MPC} \right] \quad (11)$$

where Q is the amount of radionuclide to be disposed (curies); MPC is the

maximum permissible concentration of that radionuclide in water ($\mu\text{Ci/ml}$), found in the Standard for Protection Against Radiation [Code of Federal Regulations (10 CFR Part 20, Appendix B, 1976)], and TF is a transport factor for the radionuclide. The transport factor selected here is the inverse of the retardation factor (Rf) since HA should be larger (all other things equal) for a radionuclide having a low retardation factor (high mobility) than for an element with a high Rf (or low mobility).

Inventories for the radionuclides (Q) were taken from the final environmental impact statement on management of commercially generated radionuclide waste (Department of Energy, 1980). Table A.2.3A of that document was used for spent fuel, and Table A.2.6b was used for high-level waste. If a radionuclide was not present at times greater than 1000 yr (as a result of a decay), it was not included in the analysis.

The logarithmic average retardation factors for the five geologic environments under consideration (domed salt, bedded salt, basalt, granite, and tuff) were calculated from Rd values shown in Tables 6 and 7. For the "redox sensitive" elements in Table 7, the lower values were chosen to maintain conservatism. The Rd value was converted to an Rf value ($Rf = 1 + 10 Rd$, where the constant 10 represents a gross average of the ratio of rock bulk density to porosity or fracture surface area to a fracture volume for porous or fractured rock, respectively). Hazards available indexes for each radionuclide were calculated for three times, for 10^3 , 10^4 , and 10^5 yr. Table 9 lists radionuclide rankings and the average HA. Both spent fuel and high-level waste forms are averaged for this table, as are the hazards available indexes for each of the three times. The exact ratings, which are a function of time, are available on request from the authors.

For example, at 1000 yr ^{241}Am has an average HA of 10.4, and at 10^5 yr it has a value of 3.9. The remarks column identifies isotopes whose hazards available indexes change significantly with time.

The priority listing in Table 9 is based on all five rock types and compares with Barney and Wood (1980) on basalt, except that the rating in Table 9 significantly increases the

hazard of ^{239}Pu , whereas the rating of Barney and Wood increases the hazards of ^{107}Pd and ^{230}Th . In the basalt environment under reducing conditions, plutonium is expected to be quite insoluble (Wood and Rai, 1981) and, thus, less hazardous. The estimated Rd values used by Barney and Wood for palladium and thorium (10 and 100 ml/g, respectively) seem too conservative to the WRIT staff. If

Table 9 WRIT Nuclide Priority List

Ranking	Isotope	Average HA*	Remarks
1	^{129}I	11.1	
2	^{99}Tc	10.0	
3	^{226}Ra	9.8	HA increases with time
4	^{237}Np	9.6	
5	^{239}Pu	9.6	
6	^{210}Pb	9.4	HA increases with time
7	^{79}Se	8.9	
8	^{126}Sn	8.9	
9	^{240}Pu	8.6	HA is greater at $t < 10^4$ yr
10	^{234}U	8.5	
11	^{107}Pd	8.1	
12	^{243}Am	7.9	HA is greater at $t < 10^4$ yr
13	^{242}Pu	7.9	
14	^{59}Ni	7.8	
15	^{238}U	7.6	
16	^{236}U	7.5	
17	^{233}U	7.3	HA increases with time
18	^{241}Am	7.1	HA decreases with time
19	^{235}U	6.6	
20	^{229}Th	6.6	HA increases with time
21	^{14}C	6.5	HA is greater at $t < 10^4$ yr
22	^{230}Th	6.3	
23	^{245}Cm	6.2	HA is greater at $t < 10^4$ yr
24	^{227}Ac	6.0	
25	^{135}Cs	5.9	
26	^{231}Pa	5.4	
27	^{93}Zr	5.0	
28	^{241}Pu	4.9	
29	^{238}Pu	2.7	HA is greater at $t < 10^4$ yr
30	^{63}Ni	2.3	HA is greater at $t < 10^3$ yr
31	^{242}Cm	2.1	
32	^{151}Sm	1.9	
33	^{90}Sr	1.5	
34	^{137}Cs	0.9	

*HA averaged over 5 rock types and three times, 10^3 , 10^4 and 10^5 years.

the estimates were increased, the priorities would drop and would agree better with Table 9.

The WRIT staff has also reviewed the safety assessment calculations presented in Swedish, English, and American waste isolation literature. A list of key nuclides that contribute to potential doses to man was constructed (see Chikalla and Powell, 1981), assuming that the scenarios chosen for study in the various rocks (granite, basalt, and salt) are reasonable. The most frequently identified isotopes contributing the majority of the calculated dose are ^{129}I , ^{99}Tc , ^{237}Np , ^{226}Ra , and ^{14}C . Neptunium daughter products ^{233}U , ^{229}Th , and ^{225}Ra and radium daughter products ^{234}U , ^{210}Pb , and ^{210}Po also appear frequently. For extremely short travel times to the biosphere, ^{90}Sr and ^{137}Cs will contribute significantly.

In view of the limited funds available and the large size of the areas requiring support, this nuclide prioritization exercise can be used to make objective recommendations as to which nuclides deserve detailed study. In each of the analyses discussed, the four most hazardous radionuclides are I, Tc, Np, and Ra; thus it appears that they should receive top priority in experimentation. WRIT has focused on technetium and neptunium and has used barium as an analog for radium. Adsorption studies of iodine have been performed, but natural rocks show little affinity for sorption of iodine. Outside of WRIT, certain minerals and insoluble iodide-generating salts are being investigated for addition to backfills and engineered barriers (Bird and Lopata, 1980; Strickert, Friedman, and Fried, 1980).

The WRIT staff formulated several other recommendations after reviewing the available knowledge of nuclides present in Table 9. Very little work has been performed on adsorp-

tion of selenium (see Ames and McGarrah, 1980; Coles, Weed, and Tewhey, 1980), tin, lead, palladium, and thorium. Some efforts should be started on these elements, but we recommend that efforts on I, Tc, Np, Ra, Pu, U, and Am continue until the basic retardation mechanisms are clearly identified. Continued work on strontium, cesium, and such lanthanides as europium and cerium, aside from studies needed to elucidate nuclide adsorption mechanisms, does not seem warranted.

Thermodynamic data suggest that solubility constraints similar to those discussed by Wood and Rai (1981) can be used to lower the concentrations of tin, palladium, and thorium to acceptable levels and, thus, diminish the need for comprehensive nuclide adsorption studies. If thermodynamic solubility constraints lower the hazards of tin, palladium, and thorium below those currently perceived, the two remaining priority elements that have not as yet received adequate study are selenium and lead.

Brief Discussion of Relationships Between Laboratory and Field Nuclide Migration Studies

The NWTS program has several ongoing field nuclide migration experiments. Two tests are being performed at the Nevada Test Site in fractured granite (Isherwood et al., 1980) and fractured tuff (Erdal et al., 1981). A third ongoing effort is an international cooperative program entitled Migration in a Single Fracture—Experiments in Stripa, which is being directed by Ivars Neretnieks of the Royal Institute of Technology, Stockholm, Sweden. In the first two tests the WRIT program maintained formal ties and participated in several program plan reviews and technical discussions in 1979 and 1980. The WRIT staff plans to keep

abreast of all three projects and to work cooperatively with the respective project managers to ascertain the degree to which laboratory nuclide migration predictions agree with actual field observations of nuclide transport. It is hoped that these collaborative assessments and future written findings can address and alleviate most of the concerns raised by review groups (Bredehoeft et al., 1978; Giletti et al., 1978) and other scientists (de Marsily et al., 1977) on the applicability of laboratory sorption studies to deep geologic disposal.

Although it is premature to close the debate on this issue and debate is outside the scope of this paper, several available works compare laboratory predictions and field observations of radionuclide migration. For example, Landstrom et al. (1978) discussed a joint laboratory-field program at Studsvik, Sweden, on nuclide migration in granite. Robertson (1977) discussed the migration of radionuclides below waste seepage ponds in Idaho. Several other field tracer experiments with reactive solutes have been performed in near-surface porous media (e.g., Pickens et al., 1981; Kaufman, 1960; Inoue and Kaufman, 1963; Parsons, 1963; Sterneau et al., 1967).

At the Nevada Test Site, a few of the underground bomb tests that detonated below the water table are being monitored. At one test site, the Cambrian event, a satellite well has been drilled about 100 m away. Since October 1975 this well has been pumped at rates between 1 and 2.3 m³/min. To date only ³H, ⁸⁵Kr, and a trace amount of ¹⁰⁶Ru have been detected in the water samples even though over one billion gallons of water have been removed. When the bomb cavity was re-entered 10 yr after the detonation, such isotopes as ³H, ⁸⁵Kr, ⁹⁰Sr, ¹⁰⁶Ru, ¹²⁵Sb, ¹³⁷Cs, ¹⁴⁴Ce, ¹⁴⁷Pm, ¹⁵⁵Eu, and ²³⁹Pu were readily detected in the water and fused rock. Except for the results for ¹⁰⁶Ru,

laboratory empirical distribution coefficients support the observed data and predict very long travel times to the well (80 to 10⁴ yr) for the radionuclides present. The discrepancy between nuclide migration predictions for ruthenium, which were based on batch distribution coefficients, and the field measurements may be caused by multiple species of ruthenium. As mentioned, the batch sorption test measures a gross average distribution ratio, and perhaps the ruthenium observed in the satellite well water represents a mobile species. We should note that observed ruthenium represents only 1% of the total present in the groundwater, melt glass, and fused rock found in the cavity upon re-entry. Details on field tests and laboratory studies of nuclide sorption, which have been performed at Nevada Test Site, can be found in Borg et al. (1976), Hoffman, Stone, and Dudley (1977), Hoffman (1979), Hoffman and Daniels (1980), and Coles and Ramspott (1982).

In general, most of these investigators were pleased with the agreement between radionuclide migration predictions based on laboratory experiments and observations in the field. Thus laboratory data can be expected to predict nuclide migration in the field. It should be acknowledged that most of the field studies mentioned were performed within simple and well-characterized hydrologic regimes and that the elements chosen for study are known for their simple and "well-behaved" chemistry (e.g., Sr, H, and I). These ideal circumstances need to be expanded upon, and more complicated field tests that use a wider range of radionuclides need to be performed. The three ongoing studies in fractured granite and tuff are designed to expand on past studies.

Field testing of nuclide migration expands on the time and spatial scales typically used in laboratory testing but still lacks several orders of magni-

tude in comparison to long-term safety assessment requirements. Thus NWTs is actively observing natural systems, often called natural analogs. Two such studies are the natural reactor Oklo (Bryant et al., 1976; Cowan, 1978) and the Morro do Ferro thorium deposit (Eisenbud et al., 1981).

At present it appears difficult to compare nuclide migration from either of these sites quantitatively with laboratory distribution coefficients. The complexity and numerous changes in the hydrologic and geochemical environments over the geologic time frame (10^9 yr) since the formation of the original ore deposits make the calculation of a retardation factor (Rf) or empirical distribution coefficient (Rd) very difficult. On the other hand, qualitative and semiquantitative evaluations of element migration are possible. These field evaluations can then be compared with theoretical constructs, such as thermodynamics. Diagrams of Eh and pH for important radionuclides, based on dissolution-precipitation and solution complexation reactions, have been constructed for the probable environment right after the fissioning process ended at Oklo. It was possible to make qualitative predictions of expected nuclide mobility from these diagrams. When the thermodynamic predictions and field observations were compared (see Brookins, 1978a, 1978b, 1979), they were found to agree for the elements Y, Zr, Nb, Mo, Rh, Pd, Ag, Cd, In, rare earths, Pb, Bi, Po, Th, U, Np, Pu. Predictions for ruthenium and technetium were difficult because of sensitivity to assumed temperatures between 25 and 200°C. Gancarz et al. (1980) presented data that show technetium mobilized relative to ruthenium. These studies reinforce the point made earlier that nuclide migration is best studied with both adsorption and solubility concepts. The two approaches combined are quite successful in explaining observations of

nuclide migration from laboratory and field experiments or natural analogs.

Although it does not directly perform field or analog studies, the WRIT program maintains close ties with and offers theoretical, experimental, and computer modeling tools and data to investigators active in these pursuits. Together investigators are ascertaining the potential for nuclide migration from all avenues, and their various activities supply test data to make comparisons and verify each others' models and hypotheses.

Summary and Conclusions

Numerous studies have identified radionuclide transport by groundwater as the most credible means for nuclear wastes buried in deep geologic repositories to impact the biosphere. Since physicochemical interactions, such as adsorption, precipitation, and filtration, can significantly delay or reduce the mass transport of such radionuclides, these interactions should be described in quantitative terms. The identification and quantification of these interactions are goals of the WRIT program, and their status is the subject of this paper.

Two approaches have been pursued in concert to identify and quantify adsorption processes: (1) An empirical approach, which allows rapid measurement of distribution coefficients (Rd); and (2) mechanism studies that strive to identify, differentiate, and quantify the various physicochemical processes that control nuclide adsorption. The empirical distribution coefficient (Rd), which is readily measured by laboratory studies, is currently the basis for nuclide mass transport calculations for almost every existing safety assessment and site selection model. Other studies cited show the usage and importance of nuclide retardation in guiding waste package design and preliminary site selection.

From 1976 through 1980, WRIT performed empirical sorption studies on a wide range of groundwater-rock-nuclide combinations to develop bounding nuclide retardation values.

The WRIT program pursued laboratory methodology standardization. A wide range of rocks, sediments, and minerals in contact with radionuclide-laden solutions have been used to assess the precision of R_d analysis; ease of method used; time, equipment, and cost expenditures; and method limitations. Laboratory methods investigated include batch, axial filtration, channel chromatography, once-through-flow column on disaggregated or permeable rock, high pressure once-through-flow column on fractured or intact low permeability rock, and recirculating flow column. The WRIT staff concluded that no one laboratory method best simulates all possible rock-groundwater-nuclide combinations. As a result, the use of at least two methods in concert to bound radionuclide migration is currently recommended. The two most used methods are batch and once-through-flow column. Together these two methods alleviate most of the limitations that each exhibits individually. The observed nonlinearity in radionuclide sorption isotherms on rocks leads to the recommendation that, rather than making only one analysis at fixed conditions, investigators determine R_d values over a realistic range of nuclide concentrations and groundwater compositions. The empirical Freundlich sorption isotherm is a suggested approach to reducing the numerous experimental observations to mathematical descriptions.

The two laboratory methods, batch and once-through-flow column, are described in some detail. The results of the first WRIT round-robin batch sorption exercise and numerous WRIT methodology sensitivity studies have identified the cause of much of the

previously observed variability in reported R_d values. Phenomena that contributed to past variability include fine particulate formation during slurry agitation, incomplete solid-liquid phase separations, tracer addition technique, variations in container sorption corrections, variations in defining the influent nuclide concentration, variable solution-to-solids ratio, and nonlinear adsorption. Knowledge gained in these studies allowed the first detailed recommendation for a proposed standard batch sorption method (Relyea, Serne, and Rai, 1980). Further work is necessary, however, to discover the cause of R_d dependency on solution-to-solids ratio, to evaluate the surface area relationship between disaggregated and intact rock, and to quantify conversion factors that allow R_d values based on rock weight to be recalculated as R_d values based on surface area.

The greatest limitation of the batch method is its inability to differentiate multiple species of a radionuclide. The use of total radioactivity in original and post-contact solutions or in post-contact solutions and on the solid cannot separate the distinct sorption values for different species. This inadequacy in the batch sorption method may be the cause of the recent discrepancy between laboratory predictions (based on batch R_d) and field observations of ^{106}Ru migration at the Nevada Test Site (Coles and Ramspott, 1982).

The once-through-flow column sorption experiment is the second most used laboratory method. Its strengths include allowing nuclide migration study without significant rock alteration, differentiation of multiple species, and study of reversibility, colloid transport, and hydrodynamic effects. Its limitations include large equipment requirements; long time frames needed for quantitative study of nuclides that exhibit appreciable sorption; experimental

problems, such as water short-circuiting or channeling along the interface between the rock and the containment vessel wall; and data reduction complications for asymmetric or peakless breakthrough curves.

At present the WRIT staff recommends that once-through-flow column experiments be used in conjunction with batch sorption experiments to produce the most credible bounding R_d values for nuclide retardation. Replicated batch tests should be performed over a range of nuclide concentrations and groundwater compositions on several samples of the rock to delineate the probable range of R_d values for each nuclide. In addition, such batch tests would delineate the concentration of nuclides at which confounding reactions, such as precipitation or polymerization, might occur. Studies of R_d vs. time should allow estimates of the importance of kinetics on sorption. Once-through-flow column experiments at nuclide concentrations below solubility constraints and at realistic residence times should be performed to verify the batch R_d values. Effluent breakthrough curves should be monitored for low sorbing elements and for "leakage" of highly sorbing elements. Attempts should be made to verify whether the leakage is caused by actual mobile species, colloid transport, or column short-circuiting. After a reasonable period of time (3 to 6 months), the column should be sectioned and the distribution vs. distance of strongly adsorbing nuclides should be determined to verify batch R_d values qualitatively.

Since few complementary batch and once-through-flow column adsorption studies have been performed to allow detailed comparison, the following recommendations are offered. To facilitate conservatism in safety assessment calculations on crystalline or fractured rock where only batch R_d values are available, we should reduce

the batch R_d values by a factor of 3 for batch R_d values less than 50 ml/g, a factor of 5 for R_d values between 50 and 300 ml/g, and a factor of 10 for batch R_d values more than 300 ml/g. Such a policy should be acceptable for preliminary safety assessment and/or site selection activities, but we should gather detailed laboratory and field data for final licensing activities.

The types of empirical R_d data available are discussed, and two summary tables containing average conservative R_d values for the five most promising host rocks—bedded salt, domed salt, basalt, granite, and tuff—are included. Of these rocks, R_d data availability for domed salt is poorest, whereas availability of R_d data for basalt, tuff, and granite, in that order, is best. Bedded salt R_d data availability is intermediate. In general, laboratory data for sorption under reducing conditions for all rock types need improvement in quantity and quality. The tables can be used to aid preliminary safety, siting, and licensing activities.

The advantages of computerized R_d data management and statistical analysis to create empirical mathematical predictive equations are briefly discussed. Example results for strontium and americium R_d predictions based on the nonlinear statistical analysis method, adaptive learning networks, are discussed.

Results from the empirical approach to describing adsorption-desorption, although useful in assessing the migration potential of radionuclides, are very specific to the particular rocks and groundwater studied; i.e., the empirical results do not lend themselves to extrapolation to other conditions. Therefore mechanism studies are used to investigate the factors and interactions that control the adsorption-desorption behavior of nuclides. With knowledge of the nuclide retardation mechanisms, we can make more defensible

migration rate predictions for any proposed storage environment.

Five types of mechanism studies are discussed: (1) Scouting studies to identify the most important ground-water and rock sorption controlling parameters; (2) ideal ion-exchange studies; (3) site-binding electrical double-layer model studies; (4) redox-mediated nuclide retardation studies; and (5) rock surface adsorption site identification studies.

Results of ideal ion-exchange theory show that this theoretical construct favorably predicts the adsorption behavior of only a few elements, e.g., strontium and cesium onto clays and clay mixtures. The adsorption of other elements, such as actinides and lanthanides, are not readily modeled by ideal ion-exchange constructs. Several possible reasons for the narrow range of applicability of ideal ion-exchange theory to deep geologic isolation are discussed. In contrast, preliminary experimental studies are described which agree favorably with predictions based on generalized ion-exchange and site-binding electrical double-layer constructs. These preliminary results and the available literature on transition metal sorption on oxide surfaces have led the WRIT staff to focus adsorption modeling efforts on the site-binding electrical double-layer model, but the generalized ion-exchange model also appears useful.

Experimental studies of redox-mediated nuclide retardation have concentrated on three multivalent elements, technetium, neptunium, and plutonium. It appears that dominant solution redox couples, such as Fe(II)-Fe(III), can cause reduction of nuclides and removal as insoluble precipitates. Thermodynamic calculations based on measured Fe(II)-Fe(III) solution concentration in laboratory experiments predict that for igneous rocks, such as basalt and granite, reduction of Tc(VII), Pu(V or VI), and

Np(V) should occur. Experimental results do show significantly reduced nuclide solution concentrations. It appears that Tc(VII) reduction forms Tc(IV) hydroxide precipitates, and it is reasonable to surmise that plutonium and neptunium would also. In addition, some laboratory studies are described in which the reduction of plutonium appears to occur at the solid-solution interface even though the bulk solution is oxidized. Minerals with large percentages of structural Fe(II) appear to reduce the plutonium in a heterogeneous solid-solution redox reaction.

Autoradiography, microscopy, and electron microprobe studies of rock surfaces on which radionuclides were adsorbed have identified specific adsorption sites and have shown that it is possible for minor phases within the bulk rock to completely dominate the mass of radionuclides adsorbed. Minor phases identified to date to be most active in adsorption include the alteration products, clays, and zeolites. Slightly soluble actinides and lanthanides have been found to give random autoradiographs; this suggests that precipitation reactions are a dominant nuclide retardation mechanism for these elements.

As an aid to future laboratory experimentation, radionuclide hazards potential was ranked quantitatively, and the WRIT findings were compared with three other analyses. All four analyses conclude that the four most hazardous elements in the long term are I, Tc, Np, and Ra. Thus continued nuclide retardation studies of these four elements should receive top priority. Other elements that exhibit significant hazards potential include Pu, U, Am, Se, Sn, Pb, Pd, and Th. Numerous studies of plutonium, uranium, and americium nuclide retardation properties are under way. For the other elements, solubility constraints may lower the hazards and thus diminish the need for detailed

study for tin, palladium, and thorium. The two remaining elements selenium and lead, appear to require new efforts to generate enough data to assess their retardation potential.

A brief review of field nuclide migration experiments is given. In general, past studies in which nuclide migration was monitored in the field and compared with predictions based on laboratory studies showed satisfactory agreement. The range of hydrologic conditions and nuclides studied has been quite limited, however. Three ongoing field nuclide migration projects in fractured rock should help expand the range of environments and nuclides studied.

The limitations of both laboratory and field testing in addressing geologic time scales necessitate a third type of study, called natural analogs. Qualitative comparisons between field observations of nuclide migration at Oklo and thermodynamic predictions have been quite successful. The combination of laboratory and computer-based modeling studies, field testing, and natural analogs appears to address the long-term potential of nuclide migration adequately. The WRIT program's main activities fall within the former area, but close ties are maintained with other NWTs participants to facilitate data and model verification.

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The Oklo Reactors: Natural Analogs to Nuclear Waste Repositories

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The real world is immensely complex (and) continuous. Isolated structures are therefore subjective and artificial portions of reality, and the biggest initial problem is the identification and separation of meaningful sections of the real world. On the one hand, every section or structure must be sufficiently complex . . . so that its study will yield significance and useful results; on the other, every section must be simple enough for comprehension and investigation.

R. J. Chorley and B. A. Kennedy (1971)

The 2-billion-year-old fossil reactors at Oklo are ancient natural nuclear waste sites. Isotope dilution mass spectrometric analyses of the fission products in the reactor core uraninite and the peripheral pelitic sandstone provide data for calculating the reactor operating parameters, the quantities of fissiogenic isotopes produced, the fraction of these isotopes retained in the cores, and the location in the peripheral rocks of the fissiogenic fraction lost from the cores. For a duration of criticality of 3×10^5 yrs, the thermal plus resonance neutron fluence ranged between 10^{20} and 10^{21} neutrons/cm². The fraction of technetium (60 to 85%), ruthenium (75 to 90%), and neodymium (85 to 100%) retained is negatively correlated with fluence. The lost fission products are contained within a few tens of meters of their source, the reactor cores.

The systematics of the decay of ⁹⁹Tc ($t_{1/2} = 2.13 \times 10^5$ yr) to ⁹⁹Ru limits the period of fissiogenic element migration to approximately 1 million yr at a time 2 billion yr ago. Thermodynamic calculations of the temperature-dependent solubilities indicate that the loss of fissiogenic elements is diffusion controlled, whereas retention in the surrounding rocks is a result of temperature-dependent deposition from an aqueous solution. These results concerning the geochemistry of technetium, ruthenium, and neodymium at a natural waste site support the concept of geologic burial of man-made radioactive wastes.

Introduction

The currently favored method for disposing of commercially generated high-level radioactive wastes in the United States is deep burial in mined repositories. Successful isolation of hazardous wastes from the biosphere by this method relies on a philosophy of redundant containment commonly called the multiple barrier concept. This approach uses a series of engineered and natural barriers, each selected to isolate the wastes for sufficient periods of time to allow the radioactive elements to decay below some predetermined level. Such a philosophy places new demands on the predictive capabilities of the science and engineering communities. The concept of multiple barriers requires defensible predictions of the mechani-

cal, thermal, hydrologic, and chemical properties of the geosphere over periods as long as 1 million yr and of the effects of these properties on the chemical stability of radionuclides. The difficulty lies in extracting information from a system that is "sufficiently complex . . . that its study will yield significance" but "simple enough for comprehension and investigation." Information obtained from laboratory measurements and mathematical models may reflect conditions that are too simple to be meaningful. In contrast, it is difficult to extract conclusions from the geologic record where the periods of time and the complexity of conditions bear directly on the problem of long-term management of nuclear wastes.

Thick lenses of uraninite at the Oklo uranium mines in the Republic of Gabon in equatorial Africa sustained nuclear fission for a period of a few hundred thousand years about 2 billion yr ago. The mere existence of these remnants of naturally occurring fission reactors attests to their remarkable stability for about half the age of the earth. They are a direct demonstration that waste from nuclear reactors can be contained in the earth's crust for geologic periods of time. As such, they validate, in principle, the concept of geologic disposal of such wastes. More significant, however, is the opportunity to characterize quantitatively the stability of the reactors and the rocks that contain them with respect to more than 30 elements, which are the products of neutron capture, nuclear fission, and radioactive decay, and to study the transport of these elements into the geologic surroundings. This quantitative examination can be done on a system that has many physical and chemical properties that are similar to proposed repositories, has existed in a crustal environment for geologic periods of time, and has been subjected to many of the conditions

that must be considered in evaluating the stability of the man-made facilities.

We summarize here some of the possible properties and conditions that may have affected the stability of the Oklo reactors and discuss the methods used to evaluate the gain or loss of elements, the distances over which elements have been transported, the time in the past when this redistribution occurred, and the duration of the redistribution processes. These methods are used to examine the stability and redistribution of ruthenium, ^{99}Tc , neodymium, and uranium in and around the zones of nuclear activity.

The Oklo Reactors as Analogs of Geologic Repositories of Nuclear Wastes

Characteristics and Geologic Setting. As of 1978 four distinct sites of sustained nuclear fission had been distinguished at the Oklo mines. The total uranium involved in the nuclear reactions was estimated to be 8×10^5 kg. At present the rocks contain about 6×10^2 kg of ^{235}U ; this corresponds to 6×10^3 kg of fissioned ^{235}U at 2×10^9 yr ago (Naudet, 1978b). Of the 2×10^3 kg of ^{239}Pu that was produced, some small fraction fissioned or underwent neutron capture, and the majority decayed to ^{235}U . At the present time 13 reactor zones have been discovered, and the estimate of fissioned ^{235}U has been increased to approximately 1.2×10^4 kg. The inventory at Oklo corresponds to 10 to 20% of the uranium and 1 to 2% of the plutonium and fission products in the United States spent-fuel inventory as of 1980 (Department of Energy, 1980).

The natural reactors are located in the Franceville Basin. Strata of the Francevillian Series consist of middle Precambrian unmetamorphosed volcanic and sedimentary rocks (Weber, 1973). They lie uncon-

formably on the metamorphosed basement of the Du Chaillu and North Gabon massifs. To the east they are overlain by Cretaceous-Tertiary sediments. The series is divided into five major formations, F_A through F_E . Uranium mineralization at Oklo occurs at the top of the F_A formation in a layer identified as C-1. The F_A formation is approximately 900 m thick and consists of fluviatile sandstone and conglomerate with argillaceous and carbonate cement. The overlying F_B formation is composed of variegated and black pelites, dolomite, and manganese-rich carbonates (Gauthier-Lafaye, Besnus, and Weber, 1978).

The stratigraphy and mineralogy of the mineralized layer, C-1, has been defined in detail (Gauthier-Lafaye, Besnus, and Weber, 1978). It is underlain by a silicified quartz pebble conglomerate. This stratum forms the west wall of the Oklo quarry. The mineralized strata are 5 to 6 m thick and consist of a basal sandstone layer with minor pelite, a crossbedded and lenticular sandstone unit, followed by four sequences, each consisting of a basal conglomerate grading upwards into medium- to coarse-grained sandstone. Normal sandstone contains ~10% clay, predominantly illite and iron-rich chlorite in various proportions. Pelite may contain up to 80% of these clay minerals.

Isotopically normal uranium ores are generally of two types. The first is highly recrystallized black sandstone with a UO_2 content that rarely exceeds 1%. Uranium mineralization occurs as pitchblende, which is associated with carbonaceous materials. Chlorite and illite are present in varying proportions with abundant sulfide minerals. The second type contains 5 to 25% UO_2 , again in the form of pitchblende, and there is no association with carbonaceous materials. This ore usually occurs in what were

tectonically active zones. The pitchblende fills microfractures in both the quartz and the matrix material. There is an apparent association between this uranium mineralization and spots of hematite (Gauthier-Lafaye, Besnus, and Weber, 1978).

Relative to normal C-1, the reactor zones and their immediate surroundings are anomalous in almost every sense. In this sandstone environment the reactors are always associated with a disappearance of sedimentary features and an almost complete lack of quartz. In addition, aureoles of clay that are associated with the reaction zones are mineralogically unique in the Francevillian Series. The principal change in the clay mineralogy involves a polymorphic transformation of illite correlated with the progression from "normal" sandstone to the reactors. Chlorite changes from ferruginous to magnesian and is found in association with vermiculite in the interior portions of the aureoles. Total silica content decreases from ~90% in the sandstone to ~35% in the reactors because of a complete removal of quartz. The remaining silica is in clay minerals. The gangue associated with the reactor zones is argillaceous with little or no quartz in most cases (Gauthier-Lafaye, Besnus, and Weber, 1978). At present the uranium content of these zones is 25 to 60%, in the form of coarsely crystalline uranium dioxide, uraninite. The presence of radiation-produced crystallites in UO_2 and a correlation between the density of these crystallites and the degree of ^{235}U depletion suggests that grains of uraninite have been thermally and mechanically stable since the reactors were functional. There is a notable lack of radiation damage in the clay minerals that comprise the reactor gangue; this indicates total recrystallization (Dran et al., 1978).

Interpretations of uranium and lead isotopic analyses suggest that the

uranium mineralization occurred 2.05×10^9 yr ago (Devillers et al., 1975; Devillers and Menes, 1978; Gancarz, 1978). The time when the reactors were critical, inferred from isotopic analyses of the uranium fuel and fission product neodymium, was from 1.6 to 2.1 (Cowan et al., 1975) or 1.93 to 2.05 billion yr ago (Ruffenach, 1978). It seems reasonable to assume that the time of reactor criticality was very soon after the time of uranium mineralization. Studies of the operating parameters of the reactors restrict the duration of criticality to periods of 10^5 to 5×10^5 yr (Ruffenach, 1978). The age of pelite from several stratigraphic levels in the Francevillian Series, inferred from potassium-argon and rubidium-strontium isotopic analyses, is consistently about 1.8×10^9 yr (Bonhomme and Weber, 1978; Weber and Bonhomme, 1975). This age probably corresponds to the time of diagenesis and not to the age of sedimentation of the Francevillian Series (Gauthier-Lafaye, Besnus, and Weber, 1978). The latter interpretation would be inconsistent with the age of uranium mineralization.

Physical and Chemical Environment of the Reactors.

The natural fission reactors and the sedimentary host rocks were subjected to distinctly different physiochemical conditions at different times throughout their history. We have tried to ascertain the time and duration of these periods and the conditions that prevailed during each so that we can determine the conditions that may have influenced the retention or redistribution of the nuclear products at Oklo. The periods were (1) a thermal period lasting as long as 1 million yr during and immediately after the reactors were operative; (2) the period of diagenesis, extending for about 200 million yr after the reactors ceased nuclear criticality; and (3) the 1.8 billion yr that have elapsed

since the last stages of diagenesis reset some of the isotopic clocks.

Thermal Period. During the time of reactor criticality, the rocks that comprised the reactors were subjected to much larger radiation doses from a greater variety of radioactive emanations than would be encountered by materials in a proposed repository. Thermal plus resonance neutron fluences in the natural reactors were as high as 10^{21} neutrons/cm² (Cowan et al., 1975) (see Table 1). Decaying fission products produced $\sim 10^{28}$ beta-gamma emitting disintegrations during the reactors' lifetime (Glasstone and Sesonske, 1980). Total energy production of the Oklo reactors is estimated to have been 1.65×10^4 MW-yr (Naudet, 1978b). This is about 15 times the total amount of energy that would be released in a repository if it were filled with the entire 1980 U. S. inventory of spent commercial fuels (Department of Energy, 1980). The duration of nuclear criticality was a few hundred thousand years. This corresponds to an average thermal loading *within the reactor zones* of about 50 W/m², two to five times greater than the local thermal loadings determined for reference waste repositories (Raines et al., 1981). In response to the dissipation of this energy, the temperature increased in a manner analogous to the near-field environment during the thermal period of proposed repositories (Raines et al., 1981).

During the high-temperature phase of reactor criticality, hot aqueous solutions convectively circulated through the rocks within the critical zone. Nuclear reactors require a neutron moderator to sustain criticality. Water was the most likely neutron moderator in the Oklo reactor zones, and its partial loss is proposed as a control of the reactor criticality (Naudet, 1978a). Inclusions in mineral grains that formed during the period

of nuclear fission contain fluids that were heated to temperatures between 450°C and 600°C at a pressure of about 1 kbar (Openshaw, Pagel, and Poty, 1978). These studies, furthermore, suggest that the aqueous phase from the reactors had a highly variable composition. This fluid was found up to 30 m from the zones of criticality (Openshaw, Pagel, and Poty, 1978). The picture that develops is one of circulating hydrothermal fluids convectively driven by heat produced by the nuclear reactions.

It seems certain that the unique lithology associated with the Oklo reactors was caused by dissolution and modification of minerals as a result of the thermal-radiation environment and chemical redistribution associated with the convective flow of hot aqueous fluids. In particular, the extreme enrichment of argillaceous material is thought to represent a desilicification of "normal" C-1 sandstone by dissolution and mobilization of quartz, leaving behind the interstitial clay minerals. Clay mineralogy in the aureoles may represent modifications of "normal" Francevillian clays in response to the extreme conditions during the nuclear event (Gauthier-Lafaye and Weber, 1978). The lack of severe radiation damage in clay minerals from the reactor zones is probably a result of recrystallization during or after the criticality in response to intense radiation damage and the hot aqueous environment (Dran et al., 1978).

Despite the apparent mechanical stability of the host uraninite grains, some fission products are missing from their sites of production. There are extreme deficiencies of rare gases, halogens, molybdenum, and the alkali and alkaline earth elements (Bryant et al., 1976). Uranium, rare earth elements, and others appear to have suffered some local redistribution but were largely retained within or near

the reactor zones (Naudet, 1978c). In general, it is difficult to correlate the transport of fission products with the convective movement of hydrothermal fluids during the thermal period. As shown below, however, observed fractionations of ^{99}Tc from ruthenium occurred within 1 million yr after the end of reactor criticality (Gancarz et al., 1980). The spatial redistribution of these two elements is consistent with convective fluid flow, and the mobilization and transport of ^{99}Tc must have occurred during this time.

Diagenetic Period. Conditions postdating reactor criticality are not well defined. Until they are more completely delineated, it will be difficult to ascribe element migration and redistribution events to processes attendant with diagenesis. Diagenesis of the Francevillian Series sediments is characterized by: (1) Silicification of sandstone as a result of recrystallization of the quartz detritus. Fluid inclusions suggest that one episode of silicification predated the uranium mineralization and another postdated it. Fluid temperatures were 240°C, and pressures were 1 kbar for the periods of silicification. These two events bracketed the ore-forming events and indicate ore formation under deep diagenetic conditions (Openshaw, Pagel, and Poty, 1978). (2) Homogenization of the clays into illite and chlorite. (3) Alteration of plagioclase and micas by silicification and the formation of sericite and chlorite (Gauthier-Lafaye, Besnus, and Weber, 1978). A late stage of dolomite cementation is also seen in the upper F_A formation. Oxides and sulfides have been redistributed in the sandstone. The carbonate diagenesis is believed to have occurred at a fluid temperature of 150°C and a pressure of 800 bars. Divalent cations, such as Ca^{+2} and Mg^{+2} , were present in the fluids (Openshaw, Pagel, and Poty, 1978).

Postdiagenetic Period. Little can be said about the conditions at Oklo for the last 1.8×10^9 yr. However, both element data (Gauthier-Lafaye, Besnus, and Weber, 1978) and isotopic analyses of lead and uranium (Devillers and Menes, 1978; Gancarz, 1978; Gancarz et al., 1980) show that massive amounts of radiogenic lead have been redistributed at the Oklo deposit. The long half-life of the parent uranium isotopes relative to the duration of nuclear criticality precludes the detection of lead-uranium fractionation during the thermal period. Observed fractionation must postdate reactor criticality. Gancarz et al. (1980) postulated that processes of lead redistribution have been operative for the entire history of the ore body. Other physiochemical effects associated with this element transport have yet to be defined.

Methods of Measuring Material Stability and Element Transport at the Oklo Reactors

Reactor Operating Parameters and Nuclear Product Inventory. Chemical elements were produced and destroyed in the natural reactors. With the exception of the decay and formation of naturally occurring radioactive elements, such processes are not known to have occurred at any other place in the earth. The list of these nuclear products includes a third of the naturally occurring elements and several that are principally man-made. They are the result of the three important nuclear processes—fission, neutron capture, and radioactive decay. Each process may operate on different nuclides. For example, ^{235}U , ^{239}Pu , and ^{238}U can all undergo nuclear fission. In addition, more than one process may affect a particular nuclide; for instance, ^{239}Pu is produced by neutron capture on ^{238}U and destroyed by fis-

sion, neutron capture, and decay. The extent to which each process affects each of the different nuclides determines the abundances of the nuclear products. The composition of the nuclear material depends on the following parameters: (1) The elapsed time since the reactors were critical defines the initial abundances of the naturally occurring isotopes of uranium, the primary fuel for the reactors. (2) The duration of nuclear criticality determines the relative contributions of time-dependent nuclear processes. (3) The neutron fluence and neutron energy distribution determine the number and proportion of products from energy-dependent neutron-induced processes. The energy distribution itself depends on a number of factors in the geologic environment, e.g., the abundance of elements with large neutron capture cross sections (poisons), the relative quantities of neutron scattering elements, such as hydrogen (moderators), and the amount of uranium (fuel). To calculate the abundance of any element produced or destroyed in the reactor zone, we must determine these operating parameters.

Operating parameters are calculated by measuring absolute or relative abundances of nuclides that are particularly sensitive to at least one of the nuclear parameters. These calculations are also based on the premise that during criticality there was neither migration of elements out of nor transport and deposition of elements into the reactor zones. The ratio of ^{144}Nd to ^{143}Nd is used as a measure of the "total" (resonance plus thermal) neutron fluence in a sample. The ^{143}Nd neutron capture cross section is roughly 100 times larger than that of ^{144}Nd . Therefore exposure to neutrons results in a more rapid depletion of ^{143}Nd (forming ^{144}Nd) than of ^{144}Nd , and the $^{144}\text{Nd}/^{143}\text{Nd}$ ratio increases in proportion to the neutron fluence. Since the thermal and resonance

capture cross sections differ by less than a factor of 3, the $^{144}\text{Nd}/^{143}\text{Nd}$ ratio is relatively insensitive to the proportions of thermal and resonance neutrons.

In contrast, the $^{235}\text{U}/^{238}\text{U}$ ratio is sensitive to the neutron energy distribution. Although the thermal and resonance cross sections of ^{235}U differ by only a factor of 2, the ^{238}U resonance neutron capture cross section is 10 times greater than the corresponding thermal neutron capture cross section. The sensitivity to the proportion of resonance neutrons is not caused by the small depletion in ^{238}U , but rather by the relatively large production of ^{235}U as an end product of neutron capture by ^{238}U . This capture yields ^{239}Pu , which undergoes neutron capture and neutron-induced fission, but, more importantly, 90 to 99% of the ^{239}Pu alpha decays to ^{235}U ; this results in a measurable increase in the $^{235}\text{U}/^{238}\text{U}$ ratio.

Differential equations describing the time-dependent variation of these parameter-sensitive abundances were formulated and solved. These are of the form

$$\frac{dY}{dt} = -l(t)Y + g(t) \quad (1)$$

where $l(t)$ is the loss with time of isotope Y by neutron capture and, when applicable, neutron-induced fission and radioactive decay and $g(t)$ is the gain of isotope Y from the capture, fission, and decay of appropriate nuclides. An example for ^{238}U is shown in Eq. 2, and the solution is given in Eq. 3. The calculations ignore the 3 to 4% contribution from fast-neutron-induced fission of ^{238}U and the spontaneous decay of ^{238}U during the period of criticality.

$$\frac{d^{238}\text{U}}{dt} = -[^{238}\sigma_c^{\text{th}} (1 - X) + ^{238}\sigma_c^{\text{rs}} XS] \phi (^{238}\text{U})_t \quad (2)$$

$$(^{238}\text{U})_t = (^{238}\text{U})_0 \times e^{-[^{238}\sigma_c^{\text{th}}(1-X) + ^{238}\sigma_c^{\text{rs}}XS]\phi t} \quad (3)$$

where $^{238}\sigma_c^{\text{th}}$ = thermal neutron capture cross section*

$^{238}\sigma_c^{\text{rs}}$ = resonance neutron capture cross sections*

X = proportion of resonance neutrons

S = self-shielding factor

ϕ = "total" neutron flux

t = duration of nuclear criticality

These are the parameters to be calculated: the latter two in the form ϕt , the neutron fluence. The value of $^{238}\text{U}_0$, the concentration at the beginning of criticality, depends on the time that has elapsed since the event and the neutron capture effects during the critical period. In general, this second correction amounts to only about 5% of the first correction. Consequently, large uncertainties in the neutron capture correction do not significantly affect the calculated operating parameters. An age of $2.05 \pm 0.03 \times 10^9$ yr (Gancarz, 1978) was used to calculate $^{238}\text{U}_0$ from measured uranium abundances. Variations in age of three standard deviations do not alter any of the conclusions in this paper.

The self-shielding factor (S) is difficult to quantify. It is a measure of the rate of depletion of specific energy-interval resonance neutrons by ^{238}U capture in relation to the rate of population of these energies by neutron scattering. Values of S depend on the relative abundances of moderator (H_2O) and fuel (uranium). A value of unity corresponds to an infinite dilution of uranium. Values less than unity reduce the effective resonance energy cross section for ^{238}U and

*All cross sections were taken from Mughabghab and Garber (1973).

increase the proportion of resonance energy neutrons (X) required to produce the observed $^{235}\text{U}/^{238}\text{U}$ ratio. Most calculations for samples from the reactor zones used $S = 0.115$, a value calculated from the minimum uranium concentration required for criticality and the optimum hydrogen-to-uranium ratio at that concentration (Apt, 1976). Occasionally this value of S (0.115) yielded unreasonably high values of X ($>50\%$). In these cases the calculation was repeated using $S = 1.0$; e.g., calculations for most samples peripheral to the reactor zones required a self-shielding factor of 1.0. These choices were somewhat arbitrary. Even though different values of S make large differences in calculated values of X , they make relatively small differences in the abundances of the nuclear products that are of most interest to us.

Finally, the parameters were iteratively adjusted to match the solutions to the differential equations with the isotopic ratios or nuclide abundances of the parameter-sensitive species. Matching measured and calculated $^{144}\text{Nd}/^{143}\text{Nd}$ and $^{235}\text{U}/^{238}\text{U}$ ratios yields values of the total fluence (ϕt) and the proportion of resonance neutrons (X). Three time intervals of reactor operation were considered—1, 3, and 5×10^5 yr. These encompass the most plausible durations of reactor criticality (Cowan et al., 1975). Since none of the measured abundances are markedly sensitive to duration, this parameter is not constrained by these calculations and the results are not sensitive to the choice of duration. Results for an operating period of 3×10^5 yr are discussed.

Calculated values for reactor operating parameters are presented in Table 1. The several investigators whose data are used in constructing this table in most cases used the data and a variation of the methods

described here to determine reactor operating parameters.

Once plausible operating parameters were chosen, they were used to calculate the abundance of nuclides produced or destroyed during nuclear criticality. These abundances are model dependent! They are based on two assumptions—(1) that uranium has been neither chemically depleted nor enriched in the sample during or after the reactors were active and (2) that neodymium has been neither *added to the rocks at any time* nor *lost during criticality*. It is important to note that small deviations from the model assumptions do not significantly alter the solutions to the calculated parameters or any conclusion. The samples with no solutions must have suffered large perturbations in uranium and/or neodymium. The calculated abundance is that which was produced in the reactor zones and would be measured in the rocks if there were no chemical fractionation during or after criticality. These abundances are specified in the table by the subscript “prod.”

Present Inventory of Nuclear Products and Measurement of Element Fractionation. The rocks that supported nuclear fission 2 billion yr ago are composed of elements containing distinct components—natural and nuclear. Although the chemical properties of these components are identical, they can be distinguished by their isotopic composition. The isotopic composition of the natural component is that which is found in natural materials throughout the earth, whereas that of the nuclear component is a function of the relative proportions of the various nuclear processes.

Isotopic abundances are measured by high-precision mass spectrometric isotope dilution techniques. Measured abundances are mixtures, in various proportions, of the natural and

Table 1 Oklo Nuclear Parameters†‡

Sample	Duration (t), 10 ⁵ yr	Criteria of fit §	Fluence (φ), 10 ²⁰ neu- trons/cm ²	Resonance proportion (X), %	U, g/g rock	²³⁵ U/ ²³⁸ U, 10 ⁻³ (atomic)	(²³⁹ Pu/ ²³⁵ U) _{fin} , 10 ⁻² (atomic)	Natural Nd, 10 ⁻⁶ g/g rock	FP Nd, 10 ⁻⁶ g/g rock	Nd*¶
Reactor Zone 2										
1408/4-SC36-CLSA	1	1 H	10.6	30.4	2.33 × 10 ⁻¹	5.45	8.56	1.18 × 10 ⁻²	5.52 × 10 ⁻²	0.719
	3	1 H	10.3	29.0			3.67			0.715
	5	1 H	10.3	28.6			2.32			0.716
1410/3-SC36-CLSA	3	1 H	12.9	31.0	5.78 × 10 ⁻¹	5.27	4.76	1.37 × 10 ⁻²	1.84 × 10 ⁻³	0.784
1413/3a-SC36-CLSA	3	1 H	15.5	17.7	3.72 × 10 ⁻¹	4.10	4.37	6.06 × 10 ⁻¹	1.52 × 10 ⁻³	0.887
1413/3b-SC36	3	1 H	15.5	17.6	3.72 × 10 ⁻¹	4.10	4.35	5.96 × 10 ⁻¹	1.51 × 10 ⁻³	0.886
1418a-SC36-CLSA	3	1 H	11.4	36.3	5.79 × 10 ⁻¹	5.74	4.57	5.98 × 10 ⁻¹	1.68 × 10 ⁻³	0.793
1418b-SC36	3	1 H	11.4	36.4	5.8 × 10 ⁻¹	5.74	4.59	6.00 × 10 ⁻¹	1.69 × 10 ⁻³	0.793
1421/5-SC36-CLSA	-	-	-	-	8.55 × 10 ⁻²	5.32	-	1.22 × 10 ⁻²	2.18 × 10 ⁻²	-
1424/5-SC36-CLSA	3	1.23	4.54	29.9	1.50 × 10 ⁻²	6.36	1.64	1.03 × 10 ⁻²	7.60 × 10 ⁻¹	3.38
1425/1-SC36-CLSA	3	1.16	6.56	38.9	2.03 × 10 ⁻²	6.38	2.77	1.04 × 10 ⁻²	7.74 × 10 ⁻¹	1.80
1892-SC36-CLSA	3	1.09	7.54	48.7	2.8 × 10 ⁻³	6.71	3.62	1.50 × 10 ⁻¹	5.49	0.819
1897/5-SC36	-	-	-	-	9.1 × 10 ⁻³	6.99	-	1.69 × 10 ⁻²	2.13 × 10 ⁻¹	-
1899/5-SC36	-	-	-	-	1.71 × 10 ⁻²	7.20	-	2.93 × 10 ⁻³	7.11 × 10 ⁻¹	-
1901-SC36-CLSA	3	1.03	1 × 10 ⁻⁵	0	9.48 × 10 ⁻²	7.25	0	1.12 × 10 ⁻¹	7.11 × 10 ⁻¹	2 × 10 ⁻¹
3548 KN50	3	1 H	15.4	25.7	5.5 × 10 ⁻¹	4.65	5.21	1.42 × 10 ⁻²	2.14 × 10 ⁻³	0.827
323-KN50	3	1 H	12.4	22.8	7 × 10 ⁻²	4.82	3.88	2.06 × 10 ⁻¹	2.43 × 10 ⁻²	0.897
401/3-2L-CLSA	3	1 H	13.3	13.2	3.43 × 10 ⁻¹	4.12	3.19	5.10 × 10 ⁻¹	1.16 × 10 ⁻³	0.844
404/4-2L-CLSA	3	1 H	10.1	32.2	6.15 × 10 ⁻¹	5.65	3.79	1.07 × 10 ⁻²	1.57 × 10 ⁻³	0.784
1177-2 P-CLSA	3	1 H	13.8	33.9	5.60 × 10 ⁻¹	5.36	5.34	2.03 × 10 ⁻²	2.20 × 10 ⁻³	0.898
1179-2 P-CLSA	3	1 H	16.2	33.0	5.54 × 10 ⁻¹	5.08	6.23	7.78 × 10 ⁻¹	2.10 × 10 ⁻³	0.749
1181-2 P-CLSA	3	1 H	16.1	2.93	2.11 × 10 ⁻¹	3.07	2.38	4.97 × 10 ⁻¹	9.06 × 10 ⁻²	0.980
1184-2 P-CLSA	3	1 H	17.5	16.9	2.52 × 10 ⁻¹	3.81	4.88	5.35 × 10 ⁻¹	1.16 × 10 ⁻³	0.911
1187-2 P-CLSA	3	1 H	16.0	20.5	4.76 × 10 ⁻¹	4.23	4.84	1.43 × 10 ⁻²	2.05 × 10 ⁻³	0.904
Reactor Zone 3-4										
1763-SC53	3	1 L	0.0739	86.0	3.642 × 10 ⁻¹	7.267	0.06	1.92 × 10 ⁻²	1.19 × 10 ⁻¹	2.04
1763-SC53‡	3	1 L	0.0439	14.5	3.642 × 10 ⁻¹	7.267	0.06	1.92 × 10 ⁻²	1.19 × 10 ⁻¹	2.04
1876-SC54	3	1 L	0.178	60.0	5.98 × 10 ⁻²	7.253	0.11	1.91 × 10 ⁻¹	3.16	1.09
1876-SC54‡	3	1 L	0.128	8.31	5.98 × 10 ⁻²	7.253	0.11	1.91 × 10 ⁻¹	3.16	1.09
1844M-SC55	3	1 L	1.08	22.8	2.748 × 10 ⁻¹	6.966	0.32	1.08 × 10 ⁻²	9.87 × 10 ⁻¹	0.964
1852M-SC55	3	1 L	1.03	12.6	4.927 × 10 ⁻¹	6.903	0.22	1.25 × 10 ⁻²	1.90 × 10 ⁻²	1.03
1856-SC55	3	1 L	1.31	20.8	2.196 × 10 ⁻¹	6.889	0.37	9.61 × 10 ⁻¹	1.00 × 10 ⁻²	1.00
1860-SC55	3	1 L	1.19	10.9	1.263 × 10 ⁻¹	6.838	0.23	6.75 × 10 ⁻¹	5.51 × 10 ⁻¹	1.00
1864-SC55	3	1 L	4.36	44.2	3.03 × 10 ⁻²	6.793	2.03	6.15 × 10 ⁻¹	2.73 × 10 ⁻¹	0.656
1877-SC56	3	1 L	0.924	24.3	4.791 × 10 ⁻¹	7.016	0.29	5.99 × 10 ⁻¹	1.72 × 10 ⁻²	1.13
2223-SC57	3	1 L	0.666	15.2	3.196 × 10 ⁻¹	7.037	0.15	1.22 × 10 ⁻²	8.02 × 10 ⁻¹	1.05

Table 1 (Continued)

Sample	Duration (t), 10 ⁵ yr	Criteria of fit §	Fluence (φ), 10 ²⁰ neu- trons/cm ²	Resonance proportion (X), %	U, g/g rock	²³⁵ U/ ²³⁸ U, 10 ⁻³ (atomic)	(²³⁹ Pu/ ²³⁵ U) _{fiss} , 10 ⁻² (atomic)	Natural Nd, 10 ⁻⁶ g/g rock	FP Nd, 10 ⁻⁶ g/g rock	Nd*†
Peripheral										
2650-KN224	3	1 L	0 0541	34 0	3 06 × 10 ⁻²	7 242	0 02	5 14	5 45 × 10 ⁻¹	1 01
2665-KN236††	3	1 H	27 8	7 81	1 52 × 10 ⁻²	6 517	17 1	1 12 × 10 ⁻¹	0	0
2669-KN241††	3	1 L	0 0434	8 00	8 56 × 10 ⁻²	7 252	0 03	2 32 × 10 ⁻²	0	0
2673-KN244††	3	1 L	0 00371	28 0	3 0 × 10 ⁻²	7 257	0 01	1 21 × 10 ⁻¹	0	0
2690-KN255††	3	1 L	0 117	7 67	5 34 × 10 ⁻²	7 249	0 09	7 88 × 10 ⁻¹	9 55 × 10 ⁻¹	2 50
2191-KN258	3	1 L	0 0186	25 0	1 74 × 10 ⁻²	7 248	0 01	1 32 × 10 ⁻¹	0	0
2703-KN266††	3	1 L	0 00226	35 0	8 37 × 10 ⁻²	7 256	0 01	9 44	0	0
2197-KN268††	3	1 L	0 0132	0	9 93 × 10 ⁻³	7 245	0	1 36 × 10 ⁻¹	8 79 × 10 ⁻²	0 591
2705-KN270††	3	1 L	0 0259	0	1 22 × 10 ⁻¹	7 241	0	1 41 × 10 ⁻¹	1 51	0 827
2252-SCO††	3	1 L	0 00663	10 0	3 0 × 10 ⁻²	7 253	0 01	1 03 × 10 ⁻¹	0	0

†Data from Cowan et al. (1975), Ruffenach (1978), Gancarz et al. (1980), Apt (1976), Maeck and Delmore (1982), Naudet and Renson (1978b), Hagemann, Devillers, and Lecomte (1978), and Ruffenach et al. (1975)

‡Self-shielding factor (S) is 0 115 unless otherwise indicated.

§Because of the presence of natural neodymium, the solution of the constraint

$$\frac{(^{144}\text{Nd}/^{143}\text{Nd})_{\text{meas}}}{(^{144}\text{Nd}/^{143}\text{Nd})_{\text{prod}}} = 1$$

is double valued in φ, i.e., solutions are obtained at both a low (L) and a high (H) fluence and different values of X. Unique solutions are obtained by matching the ²³⁵U/²³⁸U ratio and, if necessary, the absolute neodymium abundances. For many samples the ²³⁵U/²³⁸U ratio cannot be matched at φ_L, thus φ_H becomes the sole solution. Other samples that match ²³⁵U/²³⁸U at φ_L invariably also match at φ_H, but, φ_L yields approximately the observed number of fissiogenic neodymium atoms, and φ_H yields one to two orders of magnitude more neodymium than observed. In these cases φ_L is taken as the correct solution. Choice of solution is designated under criteria of fit by L or H. Three samples, 1421/5, 1897/5, and 1899/5 produced no solution for either fluence (φ) or resonance proportion (X). Several samples had ²³⁵U/²³⁸U ratios that produced reasonable values of X, but the calculated neodymium isotopic ratio was always greater than the measured ratio. Operating parameters were calculated for minimum values of Nd. Samples showing no designation for the criteria of fit or having values different than unity have been altered chemically and isotopically. They are all from the periphery of the reactor zones, regions that have previously been identified as having suffered chemical fractionation. Naudet (1978c) presented a detailed discussion of the redistribution of uranium and rare earth elements in these peripheral regions. These samples were not considered further.

Nd = ratio of measured fissiogenic neodymium to total fissiogenic neodymium produced.

††Self-shielding factor (S) is 10

neodymium components. Let us consider neodymium, for example. The components contributing to measured ratios of neodymium isotopes were deconvoluted using a constrained least-squares analysis (CLSA) (Reid, Gancarz, and Albee, 1973). Combinations of five different components were considered in the CLSA— ^{141}Pr capture, natural neodymium (DePaolo and Wasserburg, 1976), ^{235}U fission, ^{239}Pu fission, and ^{238}U fast fission. All fission yields are from Meek and Rider (1974). The results of these analyses are shown in Table 1. The CLSA ratios of fissioned ^{239}Pu to fissioned ^{235}U are compatible with the calculated operating parameters and show that ^{235}U was overwhelmingly the major fissioning species; ^{141}Pr capture does not appear to have produced significant quantities of ^{142}Nd . Measured concentrations of natural neodymium and fissiogenic neodymium (from all sources) are presented in Table 1.

Loss or gain of a fissiogenic species during or after criticality is determined by comparing the measured abundance of the nuclear product with the abundance produced in the sample by the nuclear reactions. This comparison is a measure of element fractionation relative to immobile uranium. Abundances for fission-produced neodymium are compared in Table 1 in the column headed Nd*. The magnitude of this ratio is the proportion of the fissiogenic element remaining in the rock. Values of 1 indicate no fractionation of neodymium relative to uranium; those less than unity, relative loss of neodymium; and those more than unity, relative gain of neodymium.

Ruthenium-Techneium Fractionation. Technetium-99 is a radionuclide of particular concern in the storage of radioactive wastes. It has a half-life of 2.13×10^5 yr, which necessitates storage times on the

order of a million years. After such an interval, 96% of the ^{99}Tc will have decayed to the stable nuclide ^{99}Ru . Since technetium does not occur naturally on the earth in significant quantities, its geochemical properties must be inferred from experimental and theoretical considerations. At the Oklo reactors approximately 730 kg of ^{99}Tc were produced. It is fortunate that we can study the isolation and transport of this extinct radionuclide by measuring the isotopes of ruthenium. Four isotopes of this element are produced by fission— ^{99}Ru , ^{101}Ru , ^{102}Ru , and ^{104}Ru . The latter three are produced “instantaneously”; i.e., the isobaric precursors are short-lived relative to the time scale of relevant geologic processes. The formation of fissiogenic ^{99}Ru is delayed by the long-lived precursor ^{99}Tc . If, at some time within approximately 1 million yr after their production, conditions were such that ruthenium and technetium were chemically fractionated, then, the fractionation would be observed today by depletion or enrichment of ^{99}Ru in relation to the other fissiogenic isotopes of ruthenium.

Like all the fissiogenic elements, isotopes of ruthenium separated from the Oklo reactors may represent a complex mixture of a natural component and various nuclear components. Figure 1 shows the isotopic composition of three of the principal ruthenium components. Natural ruthenium is composed of seven isotopes; three of them (^{96}Ru , ^{98}Ru , and ^{100}Ru) are not produced by fission. Consequently, the natural component can be removed easily by subtracting from the measured isotopic abundances the appropriate natural quantities of ^{99}Ru , ^{101}Ru , ^{102}Ru , and ^{104}Ru relative to ^{96}Ru or ^{98}Ru . Fission product abundances of ruthenium, reported in Table 2, are residuals of the total ruthenium corrected for the natural component. They represent a

Figure 1 Relative abundances of isotopes of ruthenium from different sources. Samples from the reactor zone usually contain ruthenium with the isotopic composition of the ^{235}U fission product. Samples from the periphery contain various proportions of natural and fissiogenic ruthenium.

mixture of various nuclear components—those produced by fission of ^{235}U and ^{239}Pu during the period of sustained nuclear reaction and one produced by spontaneous fission of ^{238}U during the entire 2×10^9 yr since the rocks were formed. In samples from the reactor zones, natural ruthenium and that produced by spontaneous fission are an insignificant portion of the total abundance. Outside the zones of criticality, both

components may be important constituents. Because of the large natural component in the peripheral samples, there are large uncertainties in the residual, fission-produced ruthenium. Therefore no correction for ^{238}U spontaneous fission was attempted (compare with Gancarz et al., 1980). No conclusion is significantly affected by this omission.

An additional complication that must be considered is that both ^{99}Ru

Table 2 Oklo Ruthenium Inventory and Isotopes

Sample	Duration (t), 10 ⁵ yr	FP Ru, 10 ⁻⁶ g/g rock	$\frac{(^{99}\text{Ru} + ^{100}\text{Ru})}{(^{101}\text{Ru} + ^{102}\text{Ru})_{\text{meas}}}$	$\frac{^{102}\text{Ru}}{^{101}\text{Ru}_{\text{meas}}}$	99*†	Ru*‡	Δ*§	Maximum time, T _p ,¶ 10 ⁵ yr
Reactor Zone 2								
1408/4-SC36-CLSA	1	3.85 × 10 ²	0.6040	0.8556	0.795	0.854	0.931	8.2
	3				0.798	0.868	0.919	7.7
	5				0.800	0.874	0.915	7.6
1410/3-SC36-CLSA	3	1.00 × 10 ³	0.5200	0.8737	0.611	0.770	0.794	4.9
1413/3a-SC36-CLSA	3	6.04 × 10 ²	0.5371	0.8760	0.516	0.632	0.816	5.2
1413/3b-SC36	3	5.62 × 10 ²	0.5084	0.9746	0.481	0.620	0.776	4.6
1418a-SC36-CLSA	3	8.25 × 10 ²	0.4892	0.8825	0.534	0.715	0.747	4.2
1418b-SC36	3	8.25 × 10 ²	0.4892	0.8825	0.531	0.711	0.747	4.2
1421/5-SC36-CLSA	-	5.72 × 10 ¹	0.7596	0.8483	-	-	-	-
1424/5-SC36-CLSA	3	3.21	0.7017	0.8339	0.253	0.238	1.06	-
1425/1-SC36-CLSA	3	5	0.6624	0.8323	0.199	0.198	1.01	-
1892-SC36-CLSA	3	6.7 × 10 ⁻¹	0.7929	0.8651	0.189	0.157	1.21	-
1897/5-SC36	-	1.08 × 10 ¹	0.5832	0.8476	-	-	-	-
1899/5-SC36	-	5.87 × 10 ⁻¹	0.6150	0.8515	-	-	-	-
1901-SC36-CLSA	3	1	0.6617	0.8601	5 × 10 ³	5 × 10 ³	1	-
3548-KN50	3	1.17 × 10 ³	0.5836	0.8775	0.697	0.781	0.892	6.9
323-KN50	3	1.53 × 10 ²	0.6612	0.8624	0.948	0.941	1.01	-
401/3-2L-CLSA	3	6.07 × 10 ²	0.6243	0.8618	0.717	0.755	0.949	9.2
404/4-2L-CLSA	3	6.39 × 10 ²	0.6167	0.8739	0.516	0.550	0.939	8.6
1177-2'P'-CLSA	3	7.27 × 10 ²	0.5369	0.8818	0.432	0.526	0.821	5.3
1179-2'P'-CLSA	3	6.85 × 10 ²	0.5296	0.8839	0.351	0.433	0.812	5.1
1181-2'P'-CLSA	3	6.42 × 10 ²	0.6310	0.8807	1.13	1.18	0.958	9.7
1184-2'P'-CLSA	3	6.15 × 10 ²	0.5478	0.8911	0.713	0.852	0.836	5.6
1187-2'P'-CLSA	3	9.21 × 10 ²	0.6252	0.8955	0.652	0.683	0.955	9.5
Reactor Zone 3-4								
1763-SC53	3	2.58	0.5846	0.8333	0.692	0.785	0.881	6.5
1763-SC53¶	3	2.58	0.5846	0.8333	0.689	0.783	0.881	6.5
1876-SC54	3	1.34	0.7015	0.8432	0.816	0.772	1.06	-
1876-SC54¶	3	1.34	0.7015	0.8432	0.815	0.771	1.06	-

Table 2 (Continued)

Sample	Duration (t), 10^5 yr	FP Ru, 10^{-6} g/g rock	$(^{99}\text{Ru} + ^{100}\text{Ru})$ $(^{101}\text{Ru} + ^{102}\text{Ru})_{\text{meas}}$	^{102}Ru $^{101}\text{Ru}_{\text{meas}}$	99*†	Ru*‡	$\Delta^*\S$	Maximum time, T_p ,¶ 10^5 yr
1844M-SC55	3	6.70×10^1	0.6994	0.8362	1.17	1.09	1.08	-
1852M-SC55	3	1.07×10^2	0.5664	0.8383	0.888	1.04	0.854	5.9
1856-SC55	3	4.51×10^1	0.6593	0.8366	0.759	0.763	0.995	16.2
1860-SC55	3	2.84×10^1	0.6069	0.8378	0.834	0.911	0.915	7.6
1864-SC55	3	1.17×10^1	0.6695	0.8373	0.482	0.475	1.02	-
1877-SC56	3	9.81×10^1	0.5614	0.8436	0.993	1.17	0.847	5.8
2223-SC57	3	5.30×10^1	0.5320	0.8383	1.02	1.27	0.802	5.0
Peripheral								
2650-KN224	3	6.66×10^{-1}	1.69	0.843	3.48	1.37	2.55	-
2665-KN236††	3	7×10^{-4}	0.416	1.12	0	0	-	-
2669-KN241††	3	3.96×10^{-2}	0.575	0.829	0.0438	0.0506	0.867	6.2
2673-KN244††	3	0	-	-	-	-	-	-
2690-KN255††	3	8.49×10^{-1}	2.06	0.841	1.08	0.349	3.10	-
2191-KN258	3	1.94×10^{-2}	0.619	0.885	0.282	0.302	0.933	8.3
2703-KN266††	3	3.49×10^{-2}	0.411	0.856	0.697	1.13	0.619	3.0
2197-KN268††	3	1.7×10^{-3}	0.654	0.822	0.0557	0.0565	0.985	13.0
2705-KN270††	3	1.42	0.400	0.855	1.36	2.25	0.603	2.8
2252-SCO††	3	7.4×10^{-3}	1.76	0.594	-	-	-	-
Natural			0.520	1.85				
^{235}U (thermal)			0.6635	0.8326				
^{239}Pu (thermal)			0.5148	1.017				
^{238}U (fast)			0.4732	1.032				
^{238}U (spontaneous)			0.3933	1.105				

†99* = Ratio of measured fissiogenic mass 99 to total fissiogenic mass 99 produced.

‡Ru* = Ratio of measured fissiogenic $^{101,102,104}\text{Ru}$ to total fissiogenic $^{101,102,104}\text{Ru}$ produced.§ Δ^* = Ratio of 99* to Ru*¶Maximum time interval between the end of nuclide production and fractionation of ^{99}Tr from ruthenium

and ^{101}Ru have significantly larger neutron capture cross sections than their neutron capture products, ^{100}Ru and ^{102}Ru , respectively. Consequently, some residual ^{100}Ru will be observed after correcting for natural, and the residual $^{101}\text{Ru}/^{102}\text{Ru}$ ratio will be lower relative to the fission yields of the two isotopes. To compare measured abundances directly with the quantities produced, we have combined ^{99}Tc with ^{100}Ru and ^{101}Ru with ^{102}Ru .

These comparisons are made as ratios of amounts measured to amounts produced and are presented as 99^* and Ru^* , respectively, in Table 2. Ratios less than unity represent depletion, and those greater than unity represent enrichment relative to uranium. The ratio 99^* represents fractionation of mass 99, either as technetium or ruthenium, from uranium. Differences between the values of the 99^* and Ru^* are manifestations of the fractionation of ruthenium from technetium. Such fractionation is quantified in Table 2 by Δ^* , which is the ratio

$$\Delta^* = 99^*/\text{Ru}^* = \frac{(^{99}\text{Ru} + ^{100}\text{Ru})/(^{101}\text{Ru} + ^{102}\text{Ru})_{\text{meas}}}{(^{99}\text{Ru} + ^{100}\text{Ru})/(^{101}\text{Ru} + ^{102}\text{Ru})_{\text{prod}}} \quad (4)$$

If this quantity is less than unity, technetium was preferentially lost relative to ruthenium. Values greater than unity represent fractionation of the two elements in the opposite sense.

Since ^{99}Tc and ^{99}Ru are related by time-dependent radioactive decay, the degree of technetium-ruthenium fractionation establishes limits on the time and extent of fractionation. If a technetium-ruthenium fractionation factor (f) is defined as

$$f = \frac{(\text{Tc}/\text{Ru})_A}{(\text{Tc}/\text{Ru})_B} \quad (5)$$

where A is the ratio immediately after fractionation and B the ratio immediately before, the relationship between f , Δ^* , and T_f , the length of time between the end of nuclide production and the time of technetium-ruthenium fractionation, is

$$f = 1 - \frac{1 - \Delta^*}{e^{-\lambda T_f}} \quad (6)$$

The functional relationships between T_f and f for values of Δ^* encompassing most of those measured are shown in Fig. 2. In the case of instantaneous fractionation ($T_f = 0$), the fractionation factor is equal to Δ^* . An upper limit is placed on the time of fractionation when $f = 0$, i.e., when all the ^{99}Tc is removed from the ruthenium. This limit is given in the column headed Maximum time, T_f , in Table 2. Calculations using Eq. 6 are based on a model of instantaneous production, which establishes an

Figure 2 Functional relationship between the time of technetium-ruthenium fractionation (T_f) and the fractionation factor (f), which is defined by Eq. 5 in the text. The relationship between T_f and f is defined by Eq. 6. Values shown for Δ^* represent extremes measured in the reactor zones.

upper limit on the time that could have elapsed between the end of nuclide production and the fractionation of ruthenium and technetium. A more realistic model of uniform and continuous production will lower the value of T_f by approximately one-half the production interval. The basic conclusion is unchanged, however. Chemical or physical processes fractionated technetium from ruthenium at some time less than a million years after the reactors ceased criticality.

Material Stability and Element Transport at the Reactor Site

Stability of Materials in the Reactor Zones. Data and calculated isotopic inventories of samples from two zones of criticality are presented in Tables 1 and 2. Although these two zones are generally deficient in fissiogenic neodymium, ruthenium, and the mass 99 elements, technetium and ruthenium, the degree of loss is significantly different in each. Ignoring samples from the periphery, which cannot be fit by the solutions to the differential equations, we find that all the samples from zone 2 are deficient in neodymium and all but one are depleted in ruthenium and/or technetium. The lone enriched sample (1181) has an anomalously low fraction of resonance neutrons. As little as 2% and as much as 30% of the fission-produced neodymium is missing from the zone 2 rocks. A simple average of the 13 samples indicates that 16% of the fissiogenic neodymium is missing from the samples. Similarly, 26% of the fissiogenic $^{101,102,104}\text{Ru}$ and 34% of the mass 99 elements are also missing. Significant proportions of these nuclear products have been removed from virtually all the rocks in zone 2. To estimate the quantity of these elements missing from the reactor zone, we normalized the deficient quantity from each sample to the uranium content in the

same sample. The simple average of these normalized abundances was multiplied by the total uranium tonnage in zone 2 (Naudet, 1978b). Such an estimate shows that ~140 kg of neodymium, ~100 kg of ruthenium, and ~70 kg of mass 99 (ruthenium and/or technetium) have been lost from reactor zone 2.

In contrast, similar estimates for zone 3-4 show a loss of ~8 kg of neodymium, ~6 kg of ruthenium, and ~4 kg of mass 99. An order of magnitude more of these elements has been lost from zone 2 than from zone 3-4. These variations reflect not only differing quantities produced in the two regions but also differences in the proportions lost. Proportionally, zone 3-4 has lost 2 to 3 times less of the same nuclear products than zone 2. In zone 3-4 no significant proportion of neodymium is missing, but 8% of the ruthenium and 15% of the mass 99 elements are missing. In this zone the samples are variably depleted and are enriched in all three elements; this suggests not only a small net loss but also a local redistribution of elements, as opposed to the pervasive loss from zone 2.

Cowan (1978), considering the nature of element redistribution processes, concluded that two types of processes controlled the transport of elements at Oklo. First, the nuclear reaction products must escape from their uraninite host. The solubility of UO_2 is so small that loss by dissolution and recrystallization is unlikely. This conclusion is supported by abundant observational evidence that uraninite has been mechanically stable since the time of reactor criticality (Dran et al., 1978). Consequently, a solid state process must be responsible for the release of nuclear products from the host grains. Escape of daughter products by recoil from alpha decay will not account for the observed deficiencies, but loss by solid-state diffusion has been demon-

strated to be a plausible mechanism for the loss of lead produced by the decay of uranium (Gancarz et al., 1980) and seems to be a likely explanation for the loss of fission products. Once the nuclear products are no longer contained by the host grain, a second set of processes controls their migration. These involve hydrology and chemistry controlling the distribution of the elements between mobile and immobile phases. The two sets of processes are interdependent. A sample deficient in a certain element must have sustained both processes. It is unlikely that processes of the second type controlled the amount of elements lost. Arguments presented later in this paper show that partial removal of trace elements by such processes requires an almost unique set of conditions. In general, such elements will be completely retained or removed by transport in a mobile phase. We feel that these losses must have been controlled primarily by diffusion of fissionogenic elements from uraninite. Differences in the fractional amounts of an element lost from different samples probably reflect differences in the rate of diffusion.

The critical value in examining diffusive loss is the effective diffusion coefficient, D/a^2 , where D is the Fickian diffusion coefficient and a is the effective radius of the host grain. To evaluate this parameter, we developed a model that considers two different aspects of the thermal period. During the time of nuclear criticality, ruthenium and technetium were produced by nuclear reactions and simultaneously diffused from the uraninite host. In addition, ^{99}Tc was destroyed and ^{99}Ru was produced by radioactive decay. This period of production was assumed to be 3×10^5 yr. For simplicity, the production function for these two elements was taken to be proportional to the concentration of ^{235}U and the respective

fission yields. After the period of nuclear criticality and for the remainder of the thermal period, there was no production; the two elements continued to diffuse, however; and ^{99}Tc continued to decay to ^{99}Ru . The interval from the end of criticality to the end of the thermal period was T_f .

Average abundances lost from each of the two reactor zones, calculated from the data in Table 2, are presented in Table 3. In the context of the model, these values were used to calculate D/a^2 for ruthenium diffusion ($^{101}\text{Ru} + ^{102}\text{Ru}$) from uraninite grains in the two reactor zones. In zone 2 the effective ruthenium diffusion coefficient was $7.8 \times 10^{-8}/\text{yr}$, and in zone 3-4 the corresponding value was $2.5 \times 10^{-8}/\text{yr}$. The larger value in samples from zone 2 indicates more diffusive loss than in zone 3-4.

Diffusion coefficients for ^{99}Tc cannot be calculated because the ratio $^{99}\text{Ru}/^{99}\text{Tc}$ at any time is not known. If it is assumed that the fraction of ^{99}Ru lost is half the fractional loss of $^{101}\text{Ru} + ^{102}\text{Ru}$, then the quantity of mass 99 lost as ^{99}Tc can be calculated. This seems to be a reasonable assumption since the residence time of the daughter ^{99}Ru during the thermal period was roughly half that of isotopes with no long-lived precursor. On the basis of this assumption, ~25% of the ^{99}Tc produced in zone 2 was lost as ^{99}Tc , in comparison with an approximately 30% loss of $^{101}+^{102}\text{Ru}$. In reactor zone 3-4 the corresponding values are 15 and 20%, respectively. These values suggest that the effective diffusion coefficients for technetium were about the same as those calculated for ruthenium. Again if we assume that the fractional loss of ^{99}Ru was half that of $^{101}+^{102}\text{Ru}$, 46 kg of the mass 99 deficiency in zone 2 can be attributed to loss of ^{99}Tc , and, similarly, 2.2 kg of ^{99}Tc were lost from zone 3-4.

Differences in the proportions of each element lost and, as a result,

calculated diffusion coefficients correlate with differences in the intensity of the nuclear reactions in each of the two zones (Table 1). Thermal plus resonance neutron fluences in zone 2 were $\sim 10^{21}$ neutrons/cm², whereas in zone 3-4 they were $\sim 10^{20}$ neutrons/cm². Energy outputs were determined by calculating the ²³⁵U fissioned in each sample, as discussed in the methods section, and then determining the total in each reactor zone by the previously discussed method of uranium normalization. Using a factor of 1 MW-d/g of ²³⁵U fissioned, an energy output of 1.5×10^4 MW-yr was estimated for zone 2 and 1.5×10^3 MW-yr for zone 3-4; these values correspond to thermal loadings of 140 W/m² and 5 W/m², respectively. These values bracket the predicted thermal loadings for proposed repositories during the thermal period (Raines et al., 1981). In this respect the Oklo reactors represent an excellent natural analog to the geologic repositories. The temperatures and radiation doses were significantly different in these two zones. Since the different element retention properties appear to correlate with these reactor operating conditions, it seems reasonable that the period of element redistribution coincided with the 0.5 to 1 million yr thermal period during and after nuclear criticality. It is likely that the differences in the rates of diffusive loss are a function of differences in phenomena temporally associated with the nuclear reactions. The values of D/a^2 for ruthenium and technetium are two or three orders of magnitude greater than those calculated for the diffusive loss of lead. Lead loss has proceeded continuously for 2 billion yr during the periods of diagenesis and post-diagenesis under milder conditions than those of the thermal period. The differences between the rates of diffusion of lead and ruthenium and technetium probably

reflect the temperature difference between ambient geologic conditions and the conditions in the natural reactors during the thermal period.

Element Transport. Distances that elements have been transported are inferred by their excesses in rocks peripheral to the zones of criticality. Analytical results from peripheral samples taken from within a few meters of the zones are given in Table 1 and 2. The location of these samples and the reactor zones are in Table 1. With a single exception, the rocks are characterized by low neutron fluences, small uranium concentrations, and ²³⁵U/²³⁸U ratios close to normal. In principle, leakage neutrons from the reactor zones could have induced nuclear processes and created nuclear products within the rocks. We assumed that this was the case and compared the calculated abundances of nuclear products produced in the rocks with measured abundances to evaluate excesses and deficiencies. All data in the tables and figures were interpreted and presented in this manner. In fact, this is a conservative approach, since all the nuclear products may have been transported from the critical zones and deposited in these peripheral rocks, and thus any measured isotopic anomaly would indicate an excess. Basic conclusions with respect to quantities and distances are not significantly altered by considering or ignoring local production of fissionogenic elements.

Figure 3 shows the spatial relationships between the reactor zone that are deficient in fissionogenic elements, and peripheral rocks, some of which, even by conservative estimates, contain excesses of the same elements. Three of the peripheral samples contain excess ruthenium; two are enriched in ⁹⁹Tc relative to ruthenium; and one is enriched in fissionogenic neodymium. Each of these samples was between 10 and 15 m from the nearest reactor zone, as identified by

Table 3 Average Abundances of Fission Products in Oklo Reactor Zones

Zone	Neodymium, 10^{-6} g/g U			Mass 99, 10^{-6} g/g U			^{101,102} Ruthenium, 10^{-6} g/g U		
	Produced	Remaining	Deficient	Produced	Remaining	Deficient	Produced	Remaining	Deficient
Zone 2	4250	3600	650	860	530	330	1300	940	360
Zone 3-4	409	360	49	84	62	22	125	100	25

Table 4 Relative Locations of Reactor Zones and Peripheral Samples

Sample	X,* m	Y,† m	Z,‡ m
Zone 2	+9-+20	+30-+50	357-368
Zone 3-4	+25-+43	-45--20	340-360
Zone 5-6	+30-+45	-7 5-+30	340-357
KN-224	+25 5	-39 2	362
KN-236	+32 5	-45 7	345
KN-241	+36 3	-56 7	341
KN-255	+25 2	+10 0	360
KN-258	+35 1	+19 8	351
KN-266	+39 1	-11 2	345
KN-268	+29 8	+27 0	353
KN-270	+4 0	+57 5	362

*Approximately east-west

†Approximately north-south.

‡Vertical (0 0 is an arbitrary datum, distances are measured upward from this datum.)

Figure 3 Projection of north-south section of Oklo mines from $Y = -60$ to $Y = +60$ showing the locations of peripheral samples relative to the reactor zones at the Oklo mine. Nd^* and Ru^* represent fractionation of neodymium and ruthenium relative to uranium, and Δ^* represents fractionation of ^{99}Tc relative to ruthenium. Open symbols ($\circ$, $\triangle$, $\square$) represent relative deficiencies of elements, and closed symbols ($\bullet$, $\blacktriangle$, $\blacksquare$) represent relative excesses.

Gauthier-Lafaye, Besnus, and Weber (1978). These distances are taken to be representative of those over which the elements were transported. Sample locations relative to the nearest reactor zone are given by Naudet and Renson (1978a). Samples KN-244 and KN-255 are in the same stratigraphic unit but up the stratigraphic dip from the nearest reactor zone, whereas KN-256, KN-258, and KN-268 are downdip. The remaining three peripheral samples were located between reactor zones. As shown in Fig. 3, for all samples updip from the reactors, $\Delta^* > 1$ and, for those either downdip

or between reactors, $\Delta^* < 1$. Therefore the direction of movement of technetium in relation to ruthenium was updip. This is consistent with mobilization by convecting hydrothermal fluids. There is no clear relationship between Ru^* and sample location.

To determine if the concentrations of excess ruthenium in the peripheral samples can reasonably account for the quantities lost from the reactor zones, we assumed that the amount missing from each zone was homogeneously distributed from a point source lying at the center of each reactor throughout a sphere of a given

Figure 4 Change in concentration of ruthenium distributed homogeneously through an increasingly large spherical rock mass with a density of 3 g/cm^3 in two reactor zones. ●, near zone 3-4; ■, near zone 2. Sample distances are from the center of the nearest reactor zone.

radius. The consequences are shown in Fig. 4, in which the concentration in different-sized spheres about each of the two reactor zones is defined by the curves. Peripheral samples containing excess ruthenium are also plotted. The radius values are distances from the center of the nearest reactor zone. The coincidence of the data with the model concentrations suggest that ruthenium arising from the reactor zones is largely contained within a few tens of meters.

The removal, transport, and redeposition of the three elements involves the second set of processes mentioned in the previous section. Elements released from containment must be suspended in a mobile phase and carried away from the rocks where they were produced. We evaluated the apparent concentration

of technetium, ruthenium, and neodymium in the aqueous phase at Oklo by considering a model of continuous flow through a reactor zone. We considered that fissiogenic elements were produced instantaneously at the start of the thermal period in 200 m^3 of rock with a 10% porosity. The volume of water that passed through a reactor zone was estimated from the limit on the quantity of uranium that could have been removed from the zone and redistributed into the surrounding ore. This quantity is the amount which, if it had moved during the thermal period, would be observable today as a 0.1% shift of the $^{235}\text{U}/^{238}\text{U}$ ratio from "normal." This is the analytical uncertainty of measurements on ores which generally have normal $^{235}\text{U}/^{238}\text{U}$ ratios. We use the average $^{235}\text{U}/^{238}\text{U}$ ratio for zone 2, assume that this uranium could have been redistributed into ore now containing $1.25 \times 10^9 \text{ g}$ of uranium (approximately one-eighth of the total estimated reserves), and calculate that $6 \times 10^6 \text{ g}$ of uranium could have been removed from a reactor zone. If the incoming water was barren and that leaving the reactor zone contained $5 \times 10^{-9} \text{ g U/ml}$, a reasonable concentration in natural waters (Rogers and Adams, 1967), then 10^{12} l of water passed through the reactor zone. This volume of water translates to molar concentrations of 10^{-10} for technetium, ruthenium, and neodymium in the fluids passing out of reactor zone 2. To estimate the concentrations, we made some rather broad assumptions. For example, we assumed that the uranium concentration in the fluid phase was like that in near-surface groundwater; this may not be the case for upper crustal rocks. Therefore these estimates may well be incorrect by several orders of magnitude. Certainly, however, they represent the most meaningful observation available on the concentration of these rare elements in aqueous solutions in crustal rocks.

To examine possible controls of the aqueous concentrations of these elements, we considered the thermodynamic stability of their oxides with respect to aqueous species. Solubilities are influenced by the formation of complexes, the ionic strength of the aqueous phase, the formation of solid solutions, multiple host phases, etc. Since virtually nothing is known about either such complexities or the conditions at Oklo during the thermal period, only the simplest cases were considered. The following reactions describe the oxidation of insoluble tetravalent oxides to produce more soluble oxidized species and the simple aqueous dissolution of oxide or hydroxide phases:

The change in either the free energy of reaction (ΔG_R) or the equilibrium constant for each reaction is either from the literature or calculated from the free energies of formation (ΔG_f°) for each compound (Cobble, Smith, and Boyd, 1953; Pizzini and Rossi, 1971; Chatterji and Vest, 1971; Tobias and Garrett, 1958; Spedding and Miller, 1952; Lemire and Tremaine, 1980; Chirico and Westrum, 1980; Tremaine and Goldman, 1978; Wagman et al., 1969). Association of hematite spots (Gauthier-Lafaye, Besnus, and Weber, 1978) suggests that the oxygen fugacity was controlled by the hematite-magnetite buffer. The pH was assumed to be 7.5. These conditions describe the middle

of the uranium ore stability field at 25°C as defined by Brookins (1978). The oxygen fugacity as a function of temperature was calculated from the temperature dependent equation of the hematite-magnetite buffer (Huebner, 1971). The pressure correction to the buffer is negligible (Huebner, 1971). We calculated the temperature dependence of ΔG_R for the oxidation of tetravalent TcO_2 from the van't Hoff equation assuming the enthalpy of reaction to be independent of temperature (Krauskopf, 1967). The temperature dependence of the uranium and plutonium reactions was determined from the data presented by Lemire and Tremaine (1980). Changes in the free energy of formation of the neodymium species as a function of temperature were calculated from data of Tremaine and Goldman (1978) and Chirico and Westrum (1980). Neither the temperature dependence of ΔG_f° for RuO_4^{-2} or the enthalpy of formation of this species could be found in the literature. Consequently, we have limited the thermodynamically controlled concentration of RuO_4^{-2} by two sets of assumptions. We calculated the lower limit assuming ΔG_R was invariant with temperature and established the upper limit assuming that ΔG_f° of the aqueous species was invariant with temperature but using the temperature-dependent value of ΔG_f° for RuO_2 (Chatterji and Vest, 1971; Pizzini and Rossi, 1971).

The equilibrium concentration of these aqueous species is plotted as a function of temperature in Fig. 5, which includes a band representing the abundances of technetium, ruthenium, and neodymium in the aqueous fluid at Oklo. An uncertainty of two orders of magnitude was superimposed on the calculated $10^{-10}M$ abundance to demonstrate that the conclusions are insensitive to such uncertainties. Note that the diagram encompasses 60 orders of magnitude

Figure 5 Temperature dependence of the equilibrium concentration of various aqueous species. The envelope for RuO_4^{2-} encompasses limits of possible concentrations. The range of possible abundances of Ru, Tc, and Nd in an aqueous phase at Oklo is superimposed on the diagram. Equilibrium concentrations greater than those in the aqueous phase indicate chemical processes and conditions that could have removed elements from the reactor zones.

in concentration. If a particular chemical reaction is to be considered as a viable control of the concentration of an element in the mobile aqueous phase, the equilibrium concentration shown by the curves in Fig. 5 must lie above the band representing the element concentrations in the Oklo fluid. For instance, at 25°C only the dissolution of $\text{Nd}(\text{OH})_3$ could produce enough aqueous ions to remove the observed amount of this element. The simple dissolution of the tetravalent oxide of ruthenium is insufficient to account for the observed deficiencies at any temperature. The concentration of oxidized ruthenate ions shows an enormous temperature dependence, however. At temperatures between 250 and 425°C, the oxidation of RuO_2 will account for the loss of this element from reactor zone 2. Similarly, the oxidation of TcO_2 to form the pertechnetate anion will account for the technetium losses at fluid temperatures between 100 and 150°C. These are within the estimated temperature range in the reactors during the thermal period. *Oxidation of technetium and ruthenium and transport of their oxyanions by convecting hydrothermal fluids can account for the deficiency of these elements in the Oklo reactor zones.* The inferred temperature dependence provides additional evidence of mobilization during the $\sim 10^6$ -yr thermal period.

Figure 5 suggests that hydrologic transport was not the primary control on the quantities of elements lost from the Oklo reactors. For example, if the fluid temperature was 125°C, just hot enough to remove the appropriate quantity of technetium, virtually no ruthenium or neodymium would have been transported away. If the fluid temperature was 350°C, hot enough to remove necessary quantities of ruthenium, all the technetium would be gone. Furthermore, if the temperature-dependent concentration of Nd^{+3} is extrapolated to this tem-

perature, neodymium would have been quantitatively retained. Since roughly equal quantities of each of these three elements were removed from each reactor zone, it is likely that the amount removed was controlled by the rate of release by diffusion of each element from the host phase rather than by the rate of subsequent transport away from the rock.

The concentration of uranium in the aqueous phase, calculated from thermodynamic data for the oxidation of the tetravalent oxide, is 10^{14} less than that used in estimating the amount of water that passed through a reactor zone. At these concentrations, a volume of water comparable to that in the oceans would be necessary to remove the quantity of uranium estimated to be missing from a reactor zone. We feel that the concentrations measured in natural water samples are more reasonable; the differences probably reflect the importance of chemical processes other than the simple one illustrated in Fig. 5.

The same caveat is applicable to the calculated plutonium abundances in aqueous solutions. In the Oklo samples, however, there have been no measured excesses of ^{235}U relative to ^{238}U ; this would indicate the redistribution and fixation of ^{239}Pu . The extreme insolubility of this element, as shown in Fig. 5, is, therefore, consistent with these observations.

The calculations show that $\text{Nd}(\text{OH})_3$ has a retrograde solubility. Sufficient quantities could have been removed only at temperatures below 75°C. Although data on the temperature dependence of this reaction were not available above 75°C, it appears that the compound is extremely insoluble at higher temperatures. This retrograde temperature dependence suggests that neodymium was redistributed after the thermal period. Such observations are consistent with observations and assumptions about neodymium which are presented in

other portions of this paper. Calculations of mass inventories assume that neodymium was not removed from the rocks until after the sustained criticality ceased. Neodymium was redistributed on a smaller scale than ruthenium or technetium.

An aspect of the waste management program that has received considerable attention is the measurement of sorption ratios. This ratio is defined as the concentration of an element on the solid phase relative to its concentration in a coexisting aqueous phase. The magnitude of the ratio is a measure of the retardation of an element by retention on an immobile phase in the presence of a mobile one. We have evaluated the sorption ratio using the expression (Davis and DeWiest, 1966)

$$K_d = \frac{(V_w/V_i) - 1}{\rho_b/n}$$

where K_d is the distribution constant (this assumes equilibrium processes, but no such interpretation is intended for the values calculated from this expression), ρ_b and n are the bulk density and porosity of the geologic media, and V_i is the velocity of the chemical species i . We observed that ruthenium and technetium were transported distances of a few tens of meters within 10^6 yr of nuclear criticality. Thus rates of transport were on the order of 10^{-5} m/yr. Velocity of the fluid phase was calculated from a model of continuous flow for 10^6 yr through a 200-m² face of the model reactor zone. Such considerations indicate a rate of fluid movement of 5 m/yr. The resulting sorption ratio is on the order of 10^4 cm³/g. This value, which is no more accurate than several orders of magnitude, is, nevertheless, a very large value and points out the remarkable ability of the Francevillian pelitic sandstones to contain these nuclear products even

after they are released from uraninite. The extreme temperature dependence of the oxidation-reduction reactions of ruthenium and technetium suggests a suitable mechanism for this retention capacity. Figure 5 shows that as the fluids left the hot reactor zones and began to cool, they quickly became supersaturated with respect to ruthenium and technetium. Supersaturation of the ruthenate ion occurs at a temperature 150 to 200°C higher than the pertechnetate. If reduction and oxidation are the chemical processes controlling the movement of these elements, ruthenium should be found closer to the reactors than technetium and the elements should form aureoles reflecting temperature profiles around the hot zones. Distribution coefficients deduced from the Oklo data are 10^2 to 10^4 times greater than the values deduced from sorption studies on granite, argillite, and tuff (Erdal et al., 1979a, 1979b; Vine et al., 1980). These differences most likely result from differing reducing conditions in the various systems. Oxygen fugacities as low as those prevalent at Oklo have not been produced and maintained in laboratory measurements of sorption.

Conclusions

In the context of the multiple barrier philosophy of nuclear waste disposal, geochemical considerations must address two issues—the stability of engineered barriers in the geologic environment and the effectiveness of such an environment as a redundant container. The fossil reactors at the Oklo mines offer an unprecedented opportunity to address these issues and to examine possible geochemical processes and conditions that may have been responsible for their stability or instability. In many respects they are directly analogous to proposed nuclear waste repositories. Radionuclides identical to those that

will be placed in repositories were contained in crystalline uraninite. This crystalline phase has been mechanically unaltered in the 2 billion yr since the period of sustained nuclear reactions. Despite this mechanical stability, selected radionuclides have been released from the uraninite, probably by solid-state diffusion. The quantities removed from the rocks were limited primarily by the rate of diffusion from the crystalline host, a rate that was dramatically accelerated by high temperatures and/or large radiation doses associated with the nuclear reactions. Failure of the containment in this sense occurred on a time scale of less than 10^6 yr.

After release from their host phase, ruthenium, ^{99}Tc , and neodymium were removed from the reactor zones and redistributed into the surrounding rocks. Conditions in the Francevillian sediments were extremely effective in containing these elements. The apparent rate of movement of the elements was on the order of 10^{-5} m/yr, in the presence of fluids that were convecting as fast as 5 m/yr. Temperature-dependent reduction-oxidation reactions provide an excellent accounting of both the transport and redeposition of ruthenium and technetium at Oklo. At the electrochemical potentials and pH conditions that must have prevailed, equilibrium concentrations of ruthenate and pertechnetate in waters at elevated temperatures were sufficiently large to transport the missing quantities away from the reactor zones. As the temperature decreased, equilibrium concentrations of both anionic species decreased dramatically, and their reduced form could have been deposited from cooling fluids in rocks adjacent to the hot regions of nuclear criticality. The equilibrium concentration of Nd^{+3} at elevated temperatures was too small for the same hot fluids to remove neodymium. The redistribu-

tion of neodymium occurred at later times after the reactors had cooled.

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Part IV Repository Design Technology

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National Waste Terminal Storage Conceptual Reference Repository Description

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The conceptual reference repository description (CRRD) discusses, from a conceptual engineering standpoint, the structures, systems, equipment, and operations necessary to (1) receive unprocessed spent fuel assemblies in standard shipping casks, (2) unload these assemblies, (3) place them in canisters, (4) transport the canisters to underground storage locations in the salt dome, and (5) place the canisters in terminal storage. The CRRD also elaborates on the concepts for retrieval and recovery of the spent fuel after burial and describes the development of the shafts and the underground areas, as well as the supporting operational utility and administrative features of the repository.

Introduction

This paper discusses the conceptual reference repository description (CRRD) for the terminal storage of spent, unprocessed fuel assemblies and low-level transuranic waste (LLW-TRU) resulting from commercial nuclear power generating operations. The repository facilities will be capable of safely receiving, unloading, and inspecting the incoming spent fuel assemblies, placing them in canisters, and placing the canisters in terminal storage in a salt dome. The annual processing capability and total capacity of the repository are one-third of the anticipated output of all the com-

mercial nuclear power plants in the United States. As a regional repository, for example, this would be sufficient to serve the southeastern portion of the United States. Retrieval or recovery of the canisters at a later date, if required, is also provided for. The facility is designed in such a way that it can be modified for terminal storage of high-level waste (HLW).

The CRRD is based on the following previously prepared conceptual design reports:

- National Waste Terminal Storage (NWTS) for spent unprocessed fuel in a bedded salt formation (Kaiser Engineers, 1978) (a conceptual design for receiving previously canistered unprocessed spent fuel assemblies and placing them in terminal storage in bedded salt)
- National Waste Terminal Storage Repository Number 1 (Stearns-Roger, 1978) (a conceptual design for receiving waste from reprocessed spent fuel assemblies and placing it in terminal storage in a salt dome)
- Spent fuel receiving and packaging facility conceptual design (Rockwell Hanford Operations and Kaiser Engineers, 1978)

These three concepts were integrated into a design for a facility to receive unprocessed spent fuel assemblies and place them in terminal storage in a salt dome. Changes were made in the basic conceptual designs only when necessary to integrate them into a single facility. This description

is not intended to be a complete conceptual design, and no attempts have been made to optimize the design. Additional engineering and analysis will be required to determine the final configuration and to perform design optimization studies.

This repository description is based on a hypothetical site model of salt domes and surface characteristics typical of the Gulf Interior Region of the United States. The CRRD will be useful in actually selecting a site and preparing repository conceptual, preliminary design, and preliminary safety analysis reports.

General Description

The NWTS-CRRD consists of a 2100-acre repository within a salt dome for storage of spent fuel assemblies and LLW-TRU. A 400-acre surface facility, shown in Fig. 1, receives and handles the nuclear waste and transfers it to the underground area. The repository has a central group of vertical-access ventilation shafts with storage rooms parallel to the long axis of the salt dome and on each side of the central shafts. A shaft pillar at the center of the underground development, beneath the surface facilities, encompasses the shaft station and underground operating facilities (Fig. 2).

The principal surface element is the waste-handling building, where spent fuel assemblies are received, unloaded, canistered, and transferred to the terminal storage area. The building is constructed over the

waste-transfer shaft. Auxiliary facilities include four additional shafts for men and materials handling, salt handling, and underground ventilation; surface salt storage; a boiler house for heating and process steam; an electrical substation; standby generators; administration, security, and maintenance buildings; a warehouse; water and sewage treatment plants; and other support and utility facilities necessary to operate the repository.

Summary of the Principal Design Bases

Age of Spent Fuel. Spent fuel shipped to the NWTS facility is nominally 10 yr old (measured after discharge from the utility reactors); however, the facility can accept and process occasional shipments of assemblies that are only 3 yr old. The age of the spent fuel affects the amount of decay heat generation and the amount of radiation shielding required; both decrease for older fuel. Repository capacity per acre, which is determined by the heat generation, is based on 10-yr-old fuel. Shielding characteristics are determined by the source strength of individual fuel assemblies and are based on 3-yr-old fuel.

Low-Level Transuranic Waste.

Low-level transuranic waste (LLW-TRU), immobilized in concrete, is received from commercial sources in steel drums that have been loaded into returnable cargo containers. These wastes are stored in the same level in the salt dome as the spent

Figure 1 Plan of surface facility. Central area containing repository surface facilities, including the unfenced parking lots and the visitor's center is approximately 400 acres. The area enclosed by the outer perimeter fence is approximately 385 acres. The high security double-fenced inner area is approximately 110 acres. The mined salt stockpile occupies approximately 50 acres and provides approximately 4,000,000 tons of salt for backfill. Prevailing winds are from the southeast and the northeast. All ponds shown are lined with impervious materials.

Figure 2 Repository isometric.

fuel. Wastes generated on site are immobilized in concrete, placed in drums, and stored in a similar manner.

Retrieval. Retrieval is defined as removing canisters and LLW-TRU from underground storage and shipping them from the facility. Retrieval can be started at any time during the first 5 yr of operation. For purposes of this project, the retrieval rate is the same as the initial storage rate. Retrieval requires that all waste handling processes, storage operations, and equipment be reversible during this period. The retrieval method for this project uses storage holes with carbon-steel sleeves and removable shield plugs in open storage rooms that have not been backfilled.

Repository Capacity and Receipt Rates.

A total of approximately 260,000 spent fuel assemblies will be received during the lifetime of the repository. Maximum spent fuel throughput rate is approximately 15,200 assemblies per year—8900 boiling-water reactor (BWR) assemblies and 6300 pressurized-water reactor (PWR) assemblies. The receiving distribution is estimated to be two PWR assemblies to three BWR assemblies. During the initial 5-yr retrieval phase (the period during which emplaced fuel elements must be easily removable from the repository) approximately 18,000 fuel assemblies will be received, canistered, and placed in the repository. The total spent fuel quantities to be stored are based on an average decay heat loading of 60 kW/acre over the repository storage area. The receipt rates are based on projections of spent fuel discharge rates, which, in turn, are based on the low-growth projection of nuclear power (Alexander et al., 1977). Table 1 gives the estimated fuel discharge and accumulation rate for one-third of the commercial reactors in the United States.

Fuel receipt estimates are based on the low-growth curves, assuming an 80% capacity for the power plants. If the current historical plant capacity factor (approximately 60%) is used, the annual receipt rate drops, and the time to fill the repository is extended.

The total low-level waste (LLW) quantities stored will be approximately 26,000 drums, including LLW generated in the repository. Maximum throughput rate is approximately 1300 drums per year. Estimated quantities of drums that will be received are based on a Union Carbide Nuclear Division letter (1977). The wastes generated on site are from the cleanup of the spent fuel lag storage pool, the waste from the various decontamination systems, and the replacement of the ventilation filter. The quantities are based on projections from the conceptual design of the waste-handling building prepared by Rockwell. Table 2 gives the annual and cumulative storage requirement for LLW for the repository.

The total repository storage capacity can be significantly affected by such unanticipated salt dome features as brine pockets, uncharted boreholes, or fault planes. The transportation mode used to ship spent fuel to the repository can also affect the processing capacity of the repository significantly.

Allowable Storage Density. Canisters containing fuel assemblies are stored so that the decay heat generated by the spent fuel is limited to 60 kW/acre averaged over the entire storage area, including the total salt dome area (2100 acres) less an 800-ft buffer zone between the storage area and the edge of the dome. This restriction limits the input of heat into the salt and, thus, reduces the potential for damage caused by expansion and uplift of the salt and overburden. The canisters are stored two rows to a room, with 4-ft center-

Table 1 Fuel Discharge and Accumulation Rate for One-Third of the Commercial Nuclear Reactors in the United States*

Discharge year	Receipt year	Total national BWR power, GWe	BWR placed		Total national PWR power, GWe	PWR placed	
			Assemblies per year	Accumulated assemblies		Assemblies per year	Accumulated assemblies
1970	1980	3.1	182	0	3.3	64	0
		4.4	259	441	4.7	92	156
		7.2	423	864	7.4	145	301
		7.2	423	1,287	12.9	252	553
		11.7	687	1,974	18.2	356	909
		15.2	893	2,867	21.8	426	1,335
		17.0	999	3,866	25.7	502	1,837
		17.8	1,046	4,912	33.4	652	2,489
		18.6	1,092	6,004	37.4	731	3,220
		20.4	1,198	7,202	40.2	785	4,005
		22.0	1,292	8,494	43.8	856	4,861
		23.0	1,368	4,862	47.5	928	5,789
		25.5	1,498	11,360	56.8	1,109	6,898
		28.1	1,651	13,041	65.4	1,277	8,175
1980	1990	32.7	1,921	14,932	76.5	1,494	9,669
		37.7	2,214	17,146	88.9	1,737	11,406
		42.3	2,484	19,630	98.3	1,918	13,324
		46.5	2,731	22,361	106.7	2,084	15,408
		50.7	2,978	25,339	115.1	2,248	17,656
		55.2	3,092	28,431	124.1	2,424	20,080
		60.2	3,536	31,967	134.2	2,621	22,701
		65.4	3,841	35,808	144.8	2,828	25,529
		70.9	4,164	39,972	156.1	3,049	28,578
		76.4	4,487	44,459	167.4	3,270	31,848
		82.6	4,851	49,310	180.1	3,518	35,366
		89.1	5,233	54,543	193.4	3,778	39,144
		95.6	5,615	60,158	206.7	4,038	43,182
1990	2000						

	2000	2010	102.1	5,993	66,151	220.0	47,474
			108.7	6,384	72,535	233.2	52,029
			115.2	6,766	79,301	246.5	56,844
		2010	121.1	7,113	86,414	258.6	61,895
			124.9	7,336	93,750	266.5	67,101
			128.6	7,553	101,303	274.3	72,459
			132.5	7,782	109,085	282.4	77,975
			136.3	8,005	117,090	290.5	83,649
			140.1	8,229	125,319	298.6	89,482
			144.0	8,458	133,777	306.7	95,475
		2018†	147.8	8,681	142,458	314.8	101,624
			151.6	8,904	151,362	321.9	107,912
			155.4	9,127	160,489	328.8	114,335
	2010	2020	157.8	9,268	169,757	335.9	120,896

*Data from Alexander et al., 1977, assuming an 80% plant capacity factor.
†Emplacement begins.
‡Facility reaches capacity.

to-center spacing along the rows and 5.5 ft of spacing between the rows.

Spent Fuel Receiving and Packaging System

The spent fuel receiving and packaging system consists of the equipment and facilities necessary to receive spent fuel assemblies in shipping casks, unload the casks, and package fuel assemblies into canisters. The section housing the spent-fuel-handling facility has six sets of rail tracks into the building and is connected to the waste shaft, which carries the fuel canister into the underground storage area. Figure 3 is the plan for the waste-handling building. Receiving and packaging includes seven major activities:

- Cask receiving and off-loading
- Cask washing and cool down
- Cask unloading
- Cask decontamination
- Spent fuel storage and transfer to packaging cells
- Spent fuel packaging into canisters
- Canister transfer to the shaft area

Cask Receiving and Off-Loading.

Spent unprocessed fuel assemblies are received by railcar or truck in shipping casks containing 1 to 24 assemblies, one cask to a carrier. The cask weights can vary from approximately 26 to 100 tons.

Carrier and cask are inspected at the outer gate for shipping damage, leakage, or possible sabotage of the cask. If sabotage is suspected, the carrier and cask are moved to the isolation area for further investigation and implementation of safety measures. Carriers with uncontaminated (nonleaking) casks are washed to remove road dirt at the outside wash-down platform and then moved into the radwaste building.

Table 2 Annual and Cumulative Storage Requirement for Low-Level Waste for the Repository

Year	Drums generated at reactor (A)	Drums generated at site (B)	Total annual drums* ($\frac{1}{3}$ A + B)	Total cumulative drums for CRRD
1988	1,979	220	880	880
1989	2,117	220	926	1,806
1990	2,262	220	974	2,780
1991	2,438	220	1,033	3,813
1992	2,589	220	1,083	4,896
1993	2,741	220	1,134	6,030
1994	2,899	220	1,186	7,216
1995	3,056	220	1,239	8,455
1996	2,423	220	1,028	9,483
1997	2,575	220	1,078	10,561
1998	2,719	220	1,126	11,687
1999	2,866	220	1,175	12,862
2000	3,011	220	1,224	14,086
2001	3,147	220	1,269	15,355
2002	3,147	220	1,269	16,624
2003	3,147	220	1,269	17,893
2004	3,147	220	1,269	19,162
2005	3,147	220	1,269	20,431
2006	3,147	220	1,269	21,700
2007	3,147	220	1,269	22,969
2008	3,147	220	1,269	24,238
2009		220	220	24,458
2010		220	220	24,678
2011		220	220	24,898
2012		220	220	25,118
2013		220	220	25,338
2014		220	220	25,558
2015		220	220	25,778
2016		220	220	25,998
2017		220	220	26,218
2018		220	220	26,438
	58,851	6,820	26,438	26,438

**To account for the handling of one-third of the total national output.*

Figure 3 Plan of waste-handling building.

Figure 3 Plan of waste-handling building.

The washed carrier and cask enter one of six preparation areas. Protective shipping devices and cask tie-downs are removed and placed in the lay-down area. The carrier and cask are then moved to the cask loading and off-loading area, where one of two 125-ton overhead bridge cranes lifts and moves the cask to a washing and cool-down pit. The empty carrier is monitored for radioactive contamination, decontaminated if necessary, loaded with an empty decontaminated cask, and moved out of the radwaste-handling facility. The carrier may wait in the railyard until an empty cask is available.

If contamination is noted during the initial inspection, the carrier is moved directly into the waste-handling building and washed in the preparation area inside the building.

Each preparation area is independent and enclosed, with air-lock doors on both ends and a 10-ton crane and lay-down area for shipping equipment. The cask loading and off-loading area includes facilities for loading and off-loading, washing and cool-down pits, unloading pools, and cask decontamination pits.

Cask Washing and Cool Down.

The cask washing and cool-down pits are provided to wash the external surface of the cask and to cool the cask and its contents. Washing prevents the transfer of dirt into an unloading pool, and cooling minimizes thermal shock to the cask and fuel assemblies and prevents steam generation and uncontrolled release of contaminated vapor.

A cask filled with fuel assemblies is brought into one of the four washing and cool-down pits by one of the two 125-ton overhead bridge cranes. In the pit, coolant supply (steam and water) and discharge hoses are connected to the cask. The cask cooling system is designed to cool both dry and wet casks.

While the cask is going through the cool-down process, its external surface is washed with a high-pressure demineralized water spray. When the cask is completely cooled, the overhead bridge crane transfers it into one of the four unloading pools.

Cask Unloading. After a cask containing spent fuel assemblies is placed in one of the unloading pools, the overhead bridge crane removes the head of the cask and places it on an adjacent underwater shelf. A gantry crane then removes the spent fuel assemblies, one by one, from the cask and, after they are identified, places them in a transfer basket located inside the unloading pool. The transfer basket will hold four PWR or nine BWR fuel assemblies. The fuel gantry cranes have an interlock system that prevents them from lifting the fuel above the safe level of submergence (12 ft of water).

When a cask in which leakage was detected is unloaded, each fuel assembly is moved separately to the sipping station in the pool to determine whether that assembly is leaking by testing the water around it for radioactivity. Depending on the degree of leakage, the leaking fuel assembly is placed in a special container, put into a fuel basket, and transferred directly to the special function cell for immediate packaging. Assemblies with large leaks are put into special containers and sealed before being transferred to either the special function cell or the presentation pool.

All spent fuel assemblies leave the unloading pool in a transfer buggy that can hold up to three fuel baskets (only one leaking fuel container would be placed in a basket). The unloading pool gantry crane moves the loaded transfer buggy from the unloading pool through the transfer canal into the lag storage pool area.

The unloading pool water is pumped to the pool cleanup system (a

filter and ion exchanger) to remove dirt particles and contaminants.

Cask Decontamination. After a cask is emptied in the unloading pool, its cover is replaced, and it is lifted out of the pool. As it is lifted, the water in it is drained, and the cask surface is rinsed with fresh demineralized water. The empty cask is then moved to one of six cask decontamination pits by an overhead bridge crane.

In the decontamination pit, the empty cask is flushed again with demineralized water. The exterior is decontaminated with demineralized water and chemical cleaning solution until a swipe test verifies that it meets requirements. When decontamination is complete, the cask is inspected and prepared for shipping. This includes testing for leakage and minor maintenance work.

Demineralized water used for flushing cask interiors is sent to a treatment system consisting of a filter and ion exchanger. Water and chemical cleaning solution used for decontaminating cask exteriors are collected and sent to the liquid radwaste treatment system (evaporation system).

Spent Fuel Storage and Transfer. Two water-filled fuel storage pools (lag storage pools), each with a capacity of 240 fuel baskets, provide operating storage. A smaller storage pool (presentation pool), with a capacity of 52 baskets, is also available for equalizing the flow of spent fuel and for storing damaged fuel containers.

The transfer buggy moves fuel baskets from the unloading pools into the entrance area of the lag storage pool, where they are taken out of the buggy by a gantry crane and either moved to the presentation pool or loaded onto the transfer canal basket buggy, which takes fuel baskets into

the packaging area. During normal operation, fuel assemblies do not go through the lag storage pools.

The demineralized water in each storage pool is continuously circulated through a heat exchanger to maintain the temperature below 120°F. The heat is rejected to the lag storage pool cooling towers. Each storage pool also continuously circulates pool water through a filter and an ion exchanger to remove contamination. The water is sampled continuously to detect any change in activity level.

Spent Fuel Packaging. Two weld and test cells, where normal (nonleaking) assemblies are canistered, and one special function cell, where damaged (leaking) assemblies are canistered, make up the spent fuel packaging facility.

A spent fuel canister is a cylindrical vessel of 0.5-in.-thick carbon steel, 14.5 in. in OD and 186.5 in. long. It has a 2.5-in.-high lifting fixture on the top and a 3-in. crush barrier on the bottom.

Normal (nonleaking) assemblies are brought in baskets to the transfer chamber section of the weld and test cells by a transfer canal buggy. A basket containing either four PWR or nine BWR assemblies is lifted by a 7.5-ton crane into one of three dryers in the transfer chamber, where fuel assemblies are dried. Dried assemblies are then inserted into empty canisters, one PWR assembly or two BWR assemblies per canister. The canister is then capped, welded, heat-treated, tested for improper welding, filled with air, tested for leakage, tested for surface contamination, decontaminated if necessary, and either stored or taken out of the cell. Canisters rejected during the weld or gas leakage tests are sent to the special function cell for repackaging.

Damaged (leaking) assemblies are brought to the special function cell in watertight containers or normal fuel

baskets, taken out of the containers, and dried before being inserted into canisters. Broken remnants of badly damaged fuel assemblies are put into a can, which is then inserted into a regular canister. Canisters rejected during the weld and gas leakage tests are transported to the special function cell via the overhead transfer corridor. Heads of rejected canisters are cut off, and the fuel assemblies are repackaged into new canisters. After filling, these new canisters are capped, welded, and transferred back to a weld and test cell via the overhead transfer corridor.

All operations in the weld and test cells and the special function cell are performed remotely through the cell wall, using manipulators, with the aid of viewing windows and television monitors.

Canister Transfer to the Shaft Area. When the fuel assembly has been packaged into a canister, the canister can be stored in one of 26 storage holes in the cell or transferred to the shaft area and thence into the underground storage area. Normally a completed canister is taken directly out of the cell without storage.

After the last step of this operation, the canister is lowered into a transfer buggy through the load-out port. The transfer buggy transports the canister from the weld and test cell to the bottom of the transfer-cask loading port. A cable attached to the inside of the transfer cask is lowered through the loading port, attaches to the canister, and raises the canister into the cask. The cask bottom is closed, as is the loading-port shielding cover.

The transfer cask containing the fuel canister is moved by an electric vehicle (cask carrier) to the waste-shaft cage area, where it is exchanged for an upcoming empty cask. The empty cask is brought back to one of the cask loading ports for reloading.

Low-Level Transuranic Waste Handling System

The LLW-TRU handling facility is housed in the waste-handling building, which also houses the spent fuel handling facility. Two separate receiving areas, each with a separate vehicle entrance and air lock, are provided. This facility is illustrated in Fig. 4. The LLW-TRU handling system receives and off-loads the shipping carriers, unloads the waste drums from the containers, and prepares the drum for underground storage. Five major activities are conducted in the LLW-handling facility:

- Container carrier receiving and off-loading
- LLW-TRU drum unloading and inspection
- Overpacking of damaged and out-of-specification LLW-TRU drums
- Drum decontamination
- Drum transfer to the waste shaft area

Container Carrier Receiving and Off-Loading. The LLW-TRU drums are shipped in containers in special container transport vehicles, trucks, or railcars. Shipping containers are of two types—the Super Tiger and the standard ISO shipping container, which holds 42 to 48 55-gal steel drums. As described earlier, the carrier with containers is inspected at the gate to check for possible shipping damage, radioactive contamination, and sabotage. If sabotage is suspected, the carrier, with the containers, is moved to the isolation area for further investigation and implementation of safety measures.

If cleared, the container carrier is moved into one of two receiving areas, where containers are off-loaded from the carrier by a 35-ton overhead bridge crane, loaded onto an air-cushion pallet, and transferred into the drum-unloading area. Containers and carrier are checked for

EXPLANATION

— (-3000) — Salt Dome Structure Contour, Elevation at the underside of the overhang

GEOLOGIC NOMENCLATURE

EC1 ... Claiborne Group
 EW1 ... Wilcox Group
 PM1 ... Midway Shale Group
 C-UJ ... Cretaceous—Upper Jurassic Sedimentary Sequence
 JLo.. Louann Salt
 Elevation (-3657 m MLS) of the Louann Salt

METERS

FEET

SCALE

ELEVATION, ft

Figure 4 Salt dome. Section C to C' is drawn through the approximate centerline of shafts.

radioactive contamination. The carrier is decontaminated, if necessary, in the receiving area. If a container is contaminated, it can be decontaminated either in the receiving area or in the off-loading area after the drums have been removed.

LLW-TRU Drum Unloading and Inspection. The container is brought into the unloading area through an air lock on an air-cushion pallet. Electric forklifts are used to unload the drums, which are then taken to the inspection station, inspected and surveyed for damage, surface contamination, and out-of-specification radiation levels. Each LLW drum is classified as:

- Normal
- Damaged, requiring overpacking
- Contaminated, requiring decontamination
- Out of specification, requiring shielded overpacking

Damaged Drum and Offspec LLW-TRU Drum Overpacking. A damaged LLW-TRU drum that may possibly leak contaminants is placed into an overpack drum (DOT 17C 83-gal steel drum), which is sealed, labeled, and moved to the storage area. An out-of-specification drum that contains higher level waste than is permitted is overpacked in a special shielded drum having up to 2.5 in. of lead shielding.

Drum Decontamination. If an intact drum is found to be contaminated with radioactive solids from a damaged drum, it is decontaminated with a demineralized water spray. Water used for decontamination is collected and piped to the radwaste treatment system.

Drum Transfer to the Waste Shaft Area. The LLW-TRU drums are lowered into the waste shaft, which is designed to carry the canister transfer casks. The LLW-TRU

drums are carried in fixtures that have the external configuration of the transfer cask, so that the same equipment can handle both.

The LLW-TRU drum fixture is a steel frame that holds five LLW-TRU drums stacked vertically, or four 55-gal drums, with an 83-gal overpack drum on top. The fixture is loaded in the LLW-TRU handling area and taken to the shaft area by one of the cask carriers.

Underground Facility

This section describes the underground emplacement area, all underground development operations, and salt-handling and other surface buildings directly associated with the underground operations.

Salt Dome. The salt dome (Fig. 4) is elliptical in cross section; the long horizontal axis measures about 12,400 ft and the short axis, about 9000 ft at the underground* level. The top surface of the dome has a slight slant, but the average surface depth is about 1200 ft. The storage level selected is 2100 ft below the surface to ensure at least 800 ft of salt layer above the underground working level.

The dome at the 2100-ft level has a horizontal cross-sectional area of 2100 acres. Including the 800-ft protective salt barrier surrounding the underground storage area, the net underground working area is approximately 1400 acres.

Underground Layout and Development. Figure 5 shows the underground arrangement.

Access to the waste repository is through shafts contained in the shaft pillar, which is located centrally to equalize any thermal loads on the shafts and minimize haul distances for both the excavated salt and the

**The underground level is the dome area 2100-ft down.*

Figure 5 Underground arrangement. Abbreviations are VSS, ventilation shaft supply; WS, waste shaft; M&MS, man and material shaft; MES, mining exhaust shaft; and SES, storage exhaust shaft. Drawing shows an ideal dome layout; room layout may change because of dome imperfections. Also, as mining machinery improves, a different room and corridor layout may be preferred in later years. Local anomalies may decrease storage area, in which case rooms affected would not be developed. Rooms are 164.59 m long, 6.10 m high, and 4.57 m wide (rooms to east and west of pillar area are 188.98 m long). For storage through year 2018, 696 rooms this size will be required. Pillars are 30.48 m wide in corridors, ducts, and pillar area and 21.34 m wide in rooms. Corridors and exhaust ducts are 9.14 m wide and 4.57 m high. Exhaust ducts are at 10.67 m higher elevation than are rooms and corridors.

waste. The shaft pillar provides structural support for the shafts and protects against the possibility of subsidence. It also contains maintenance shops and other facilities required for underground development and waste-emplacement operations.

The heat generated by the nuclear waste is distributed equally on all sides of the central pillar. This minimizes unbalanced stress on the shaft pillar caused by thermal expansion of the salt.

The spent-fuel storage rooms are 4.57 m wide by 6.10 m high by 164.59 m long, with 21.34 m-wide support pillars between rooms. The spent fuel is placed in predrilled vertical holes in the floor, 264 per room. Branch corridors provide access to the rooms.

Seven main corridors extend in each direction along the principal axis of the underground. These provide for waste transport, salt conveyors, mining equipment and materials movement, and the ventilation systems. All corridors are 9.14 m wide and 4.57 m high.

Repository Development

Sequence. The repository is developed on a retreat basis. The extremities of the repository are filled to avoid closure of an area because of temperature buildup.

After the initial 5 yr (the retrieval period), when the allotment of canisters has been placed in each room, the waste storage rooms will be backfilled with salt. At that time three activities will take place simultaneously as routine operations—storing and backfilling operations at one end of the underground workings and excavating at the other end.

The first 5-yr period of shaft sinking and underground development is on the critical path; therefore this work will proceed on a three-shift, 355 d/yr basis. Continuous mining machines will be used throughout. It

is estimated that six machines and one spare will be required during this period.

The underground area will be explored before development by horizontal core drilling from the pillar area. The core drilling axis will be the same as that for one of the planned main entry corridors along the major axis of the underground area and along the axis of a planned branch corridor along the minor axis of the underground. If the core drilling is satisfactory, exploratory corridors will be excavated, and additional data will be obtained by examining the salt structure during the excavation of the exploratory corridors. In addition, cores will be drilled perpendicular to the exploratory corridor along the principal axis of the underground area to further examine the characteristics of the salt. If these operations show no problems with the salt structure, the corridors will be excavated to full size. If the exploratory effort indicates areas of questionable suitability for canister storage, the excavation plan will be modified to exclude and isolate these areas from development.

Shafts. The following five shafts serve the underground operations:

- *Men and materials shaft.* The men and materials (M&M) shaft is 31 ft in diameter and is divided into two separate sections by a full-length partition. One side contains a single-cage M&M hoist; the other contains a double-skip salt hoist. The M&M shaft also serves as a downcast ventilation shaft for the underground development operations.
- *Waste shaft.* The waste shaft is 18 ft in diameter and has a double-cage hoist and a service-inspection hoist.
- *Ventilation supply and emergency egress shaft.* This shaft is 25.5 ft in diameter, supplies ventilation air for the storage operations, and con-

tains an underground emergency egress hoist.

- *Repository exhaust shaft.* This shaft is 22 ft in diameter and serves as ventilation exhaust for the storage area.
- *Development exhaust shaft.* This shaft is 16 ft in diameter and serves as exhaust for the development operations area.

All shafts are grouted and lined with concrete about 100 ft into the salt. Friction (Koepe) hoists are used with rope guides.

Drill-and-blast shaft-sinking techniques are assumed; however, a restudy of this subject is recommended because boring may be feasible for the initial shafts. This could speed up the construction considerably.

Underground Spent Fuel System. The spent fuel transfer cask is received at the surface station of the waste shaft, where it is picked up and transferred to the waste cage by the gantry crane. A similar crane is located at the underground station, where the cask is transferred from the waste cage to the storage-room gantry crane, which does the placement.

The storage holes used during the first 5-yr retrieval period are carbon steel lined with a concrete plug. After the retrieval period, the storage holes are no longer lined and are backfilled with salt.

The storage holes are arranged two per room, 5.5 ft between rows at a 4-ft pitch. This arrangement will result in a maximum localized heat loading rate of 98 kW/acre if all units stored are PWR canisters. An average loading of 60 kW/acre, however, will be achieved if the predicted mix of PWR/BWR canisters is produced and if this load is spread over the total underground working area.

The underground spent fuel transport system is designed for safe

heavy-equipment handling. The transfer cask is continuously supported from one of its two sets of trunnions. For increased safety, underground surge storage of the casks is not planned.

Underground LLW-TRU System. The LLW-TRU drums are placed in a five-drum special transfer fixture in the surface plant. For handling purposes, the fixture matches the spent fuel transfer casks. The drums are unloaded from the fixture at the underground shaft station and placed on pallets. A special forklift transporter transfers the pallets to the storage area, where they are stacked two high.

The primary LLW-TRU storage areas are in the buffer rooms. It is calculated that the design basis quantity can be stored in about one half of those rooms. Thus there is ample capacity. Further LLW storage is available in the corridors, which can be filled with LLW on retreat from the filled section of the underground workings.

Underground Ventilation Systems. Separate ventilation systems serve the underground development and storage operations. Supply air buildings and exhaust air buildings for each system provide air pretreatment and posttreatment on the surface. Supply and exhaust fans are located in the surface buildings, and booster fans are located in the drifts near the upcast shafts in each underground system.

The development ventilation system protects the health and safety of operators from airborne contaminants and reduces the temperature of the working environment.

The storage ventilation system reduces working environment temperatures, controls the movement of airborne radioactive material, protects the health and safety of facility operators from airborne contaminants, and,

by means of HEPA filtration systems, removes radioactive materials from facility gaseous effluents, as required to protect the health and safety of the public.

The storage and development ventilation systems are separated physically by salt pillars and brattice, which are movable tunnel seals. Any intersystem leakage is always from development to storage areas since the pressure of the development area is kept higher than that of the storage area. During the course of underground operations, developed areas will be converted into active storage areas and, thus, will be served first by development ventilation and later by storage ventilation.

Salt Mining and Handling Equipment. Continuous mining machines are used for all underground development except that early in the shaft stations area. Shuttle cars gather the mined salt and deposit it on the conveyor system, which transports it to the underground surge bins for hoisting to the surface via the salt-hoisting section of the M&M shaft.

The hoisted salt is conveyed to a surge stockpile and to either the permanent stockpile or the railroad layout system. Sufficient salt is stockpiled at any time to permit backfilling operations. Excess salt is shipped by railcar for disposal.

After the 5-yr initial phase, all filled storage rooms, abandoned access corridors, and ventilation drifts will be backfilled with salt with a centrifugal thrower. Although underground development operations continue, the salt for backfilling is transferred locally from the development face. Once development operations cease, the stockpiled salt will be reclaimed and returned to the workings. Equipment for the reclaim operations will be reversed, modified, and relocated as necessary.

Underground Facility Surface Structures. The three headframe towers and their adjoining electrical equipment rooms are earthquake- and tornado-proof, monolithic, reinforced-concrete structures. The ventilation and filtration building is earthquake- and tornado-proof in the ventilation-filtration-electrical areas.

The underground operations building serves underground personnel and materials requirements. The compressor and chiller buildings house the water-chilling and compressed-air equipment.

The salt-handling structures use corrosion-resistant materials to withstand the salt-laden atmosphere.

Underground Auxiliary Services. Underground operations use electric-powered machinery wherever practical. All other equipment is diesel powered. The major machines of the latter type are the underground spent fuel transporters.

The underground dewatering system, designed to handle emergency inflows, consists of two subsystems, one for water with high contamination potential and another for that with low contamination potential. Water pumped to the surface by the system for high contamination potential is monitored for radioactivity and, if necessary, diverted to the liquid radwaste processing system.

Electrical power cables (13.8 kV) are routed down the shafts and distributed to local load centers, where the power is transformed to 4160 or 480 V for equipment use.

Diesel fuel is taken underground in drums and stored in accordance with the requirements of the Mine Safety and Health Administration. The ventilation system is designed to handle the exhaust from the diesel engines used underground.

Instrumentation is provided to monitor critical activities from the computer center, e.g., surface and

underground radiation; temperature, velocity, pressure, and gas analysis of underground air; and rock mechanics and heat parameters in the shafts and underground workings.

Compressed air is piped underground to the pillar area and distributed for instrument and maintenance usage.

Portable cans are used for potable water and underground sewage.

Underground fire protection is provided by six portable foam generator units and multipurpose dry chemical extinguishers.

Cranes and hoists are supplied wherever needed to facilitate materials handling and maintenance. Sundry underground vehicles move men and materials.

Utility and Service System

Electrical Power Supply System. The facility is normally supplied with 69-kV, three-phase, 60-Hz commercial power purchased from a local utility. The 69-kV primary power is delivered to an outdoor substation by two independent-utility-owned transmission lines. The power is distributed to surface support systems and underground workings. On-site backup diesel generators can provide electricity for emergency and essential loads.

Steam-Generating System. The steam-generator plant or boiler supplies steam for heating, plant process (e.g., cask cool down), laundry, and domestic uses. There are three boiler units in a one-story steel-frame structure. Each boiler is rated at 62,500 lb/hr at 250 psig. Coal is used as fuel in this system, with fuel oil as a standby alternative.

Compressed Air System. The air compressors supply air for plant processes and instrumentation, boiler soot blowing, breathing, and domestic uses. Each repository facility requiring

compressed air has its own set of compressors. Air is distributed in high-pressure lines; pressure is reduced when necessary at the point of use.

Water Supply System. The repository has its own water supply system from a local source near the repository site.

Makeup water for the cooling towers and radwaste facilities represents approximately 75% of the total water demand. The remaining demands are for potable water, non-contaminated carrier washdown, boiler feed, noncontaminated laundry, general service supply, and water treatment. Except for some suspended solids and traces of organics, the quality of the water source is assumed to meet the basic U. S. national drinking water standards.

Raw water is pumped to storage tanks on site for distribution to the fire protection water storage tanks and to the raw water treatment facilities. Raw water treatment consists of filtration, activated carbon adsorption, and chlorination to supply water for drinking and process uses. Treated drinking water is stored in a separate tank.

The treated water is distributed throughout the site in two main distribution systems—one distributes the filtered effluent to all process operations; the other distributes potable water to various facilities on the site.

Nonradioactive Wastewater Management System. All wastewater streams and contaminated runoff generated on site are collected and treated. Wastewater streams are of two types—one carries all blowdown flows (with high dissolved solids); the second comprises sanitary and other flows. The major contaminated runoff originates from the salt stockpile.

The wastewater management system consists of holding ponds and

wastewater treatment facilities. The objectives of wastewater management are to comply with established federal and state environmental regulations, conserve water resources by enhanced reuse of treated wastewater streams, and protect the public health and safety and the local environment.

Fire Protection System. The fire protection system (FPS) is designed to protect the repository facilities by detecting, annunciating, and providing automated and manual extinguishing systems for all types of fires that might be encountered at the repository.

Water for the FPS is drawn from FPS storage tanks and distributed by a primary electric-driven fire pump or a standby diesel pump. Other fire extinguishing agents used are compatible with the nature of the area to be protected, especially where water could cause excessive damage or result in a safety hazard.

The fire-detection and alarm systems are interconnected with local and central fire-control panels, and a trained fire brigade equipped with fire engines and other necessary equipment and accessories responds to the alarm. The FPS complies with all applicable National Fire Protection Association, Occupational Safety and Health Administration, and other industry codes and standards.

Equipment Fueling. Fuel oil is stored at the repository site for the standby emergency electric generators, standby diesel fire pumps, steam plant boilers, vehicles, and locomotives. No. 2 diesel fuel is required to operate the standby generators in the event of an outage and for startup and as a secondary fuel for the steam plant boilers. Diesel fuel for the underground vehicles is transported in 55-gal drums down the M&M shaft for transfer to the underground storage tank.

Area Lighting Services. Outdoor lighting equipment and facilities for the repository comply with all security, safety, and process requirements and are in accordance with current industrial foot-candle levels. Sodium-vapor fixtures are used for street lighting, parking lots, entrance gates, and lighting exterior areas around buildings. Security and safety lights are energized from the essential bus bars. Normally roadway and parking lights are energized from the normal bus bars.

Communications Systems. The communications system consists of telephone, public address, two-way radio, closed-circuit TV, and visual-audio warning systems. The visual-audio system is for notification of an underground emergency, such as fire or the inadvertent release of airborne contamination into the ventilation system.

Operational Support Systems. Three operational support systems, which support the main process systems of the facility, are needed to meet radiological protection requirements:

- Facility radwaste processing system
- Radiological monitoring system
- Safeguard system

The facility radwaste processing system collects, concentrates, and prepares for disposal in the repository most of the radioactive material released during the handling of the spent fuel and LLW. The only anticipated releases of radioactive material will be gases. The activity level will be within the limits of 10 CFR 20 and in as low a concentration as is reasonably attainable.

The radiological monitoring system measures, indicates, provides alarms, and makes permanent records of radiation levels and radionuclide concentrations in selected areas and at pro-

cess and effluent discharge points. The system uses local sensing devices, local and centralized alarms, monitoring channels, and a central control data computer.

The safeguards system protects the nuclear material at the site from sabotage and theft by means of inventory control, accountability, and physical protection.

Decommissioning

When the repository is finally decommissioned, the underground areas will be isolated from the outside environment for geologic time intervals. Decommissioning consists of removing salvageable equipment, burying contaminated equipment, and sealing the five shafts. Shaft sealing is accomplished by backfilling the shafts with salt to a point about 200 ft below the shaft lining, pouring a 100-ft molten salt layer, and placing a bulkhead constructed of two concrete plugs with an interlayer of bentonite above the molten salt. The rest of the shaft above the bulkhead is filled to the surface with sand cement.

Cost and Construction Schedule Capital Costs. The capital costs of the repository are estimated in

Table 3. Excluded from the estimate were:

- Owner engineering, financing, and other costs
- Financing and interest charges during construction
- Site investigation and land acquisition
- Underground operations after first 5 yr
- Utilities and roads outside the site boundary

Annual Operating and Maintenance Cost. An estimate of annual operating costs is shown in Table 4.

Table 3 Conceptual Estimate Summary*

	10⁶ Dollars
General site facilities	29
Utilities and site distribution systems	79
Repository facilities	253
Waste handling facility	181
Other buildings	38
Total field cost	580
Home office services	90
Contingency	120
Total construction cost	790

**Second quarter, 1979, price and wage level.*

Table 4 Annual Operating and Maintenance Cost*

	10⁶ Dollars		
	Period 1 (1988–1997)	Period 2 (1998–2007)	Period 3 (2008–2018)
Supplies	16.9	24.5	34.3
Utilities	5.6	8.4	9.4
Operating and maintenance labor	21.3	17.7	21.4
Supervision	3.2	2.7	3.2
Administration and overhead	9.8	8.7	10.2
Maintenance materials	8.2	6.8	8.2
Equipment replacement	5.0	5.0	5.0
Depreciation	25.5	25.5	25.5
Allowance for uncertainty (15%)	14.5	15.7	17.8
Total estimated annual operating and maintenance cost	110.0	115.0	135.0

**Second quarter, 1979, price and wage level.*

Figure 6 Schedule for terminal waste storage.

Because the spent fuel placement rate changes during the plant's operating life (assumed to be from 1988 to 2010 for estimating purposes), the plant's lifespan was divided into three periods, as shown in the table.

Conceptual Schedule

General. The conceptual schedule for the terminal waste storage is based on the conceptual capital cost estimate. Figure 6 shows the schedule.

Construction Sequence. The construction schedule assumes completion of the design in phases consisting of work packages. Permitting, procurement, and construction will proceed as the design of a work package is complete. The schedule assumes that construction of the major work package would start according to the following lead times:

- 39 months from the date of site selection to receipt of the construction permit; construction can start immediately after receipt of the permit.
- 3 months from the start of construction to the start of M&M shaft sinking; the M&M shaft will be ready for operation 39 months after the start of shaft sinking. When this shaft is completed and in

operation, full production mining operations can start.

- 6 months from the start of construction to the start of the development exhaust shaft sinking; this shaft and lining will be completed in 18 months. Then partial mining operations can start with the use of the development ventilation shaft sinking hoists.
- 24 months after the start of full mining production until sufficient corridors and rooms are completed to start canister placing operations.

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Mining Technology Development in Crystalline Rock

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The Colorado School of Mines (CSM), under sponsorship of the Department of Energy through the Office of Nuclear Waste Isolation (ONWI), has established a hard-rock research facility at its experimental mine. Even though this site will not become a nuclear waste repository, the CSM has established and maintains an underground test room for use by its own personnel and ONWI and its contractors to conduct in situ investigations. Furthermore, CSM is designing, conducting, and reporting on a series of field research programs to develop site evaluation procedures, excavation techniques, and instrumentation required for nuclear waste repository siting, construction, and monitoring (Hustrulid, 1981).

This facility is presently being used to:

- Evaluate and develop techniques for careful excavation of hard rock
- Develop the mapping techniques required to describe adequately the structural geology
- Evaluate the structural continuity in the granitic gneiss at the CSM site
- Evaluate the structural damage done to the rock mass by blasting
- Develop techniques for evaluating fracture permeability
- Evaluate permeability changes in the rock mass as a result of blasting

Although specifically oriented toward nuclear waste storage and disposal, the techniques and procedures being developed and evaluated have wide applicability to all underground excavations in hard rock.

Background

The Edgar Mine (the proper name for the CSM experimental mine) is located at an elevation of about 2300 m at Idaho Springs, CO, approximately 40 km from the CSM campus in Golden.

The location of the experimental room (Fig. 1) was selected because:

- Excellent rock was expected on the basis of observations made in the Miami adit, A-left drift, A-left spur.
- Geologic mapping could be done in the three existing drifts, and predictions could be made regarding the expected geology in the experimental room.
- The close proximity of the A-left raise would allow a three-dimensional geologic map to be made.
- It was sufficiently far away from other openings to avoid interference.
- Access was convenient, and compressed air, water, and track haulage were available.

The two possible disadvantages were the relatively shallow cover depth (about 100 m) and the fact that it is above the water table.

The experimental room is 5 m wide, 3 m high, and 30 m long. It was

Figure 1 Test site location, CSM experimental mine, Miami portal, Idaho Springs, Clear Creek County, Colorado.

constructed by using blasting techniques developed in the United States and Sweden. After the excavation was completed and thoroughly cleaned, the location of a large block (2 m in each dimension) to be isolated from the surrounding floor rock by line drilling was selected. This block was used by Terra Tek (Salt Lake City, UT) to determine the thermomechanical response of a jointed rock mass and will remain as part of the overall

facility for use in instrument development and calibration and other experiments.

Geological Description

The depth of cover at the mine varies from near zero at the portal to 200 m in the deepest areas. It is above the water table and, therefore, is essentially dry. The average year-round temperature in the mine is 13°C. The principal rock type is a

varyingly banded and interlayered biotite gneiss (the Idaho Springs formation), which is heavily injected and extensively recrystallized by granite migmatites and massive granite pegmatites. Narrow tongues of Silver Plume granite also have intruded foliation planes of the biotite gneiss, replacing and recrystallizing it.

A study of the geologic history of the area where the mine is located revealed that it has been varyingly affected by seven tectonic and/or structural events dating back to 1.750 billion yr ago (Hutchinson, 1981).

Three of the seven events appear to have played a dominant role in establishing the structural trends present and currently being mapped underground at the CSM/ONWI test site. The Boulder Creek Orogeny (1.750 to 1.690 billion yr) initially resulted in regional metamorphism of the Precambrian basement rocks and formed a structural trend still existent today. A younger, unnamed Precambrian deformation (1.30 billion yr) was dominantly cataclastic and was accompanied by minor and local recrystallization and folding. A third event during the Late Cretaceous to Early Tertiary time (70 to 40 million yr) not only resulted in an undetermined amount of reopening of Precambrian age fracture sets but also was responsible for superposition of a younger set of fractures on a regional basis throughout the Precambrian basement rocks.

The younger Precambrian cataclastic event and the Late Cretaceous-Early Tertiary Laramide Orogeny resulted in brittle failure in the rocks of the central Colorado Front Range. Identifying the fractures or joints and their structural disposition, density of spacing, and continuity is of paramount importance to the interpretation of fracture, permeability, and overall rock mass behavior.

Excavation Technology

In mining and civil engineering practice, careful blasting techniques are normally used only when it is deemed important to minimize damage to the walls and roof of an underground rock structure. Most often, however, particularly in hard rock, "acceptable" conditions can be achieved without incurring the time and expense associated with such procedures. Rock reinforcement or support can usually be installed as needed.

A rock mass that has good containment characteristics is necessary at nuclear waste repository sites. Great care should be taken to retain these characteristics during excavation of the required chambers. This means minimizing the extent of the disturbed zone. Blast damage can markedly affect the hydrological, thermal, and mechanical properties of the host rock.

When an explosive is detonated in a confined area (e.g., in the excavation of an underground opening), the rock breaks not only in the required direction but also in the depth of the solid rock behind the last row of blast holes. The stress waves or elastic waves (dynamic) and gas pressure (quasistatic) generated from the blast result in the creation of fractures and radial cracks in the remaining rock contour (see Fig. 2).

Two phenomena occur during rock fracturing; fracture initiation (creation of new fractures) and fracture propagation (extension of radial cracks by gas expansion of cracks formed by elastic waves and extension of existing fractures in the rock formation). The extent of such fracturing into the rock contour depends on: (1) the amount of explosives used in the last row of holes, (2) pre-existing fractures, (3) static stress field, and (4) the distance to a free surface. The degree of such fracturing or extent of

Figure 2 Example of possible wall rock damage from blasting. (a) During blasting. 1, Severe damage zone. 2, Blast damage zone. 3, Transient zone. 4, Undamaged zone. (b) After blasting.

such cracks could, as previously stated, alter the hydrological, thermal, and mechanical properties of the rock surrounding the opening.

Rock has been excavated by various means since the age of the cave-man. It would seem that today the techniques for creating the desired openings should be well developed, but this, unfortunately, is not the case, at least for the care required for this application. Patterns are often developed strictly by the cut-and-try approach for a given rock type. Errors in hole location and alignment are overcome by increasing the amount of explosive used. Although attention is placed on designing the pattern used for the perimeter holes, the same care is not given to the holes in the inner rows. Engineering procedures for designing blast rounds in hard rock are available; but, unfortunately, they have not been developed or described to the point where they can be easily used by contractors.

Normally, in careful blasting applications, primary attention is focused

on preserving the roof rock and secondarily on the wall rock. In at least some designs, the waste canisters will be stored in holes drilled or excavated in the floor of the rooms. Therefore in these special applications it is important to maintain structural integrity of the floor rock as well since it is the primary holding facility for the nuclear waste.

In driving the experimental room, the best available hard-rock blasting techniques were used (Holmberg, 1981). In particular, they included the Swedish blasting technique based on the work of Langefors and Kihlström (1963) (Holmberg, 1980) and the Livingston cratering theory approach (Bauer, 1961; Grant, 1964). Ten different blast patterns were used to demonstrate design procedures, evaluate construction constraints, and provide sites for measuring variations in structure and permeability. The design principles and their application are clearly described by Holmberg (1981) so that others can follow the procedures. The technique can be easily modified for application in other rock types.

Techniques used to measure the extent of blast damage are discussed in the following sections of this paper. Nevertheless, visual observation suggests that the disturbance has been minimal. Even better results might have been achieved with better control of drill hole deviation.

Structural Continuity

Because of the great influence that permeability—particularly that caused by structural discontinuities (faults, joints, and bedding), blasting-induced or aggravated fractures, or other openings—has on the selection of sites for high-level waste disposal, methods for identifying and categorizing these features and predicting their extent and continuity are of great importance.

The purpose of this phase of the investigation is to determine the availability of technology for quantifying and modeling geologic parameters related to structural discontinuities and to evaluate the precision of the available techniques. The objectives are to: (1) evaluate existing methods of collection, analysis, and presentation of fracture data, (2) evaluate the geometric continuity and physical characteristics of fractures exposed in the ONWI test site, and (3) construct a statistical, predictive model of the geometric continuity of these fractures.

The analysis of structural discontinuities began with a detailed field study in which all physical and geometric parameters related to these features were described and recorded. Two mapping-sampling techniques were used. In the ONWI room and the two drifts parallel to it, Miami and A-left spur (Fig. 1), all fractures with trace lengths greater than or equal to 1 m were mapped and described. All fractures with trace lengths greater than or equal to 10 cm in the walls and mining faces of the ONWI room were plotted on vertical sections and described. The analysis concluded that the following variables would have to be quantified as input data for the statistical predictive model:

- Location of area mapped
- Identification number—a four-digit number
- Strike—bearing and quadrant
- Dip—angle and quadrant
- Structural type—foliation, oblique, etc.
- Geometry—planar, wavy, irregular, etc.
- Surface—rough, smooth
- Aperture—width of fracture opening
- Length—trace length of exposed fractures
- Fillings—pyrite, clay, etc.

- Spacing—observed true spacing between joints of the same set
- Termination—nature of fracture termination (only described for detailed mapping)
- Distance along a baseline (only described for large-scale mapping)

The methods by which these variables were measured and/or described are based on the techniques suggested by the International Society of Rock Mechanics, Commission on Standardization of Laboratory and Field Tests (1978).

Fracture orientation data, strike and dip, were plotted on a Schmidt net (Fig. 3) (Billings, 1972; Ragan, 1973; Bucher, 1944; Badgley, 1959; Phillips, 1971). The Schmidt net is a planar, equal area projection of the lower hemisphere of a sphere. The strike and dip of the fracture plane were transformed into bearing and inclination of the pole normal to the plane. The poles were then contoured to allow for identification of individual fracture sets.

Analysis of this data, in a manner consistent with risk assessment models, requires a probabilistic, mathematical model. Previously available data analysis techniques relied on graphical procedures and qualitative evaluations that were strongly affected by an individual geologist's bias and thus were not entirely reproducible. One of the main goals of this research program was the development of an integrated data analysis package that would use completely reproducible mathematical techniques to delineate joint sets and statistically describe such sets. The package was required to perform four basic functions:

- Preparation of data for input into a wide variety of computer programs using various data conventions and formats

- Graphical representation of the data, including stereonets and rose diagrams for the orientation data
- Clustering of fracture observations into statistically significant and geologically meaningful fracture sets
- Statistical description of the geometric and physical characteristics of the individual fracture sets

We tried to use pre-existing programs from published literature (Shanely and Mahtab, 1975; Toucher, 1979) wherever possible. This approach worked quite well for the second and third steps, but several new programs had to be written to handle data preparation and statistical descriptions.

To compare similar fracture sets derived from different locations and/or different mapping techniques, we organized the fractures into discrete joint sets and developed statistical parameters to describe the geometric and physical characteristics of each set. Consequently, the spatial distribution and continuity of each set can be evaluated. Also, the effects and usefulness of each of the mapping-sampling techniques can be examined. In addition, orientations of these fracture sets can be compared with those of regional and local tectonic and structural features, microscopic mineral alignments, fractures identified by other tasks (blast damage permeability), local stress fields, mechanical properties of rock samples,

Figure 3 Lower hemisphere, equal area plot of large (>90 cm) fractures in the ONWI test site.

and macroscopic mechanical features of the rock mass. The final product of such comparisons is a statistical predictive model of the anisotropy of the rock mass.

Much of the data collected at the site is still in the analysis phase, and thus conclusions regarding the specific geometry of discontinuities at the CSM/ONWI site are still forthcoming. A number of conclusions can be made at this time, however, regarding the availability of technology for an orientation data analysis package:

- All the variables previously listed can be reduced to numerical values and handled with a probabilistic approach.
- A large number of computer programs exist for constructing graphical displays (Schmidt net and rose diagrams, etc.) of orientation data.
- Only one published program, FRAC-TRAN (Shanely and Mahtab, 1975), which is actually the third of three similar versions of the same concept, possesses the capability of clustering orientation data into discrete sets.
- Using FRACTRAN and two additional programs, STAT and JTSTAT, written specifically for this project, allows for a completely computerized and completely reproducible statistical evaluation of joint data.
- Although the data analysis can be approached from a purely statistical viewpoint, both mathematical and geological knowledge are necessary to arrive at joint clusters that are both statistically significant and geologically meaningful.

Use of the data analysis package has allowed a much more rigorous evaluation of the data than previously allowed by graphical and qualitative procedures. For example, the Schmidt diagram for the large-scale fractures mapped in the ONWI room (Fig. 3)

displays one broad high for foliation fractures. More detailed statistical analysis indicates that this group is actually composed of at least four distinctly different statistical populations. Similarly, the one large oblique joint set striking N 54°W with a vertical dip (Fig. 3) is actually composed of two separate statistical populations, N 63°W, 84°NE and N 41°W, 86°SW.

Several recommendations have been developed for further work in this area:

- Once the analysis of the geometry of discontinuities is completed, the shear strength of each discontinuity set should be evaluated.
- Other multivariate statistical techniques should be applied to segregate the data into joint sets. Although computer programs for these techniques are not readily available at this time, the theory has been discussed extensively in the literature (Kelley, 1968; Markland, 1974; Imbrie, 1963). Using factor analysis techniques would allow for segregation of observations into joint sets based not only on orientation but also on physical characteristics.
- Use multivariate techniques to relate all the data from the various tasks at the site. This would result in an ellipsoidal, vectorial model of anisotropy (or a spherical model of isotropy) of all rock mass properties, i.e., a three-dimensional model of the rock mass. Such a model would be useful in evaluating the relative mining stabilities of various configurations of underground repositories. Knowing the dimensions and orientations of an underground excavation, the geometry of rock discontinuities, the shear strength of the discontinuities, and the in situ stress field, we can evaluate the stability of a site before excavation. Similarly, knowing the geometry of the discontinuities and their

hydraulic conductivities, we can estimate the hydraulic conductivity of a borehole before testing.

In conclusion, note that the techniques outlined are applicable not only to nuclear waste isolation but also to many other geotechnical projects, e.g., cost estimation in tunnelling work (Lindner, Einstein, and Vanmarcke, 1977) or prediction of rubblizing characteristics of oil shale (Janzon, 1977).

Damage Zone Assessment (Structural)

As shown in Fig. 4, a pattern of NX (78-mm) diameter diamond drill holes has been drilled at six locations in the experimental room for use in evaluating the extent of the damage zone surrounding the opening. In addition, three 30-m-long NX drill holes

were drilled parallel to the room for fracture permeability experiments.

The first method used to evaluate the blast damage was to view the core and log the density of the fractures. A major difficulty was distinguishing the fractures that might have been induced during the blasting process from those induced during coring. Logging the borehole walls with a borescope allowed some of the artificially induced fractures to be identified.

Furthermore, ultrasonic measurements were made in which a transmitter was located in one borehole and a receiver in another. The ultrasonic pulse method is based on the premise that the velocity of propagation of an elastic wave in the solid rock is governed primarily by the elastic properties of the rocks and by fissuration or fracture density. As measurements are made away from the site of the explosion into the rock, the fracture density decreases so that the wave velocity increases. For the arrangement of boreholes shown in Fig. 4, we can examine the rock around the drift both longitudinally and radially.

Figure 5 is a schematic of the equipment used in the ultrasonic pulse testing. The crystals used in the transmitting probes ranged from 75 to 80 kHz. Both longitudinal (P) waves and shear (S) waves were used.

The P and S wave velocity changes with respect to distance from the periphery of the room into the rock were analyzed. Three zones were isolated from the plots—damage zone (nearest to the opening), transient zone, and elastic zone. An example of the plotted P wave velocities is shown in Fig. 6, for round 1 boreholes RDD-RDE. The damage zone was estimated to be 0.34 m (1.5 ft); the transient zone, 0.34 to 1.83 m (1.5 to 6.0 ft); and the elastic zone, distances greater than 1.83 m (6 ft). Fracture envelopes

Figure 4 Plan and cross section of the CSM/ONWI experimental room showing borehole locations.

Figure 5 Diagram of ultrasonic pulse testing equipment.

for each round were delineated from the P velocities measured in the round (Fig. 7). The final analysis included in situ dynamic elastic constants from P and S wave velocities and transfer functions to determine the filter characteristics of the rock and laboratory results.

In a related study, the rock mass behavior at the site was investigated by in situ and laboratory measurements and geotechnical modeling. In situ tests included measuring stress, monitoring convergence, measuring relative movement of the roof, and determining rock mass modulus. Two different computer models were adopted to describe the behavior—a finite element model and a mine simulation model.

The in situ tests are listed in Table 1, and the test locations are shown in Figs. 8 and 9.

Table 2 summarizes the laboratory tests, and the rock properties resulting from the measurements are given in Table 3.

Conclusions from the rock mass behavior study were:

1. The response of the rock mass to the excavation technique was small and was controlled by the jointed nature of the rock.
2. The average rock mass modulus of deformation was 4.5×10^6 . This average was measured at depths greater than 0.61 m (2 ft) around the excavation.
3. Fractures detected in the borehole using the NX-CSM cell agreed with findings of the other techniques.
4. The in situ stress field measurement suggested that the horizontal stresses are greater than the vertical stress ($K = 1.2$ to 1.5) and that the

Figure 6 P wave velocity for round 1.

vertical stresses were equal to the overburden load.

The mathematical models adopted in this investigation are basically applications of the theory of elasticity. They were developed using structural mechanics in which: (1) the pertinent features of shape, size, and properties were simulated mathematically, and (2) the response of the system to a specified loading or sequence of excavation was computed using digital computer programs.

The finite element model is a two-dimensional plane stress model of the rock structure. The model is isolated and partitioned into a finite number (364 in this case) of imaginary elements connected at nodal points to create an idealized frame structure

41.2 by 33.5 m (135 by 110 ft), which can be solved by the matrix method (Fig. 10). The model initial boundary conditions used in situ measurements and different combinations of theoretical loading conditions and rock properties. The model will yield information about the stress distribution and the displacements of the rock mass around the facility.

The mine simulation model can estimate the normal stress and displacement induced by sequence of mining. The model represents the plan of the excavation divided into a finite number of "face elements," each of which effectively represents a separate dislocation. The model is 68.6 by 68.6 m (225 by 225 ft), including a 6.1-m (20-ft) incompressible zone

Figure 7 Zone contour for round 1.

Table 1 In Situ Tests and Measurements

Type of test	Number of tests	Instrument used	Purpose
Overcoring	12 17	CSIRO* cell Bureau of Mines deformation gauge	To measure stress values vs. depth and determine in situ stress field
Borehole dilation	642	NX-CSM cell	To measure rock mass modulus and detect fracture
Convergence measurement	7 locations	Soil mechanics extensometer Irad and gauge extensometers	To measure roof-floor convergence during and after excavation
Relative roof sag measurement	5 locations	Irad multipoint extensometer	To monitor real-time movement of the first 6.1 m (20 ft) of the roof
Wall convergence measurement	7 locations	Terrametric tape extensometer	To measure convergence between walls

*Commonwealth Scientific and Industrial Research Organization, Australia.

Figure 8 Cross section of CSM/ONWI room showing location of in situ stress and deformation measurements.

- SURVEYING SPAD (RP)
- ◎ ROOF-FLOOR CONVERGENCE STATION
- └ WALL-WALL CONVERGENCE STATION
- ▣ MULTIPOINT EXTENSOMETER
- ≡ OVERCORING (CSIRO GAUGE)
- ≡ OVERCORING (U.S. BUREAU OF MINES GAUGE)
- NX-BOREHOLE (CSM CELL TESTS)
- ≡ EXTENSOMETER ANCHOR

Figure 9 Plan of CSM/ONWI room showing location of in situ stress and deformation measurements.

(Fig. 11). The average excavation advance is 2.3 m (7.5 ft) per blast; hence, 13 steps of mining were used in the model. Gravity loading was used as the primitive stress field [vertical stress of 2.2 MPa (320 psi)].

Damage Zone Assessment (Permeability)

The permeability of the rock mass surrounding an underground nuclear

waste repository is extremely important in both site selection and excavation design. The instrumentation and methodology for measuring permeability in rocks such as the granitic gneiss have not been completely established, however. One purpose of the CSM hydrogeologic research program is to develop borehole instrumentation for testing extremely low-permeability rock masses. The equipment can then be used to evaluate the effects of in

Table 2 Laboratory Tests

Type of test	Number of tests	Purpose
Uniaxial compressive	100 samples	To determine elastic constants and compressive strength
Biaxial compressive	10 (0.15-m, 6-in., core)	To determine elastic constant for overcoring tests
Triaxial compressive	25 EX samples	To determine shear strength, angle of internal friction, and relationship between failure strength and confining stress
Brazilian	10 NX samples	To measure tensile strength

Table 3 Rock Properties

Density (γ)	168 lb/ft ³
Young's modulus (E)	8.98×10^5 psi
Poisson's ratio (ν)	0.22
Compressive strength (σ_c)	16,900 psi
Tensile strength (σ_t)	2476 psi
Angle of internal friction (ϕ)	50.8°
Shear strength	2314 psi
Failure strength	12,997 psi + $7.98 \times$ confining stress

situ stresses and stresses resulting from storage cavity excavation on permeability at other sites.

Crystalline rocks are always associated with fractures that may be opened or closed at greater depths as a result of an overall high stress field. Numerous laboratory and field studies have indicated that fracture conductivity is extremely sensitive to the state of the stress and pore pressure in the rock (Witherspoon and Gale, 1977; Gale, 1975; Shehata, 1971; Snow, 1968). Experiments and research concerning the effect of underground openings on the permeability of fractured rock are limited, however. Fisekci and Barron (1975), using straddle packer techniques, showed that permeability of coal reduces to a background level at a distance of

10 m from the ribs. Barron (1978), using a modified technique to investigate the integrity of coal pillars, concluded that permeability decreased sharply in the center of the pillar. Gale et al. (1977) emphasized the effect of stress and relaxation on permeability around underground repositories in crystalline rocks. Gale et al. (1981) conducted a series of permeability tests in the crystalline rocks of Stripa, Sweden. None of the experiments considered a concurrent in situ stress evaluation, however, and in all cases there was no attempt to conduct tests parallel to the long axis of the opening.

The conductivity of fractures is believed to decrease approximately one order of magnitude per order of magnitude increase in normal stress (Gale et al., 1979a, 1979b). Change of stress near the ONWI room, as indicated by in situ stress determinations, is of the order of two to three times the original state. According to the assumption, this should cause a change in hydraulic conductivity of two to three times the original state.

Such changes could completely modify the groundwater flow field, a significant factor in radionuclide transport around an underground repository. This effect can be used to advantage if the behavior of the fracture system around the opening is

Figure 10 Finite element model mesh.

known. Analysis of fracture permeability is essential to proper planning for borehole plugging and repository sealing programs. Understanding unsaturated flow through fractures is also significant in estimating water inflow during the active life of a repository and during resaturation after decommissioning. Therefore instru-

mentation, measurement methods, and data analysis techniques must be applied to thoroughly understand the behavior of the fracture system around proposed repository sites.

The purpose of this investigation was to establish a method by which the permeability of fractures in the host rock can be measured to predict

Figure 11 Mine simulation model showing 12 steps of excavation.

the possible changes in permeability as a result of blast damage and stress field alteration. In addition, we intended to take advantage of the unsaturated nature of the rock to understand the two-phase flow phenomenon in fractured rocks.

It may be possible to assess the effect of underground excavation on permeability of fractured rock by examining the pressure and permeability profiles along individual fractures in an already-existing underground room. Ideally, measurements should be made before and after excavation and the results compared. A three-dimensional deterministic fracture model is required to delineate the effect of the stress. This model was prepared in this investigation by mapping the walls of the excavation, core

logging, and making a borehole survey with a borescope.

Permeability Test Equipment and Procedure. Steady-state air- and water-injection techniques, in conjunction with pulse testing and pressure decay tests, were used to obtain data from which permeabilities were calculated for both longitudinal and radial boreholes.

Equipment for pressure profile measurements (Fig. 12) consisted of a main injection probe and two monitoring probes. The main probe has four packers, spaced to create three cavities inside the borehole, and a transducer housing. Each cavity is connected to one transducer with Tygon tubing. The central cavity is pressurized with water or air. The monitoring

Figure 12 Schematic of the components of permeability testing equipment.

probes consist of two packers and a pressure transducer. In one of three parallel boreholes, the main assembly is placed so that the central cavity straddles a preselected fracture. In the other two, the monitoring probes straddle the same fracture (Fig. 12). Several trials are required to set the packers in the correct position. After they are set, the main cavity is pressurized, and the pressure changes in the monitoring probes are observed.

Four devices have been assembled for flow measurement; they are used simultaneously to observe and compare the accuracy and applicability of each system:

- Flow tank system (Fig. 12, M1)
- Tracer-line system (Fig. 12, M2)
- Metering valve with a differential transducer (Fig. 12, M3)
- Rotometers (Fig. 12, M4)

The data acquisition system consists of a Digistrip II data logger, a

digital tape recorder, and a chart recorder. Pressure transducers are used for pressure measurements, and thermocouples are used for temperature measurements.

After the packers are set in the selected position, flow is initiated at a predetermined pressure. Injection continues until flow becomes constant and the pressure inside the zone stabilizes within the sensitivity of the pressure transducers [68.9 Pa (0.01 psi)] for at least 15 min. Flow rates, pressures, and temperatures are recorded at short intervals. The pressure is then increased in increments, and the test is repeated. Several increments are used for each zone. After the steady-state test is completed, the flow is stopped by a solenoid valve. The pressure decay is then continuously recorded. After the pressure is released and the test medium returns to its natural equilibrium, a small pressure pulse is introduced into the

Figure 13 Schematic of air-injection apparatus, the equipment used to determine fracture index.

zone by a piston and solenoid valve, and the pressure decay is monitored.

The packers were shortened, and the interval between them was adjusted to 0.75 m (30 in.) to obtain more complete coverage of the radial boreholes. Each test interval (0.3 m) was tested at one equilibrated pressure and flow. If the flow was too low to be measured by the flowmeter, a pressure decay test was conducted. The primary purpose of testing the radial boreholes was to locate conductive fractures.

Fracture Index Method. A transient air injection method, referred to as the fracture index method, was used to determine the fracture index (FI) for the radial boreholes (Fig. 4). This test is based on the principle that, when pressurized air is injected into a zone isolated by straddled packers, the rate of airflow will depend on the fracture characteristic and intensity (Barron, 1978; Gwiadza and Hladysz, 1974). The rate of flow will be greater in fractured or stress-relieved rock (low FI) formations than

in relatively competent rock (high FI); i.e., it will be inversely proportional to the permeability of the rock. A systematic FI pattern would delineate the altered envelope around the test room.

Figure 13 is a schematic of the equipment used in the air fracture index test. The equipment is a modification of Barron's (1978) system. Pressurized nitrogen was used in place of mine air, and a digital display unit was connected to a pressure transducer to record the pressure drop.

The initial pressure in the empty air cylinder (53.2 l) was 0.41 MPa (60 psi) and in the inflatable packers, approximately 0.69 MPa (100 psi). After the pressure was released into the 15-cm- (6-in.-) long measuring zone in the borehole, the cylinder pressure drop was recorded every 15 s, up to 120 s, for eight readings in all.

The results from the test were interpreted in terms of FI by the algorithm given in Barron's work.

Figure 14, parts a, b, and c are examples of the FI from boreholes

RDU-1, RDW-3, and RDE-4, respectively.

By analyzing the plots, we can isolate a definite high permeability zone (low FI) within the first 0.55 m (1.8 ft), 0.58 m (1.9 ft), and 1.04 m (3.4 ft) for holes RDU-1, RDW-3, and RDE-4, respectively.

A good correlation can be seen between FI and permeability results in the majority of cases (Fig. 15). The exceptions are believed to be caused by the fact that steady-state tests tend to ignore dead-end fractures that are not connected to a main network.

Figure 15 is a graph of the means of the logarithm of permeabilities and

inverse of the fracture index for four groups of boreholes. From the figure it is evident that a row of high permeability (or low FI) exists in all the boreholes within the first 0.5 m (1.64 ft). This, we believe, is the damage envelope induced by blasting and stress relief.

In a majority of tested intervals in the longitudinal boreholes, permeabilities calculated from air-injection testing show a strong dependency on test pressure (Fig. 16). Pressure-permeability trends are consistent and reproducible for a given test interval, however (Fig. 16a). This pressure-permeability relationship is

Figure 14 Fracture index (FI) and ΣP for fracture index test. (a) RDU-1. (b) DRW-3. (c) RDE-4. (Figure continues on following page.)

not due to fracture deformation, because the opening of the fractures as a result of increased pore pressure would have caused the permeability to increase (opposite of the trends shown in Fig. 16). This phenomenon is believed to be related to the gas properties and saturation state of the fracture (Montazer and Hustrulid, 1981). For this reason, pressure-permeability trends were used for comparison among the three longitudinal boreholes.

To be able to compare the permeability of fractures across the boreholes, we had to identify the fractures. This was accomplished by com-

paring the fracture map plotted from line mapping and core logging (Fig. 17) and the permeabilities plotted at the lowest test pressures (Fig. 18). Then the pressure-permeability results were compared for each fracture across the boreholes. Only five sufficiently distinct fractures could be isolated for permeability comparisons.

Three of these fractures show a strong diminishing trend in permeability toward the room. In one case (the shear zone) this decrease is approximately two orders of magnitude (Fig. 16, parts b, c, and d). Similar trends are shown by the results of the pressure profile testing with water

(b)

Figure 14 Continued. (Figure continues on following page.)

(Fig. 19). During steady-state injection of PA-2, the pressure drop was much greater toward the room than away from it. This confirms the diminishing trend of permeability toward the room.

The stresses in the rock immediately adjacent to the room as measured by overcoring showed that the maximum principal stress is in a plane nearly perpendicular to the main fracture set (the set tested in the longitudinal boreholes) and plunges approximately 45° to the north (Fig. 17). It has been shown by electron microscope studies that microcracks perpendicular to applied compressive stresses tend to close and

those parallel to the applied stress tend to open (Batzel, Simmons, and Robert, 1980). In addition, numerous examples show closure of fractures with increase in normal stress. The apertures would be expected to decrease in this fracture set, causing a considerable reduction in conductivity; this correlates well with the measured data. The lower the fracture stiffness, the more pronounced is the effect.

This is believed to be the reason for the markedly lower permeability observed closer to the room where the highest stress exists across the fractures. If a similar stress distribution is assumed to exist on the east side of the room, the exceptionally high frac-

Figure 14 Continued.

Figure 15 Distribution of the means of the logarithms of permeability and fracture index along four groups of boreholes., permeability (k), cm^2 ; —, inverse of FI. (a) Radial up holes. (b) Radial diagonal holes. (c) Radial horizontal holes. (d) Radial down holes.

ture permeabilities observed in the radial boreholes (Fig. 20), even at depths not suspected to be affected by blasting, can be explained by the orientation of these fractures parallel to the maximum principal stress, a condition that would cause them to open. The fact that some fractures across the longitudinal boreholes do not show significant changes in permeability may be caused by their high normal stiffness due to the nature of the filling material; this was found to be the case by examining the core.

The results accumulated thus far indicate a noticeable change in the directional permeability around the opening in the fractured metamorphic rocks around the CSM/ONWI room. Because of this alteration, the fracture permeability has decreased normal to the direction of the ultimate (post-

excavation) maximum principal stress axis and has increased parallel to this axis. Therefore the original anisotropic permeability axes around the room have been completely changed in direction and magnitude. It is most probable that the intensity of this alteration increases gradually but exponentially toward the opening.

This phenomenon is believed to be of general application in fractured rocks. During excavation of large underground openings, the original anisotropic fracture permeability of the rock mass will be completely altered around the room. Depending on the state of the original stress field (i.e., the geometry of the anisotropic stress field and the geometry of the original anisotropic permeability), the ultimate anisotropic permeability may take any position. If both the stress

Figure 16 Variation of permeability with pressure. (a) BH PA-2. (b) BH PA-1. (c) BH PA-2. (d) BH PA-3. (b), (c), and (d) are results of testing of the shear zone.

and the permeability fields are measured before excavation, the orientation and geometry of the opening could be planned so that the permeability is minimized in the radial direction with respect to the axis of the opening. This would increase the effectiveness of the immediate geologic barrier.

Summary

The CSM/ONWI test facility is being developed for a number of

important reasons. First, it provides an opportunity to evaluate excavation procedures that might be used in constructing a hard-rock repository without the pressures imposed by an actual construction timetable.

The nature and extent of the blast damage done to the surrounding rock is being quantified. With this information, we can judge the effect of the excavation process on containment and evaluate engineered remedial measures. Procedures for evaluating changes in the hydrologic, mechanical,

Figure 17 Simplified geologic map of the room showing approximate orientation of major fractures.

Figure 18 Permeabilities from air-injection testing along the longitudinal boreholes. Note that the values are relative permeabilities at the smallest test pressure.

Figure 19 Results of pressure-permeability profile testing by water injection. (a) Pressure profile along the shear zone; note the sharp pressure drop between PA-2 and PA-3 during testing of PA-2. (b) Pressure history during profile testing.

Figure 20 Permeability from air-injection tests along radial boreholes.

and thermal response of the host rock are under development and test. The instrumentation, measurement techniques, and data analysis procedures obtained can be used in initial scoping studies of actual repositories. Geologic mapping procedures and techniques for quantifying, analyzing, and storing great masses of geologic data are being developed. The significant structural features over various measurement lengths are being quantified and their continuity assessed.

For the long term, the facility will provide an opportunity for developing, evaluating, and comparing new techniques and tools for use in siting and constructing hard-rock nuclear waste repositories.

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Geochemical Factors in Borehole-Shaft Plug Longevity

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Geochemical investigations that address factors controlling the longevity of repository sealing materials in a geochemical environment are discussed. Studies are being made of cement-based materials as major candidates for seals for borehole plugging, and shaft and tunnel sealing in certain potential repository environments. Factors controlling the extent of attainment of equilibrium of the plug components with time and the rate of approach to a state of stable equilibrium of the plug component chemical subsystem within the total system are discussed. The effect of these factors on changes in physical, mechanical and thermal properties of a seal system, and the consequent effectiveness of the seal in preventing transport of radioactive waste species are the dominant features to be determined. Laboratory experiments on the effects of anticipated temperature, pressure, and environmental factors (including chemical composition and specific rock type) are described. Thermodynamic studies are used to determine the potentially stable reaction products under conditions similar to those anticipated for the repository boreholes, shafts, and tunnels during and after the operating stage. Multitemperature reaction series are studied, and reaction kinetics are investigated for the purpose of predicting the

course of likely reactions. Detailed studies of permeability, diffusion, and interfacial properties and chemical and microphase characterization of the products of experiments are carried out. Characterization studies of old and ancient cements, mortars, and concretes and prototype man-made seal materials are performed to further assess the factors associated with longevity.

Introduction

Materials for radioactive waste repository sealing constitute an essential component of the repository system since the emplaced seals will provide a major contribution to adequate waste isolation. The use of cementitious materials (cements, grouts, mortars, concrete, and other composites) provides an extensive record (Roy, Grutzeck, and Licastro, 1979) from applications for underground sealing in the oil and gas and mining industries, as well as in other underground storage (Rennick et al., 1972; Herndon and Smith, 1976; Office of Nuclear Waste Isolation, 1979). The particular range of properties of these materials and their versatility suggest that they are likely to be used extensively in geologic repositories. Applications in nuclear waste repository sealing are subject to the overriding constraint that the other desired properties must be combined with the

requirement of long-term performance. In response to this constraint, the current materials program places a strong emphasis on studies relating to longevity.

The major requirements for repository seal materials include:

(1) Mechanical adequacy; (2) good bonding to the host rock; (3) very low permeability to fluids, particularly in the interfacial zone between seal material and host rock; (4) stability and chemical durability; (5) compatibility with the surrounding rock and groundwater environment; (6) resistance to destructive expansion and contraction; and (7) resistance to radionuclide transport. These properties are important over the long time period of repository isolation.

Cementitious materials, either alone or in combination with other compatible plug component materials, are likely to satisfy the requirements, and therefore research is addressing specific problems related to their applications as repository seal materials. The studies consist of two main parts, as outlined in Table 1. First, materials selection and evaluation

studies are performed to determine the properties and characteristics related to hardening, placing, and other early stage properties. Second, starting materials and products are characterized.

Materials selected for further study on the basis of their performance in short-term tests are then investigated intensively to provide information on their longevity. This type of information is obtained from a variety of sources, including tests on experimental mixtures and formulations. The studies include detailed characterization of experimental seal materials or, where possible, specimens from plugs that have served in the field for extended time periods; evaluation of the thermodynamic stability of the material; determination of reaction rates and kinetic factors; determination of selection criteria based on knowledge of natural mineral associations; studies of ancient concrete prototype materials; and investigation of other special factors relevant to determining probable stability of seal material and host-rock–environment combinations.

Table 1 Outline of Seal Materials Studies

Materials Selection and Evaluation

Placing characteristics, hardening behavior
Mechanical properties, early stage
Characterization: Starting materials and products
Physical, thermal, and mechanical properties

Geochemical Longevity of Seal Materials

Stable modified cements and their composites
Cement–rock compatibility, stability, interface properties, and reaction kinetics
Thermodynamic properties—ultimate stability
Fluid permeability, ion diffusion, and electrochemical effects
Case histories: Old and ancient cements, mortars, and concrete
Other special studies

The information needed is further categorized into experimental, theoretical, and direct, from the geosphere; the interrelationships of this information are shown in the logic diagram in Fig. 1. The scope of the work and its relation to the information available from other sources have been described in a separate report (Roy et al., 1979), which deals with a broad range of factors considered important in assuring adequate performance and longevity of sealing and plugging materials.

Materials Selection and Evaluation

Several stages are typically followed in the design and study of potential repository seal materials.

Characterization. Thorough characterization of the starting components of a potential mixture, with respect to all factors significantly affecting their reproducibility of performance, is an important first stage in seal materials design. The factors considered include chemical composition, particle size distribution, variability within a component, and sensitivity to changes that take place during storage. The components are characterized initially and as needed after a preliminary material formulation is made. Roy et al. (1981) described the types of characterizations made during the design stage and initial phase of study of a particular cementitious grout.

Cementitious Mixture Formulation. Of particular importance in the design of seal materials for remote placement, and also when placed by normal methods, are assessment and control of the factors affecting early stage rheological properties and development of structure. The effects of changes in composition, chemical additives, particle size, and other com-

ponent parameters are determined as they affect viscosity, flow properties, and final mechanical properties. Relationships of shear stress to shear rate and yield stress and viscosity values have been determined for experimental mixtures. Figure 2 summarizes the relationship between viscosity and volume concentration of cement for a large number of mixtures; this is one type of rheological information used in designing potential seal material mixtures (Roy and Asaga, 1981). The optimum amounts of chemical admixtures and other components that produce lower viscosities or more workable mixtures were determined from a given volume concentration of cementitious solids. The effects of admixture concentration on the yield stress, one of the major factors governing workability of mixtures, are shown in Fig. 3. The data illustrate the changes with time after mixing; this provides information necessary for effective placement and optimization of workability with increasing time. The use of such data enables us to reproduce the design of low porosity seal materials, minimize volume change (Perez and Roy, 1980), and generate materials having potential for greater long-term durability (Roy, 1980).

The early stage dimensional changes of mixtures during and after hardening can be studied in detail, as shown in Fig. 4, which compares volumetric and linear dimensional change measurements for the same mixture—in this instance, one that undergoes expansion after hardening. Such determinations before and after hardening enable us to design mixtures properly to generate an adequate physical bond with the host rock.

Another important factor affecting both early stage properties and structure development is the rate of heat evolution of a hydrating mixture. Calorimetric studies are made to

Figure 1 Borehole plug longevity—stability evaluation. Logic diagram for geochemistry program.

Figure 2 Effect of volume concentration on viscosity of cementitious mixtures; measurements after 6.5 min at 128 rpm.

quantify the heat effects and indicate the time at which the peak rate of heat evolution is achieved, its magnitude, and the effect of material parameters on the total heat-effect pattern. These studies generate data such as those shown in Fig. 5. The effect of background temperature is indicated in these data, which show an increasing rate of heat evolution (i.e., the peak height of the major exotherm), a shortened time span before the heat release begins, and a shortened time for the peak rate to be achieved as curing temperature is increased. Such data can be used to change the design of a mixture and

optimize mixture formulation for the expected thermal ambient. The types of differences found are given in Table 2, which shows that, even though the second formulation was characterized by a delayed heat effect, the amplitude of the effect was higher. A theoretical model is being developed to use such calorimetric data in predicting heat buildup in concrete of different masses, geometries, and surroundings. Figure 6 illustrates the effect of temperature and the relative effects of using two different types of cement. By controlling the proportions of the mixture, we can control the thermal characteristics,

Figure 3 Changes in yield stress with admixture concentration (a sulfonated naphthalene) at increasing shear rate. (Data from Roy and Asaga, 1981.)

the consequent development of microstructures, and the resulting physical and mechanical properties.

Geochemical Investigations: Longevity of Seal Materials

Results from selection and evaluation studies are fed into the geochemi-

cal technical studies, as indicated in Fig. 1. Thus, in addition to formulation and design criteria, a number of factors more directly concerned with longevity are examined in detail.

Thermodynamic Stability. A major source of information on long-term performance is the relative thermodynamic stability of major seal material components. Portland cements hydrate relatively slowly at room temperature and atmospheric pressure; their short-term reaction products are relatively poorly crystalline; and the changes that take place under normal conditions to increase the degree of crystallinity are usually slow. A rigorous method for predicting long-term behavior of cement-based materials in a geologic environment involves determining thermodynamic equilibria and calculating the lowest free-energy (i.e., most stable) state for fixed compositional systems or subsystems under the expected environmental conditions. The studies in progress include literature reviews, calculations, and generation of needed new thermo-

Figure 4 Early stage dimensional change of a salt-compatible cementitious mixture. (Data from Roy et al., 1981.)

Figure 5 Rate of heat liberation vs. time for a set of Class C (C-5) cement slurries, as a function of background temperatures. a, height of first peak at 25°C; b, height of first peak at 35°C; and c, height of first peak at 60°C. $W/c = 0.40$.

dynamic data (Sarkar, Barnes, and Roy, 1980).

An example of the differences in the free energy of hydration (ΔG) of C_3SiO_5 , the most important cement component, according to different reaction paths is illustrated in the following three alternate calculations (Sarkar, Barnes, and Roy, 1980):

(1)

Tricalcium silicate + water = C-S-H (subcrystalline calcium silicate hydrate) + calcium hydroxide

A more favorable reaction is the transformation

Table 2 Early Heat of Hydration

Material	Maximum quantity		Second peak	
	Rate of hydration, cal/(g-h)		Start time, hr	Peak (max.) position, h
	1st peak	2nd peak		
Class H cement + deionized water at 25°C		0.66	2	8
PSU/WES* mixture 80-081† at 38°C	11.2	1.37	11	22

*Pennsylvania State University and U S Army Engineer Waterways
Experiment Station

†See Roy et al, 1981

Figure 6 Comparison of amplitudes of the second (major) exothermic peak as a function of temperature for two different cement types.

which yields crystalline hydration products, including the calcium silicate hydrate tobermorite. Finally, if the reaction product calcium hydroxide $[\text{Ca}(\text{OH})_2]$ is consumed by reacting with silica (SiO_2) to form additional

tobermorite, the ΔG change is more negative (even more favorable):

$$\Delta G = -32.24 \text{ Kcal/mole } \text{Ca}_3\text{SiO}_5$$

(when $\text{SiO}_2 = \text{quartz}$)

The important fact is that Eq. 3 is the most thermodynamically favorable of the three. In actual practice, the nearer we are to achieving the reaction product of Eq. 3, the more stable the product will be.

Continuing studies are examining the effects of groundwater compositions on the phase stabilities of cementitious materials.

Properties of Experimental Mixtures. Some examples of materials based on these thermodynamic considerations follow. In actual practice, formulations will always be based on tradeoffs between the most favorable thermodynamics and the other

relevant properties. Several mixtures were investigated in which cement compositions were modified by adding various silica-rich materials (Grutzeck et al., 1980) with different reactivities—and different proportions of alumina and minor components.

Compressive strengths of several mixtures are given in Table 3. The first three mixtures were sand-rich grouts that could be used in borehole plugs or as matrixes for preplaced aggregate concrete; the fourth was formulated with the addition of slag and quartz to a cement paste. All were designed with the goal of attaining products with an ultimate lower free-energy state. Some mixtures included salt to generate greater chemical compatibility with salt-saturated repository formations (Roy et al., 1981). The slag and quartz additives in mixture A were found to diminish the reaction rate at 27°C, as

evident from the strength development rate. However, very high strengths were developed within the time span studied at the higher two curing temperatures shown. The strengths generally increased with higher curing temperature at the shortest curing time interval. At a single temperature, regular increases in strength were found with longer curing time, except for some irregularities at the highest temperatures. The compressive strengths in general were found to range from high to very high. Studies of these and other mixtures will be extended to longer time periods.

Permeability and Bonding. Other important properties of seal material relating to long term durability include permeability of the seal system to fluids and the effectiveness of the seal-rock bond. Knowledge of

Table 3 Compressive Strength (MPa) of Experimental Mixtures

Mix number	Curing time, h	Curing temperature, °C			
		27	45	60	90
81-030*	7	41	58	63	55
	14	58	67	61	47
	28	84	87	90	93
81-050†	7	75	79	117	86
	14	80	89	87	73
	28	87	102	98	63
81-091‡	3	48	66	79	77
	7	52	85	66	76
	28	77	95	92	94
A§	7	45			57
	28	64			94

*Fly ash, ferrosilicon dust, expansive, additive, and salt additive; w/c ratio, ~0.30.

†Ferrosilicon dust, expansive additive, and slag additive, w/c ratio, ~0.30.

‡Fly ash, amorphous silica, expansive additive, and salt additives; w/c ratio, ~0.30.

§Slag- and quartz-containing cement paste; w/c ratio ~0.45.

pathways and mechanisms for fluid flow and of means for minimizing or preventing flow through cementitious materials is important because it relates to understanding mechanisms of ionic transport. Although the two mechanisms are not identical, they have certain common features (Goto and Roy, 1980). Powers (1958) discussed the importance of the pore volume and its influence on the permeability of hardened cement paste. Permeability is influenced not only by the total pore volume, however, but also by the pore size distribution and its effective interconnected porosity. Water-to-cement (w/c) ratio, curing temperature, and hydration time were investigated as experimental parameters and were related to the porosity, pore size distribution, and permeability of cement pastes.

Porosity. The porosities of hardened cement pastes calculated from measured evaporable water (that extracted from the pores of water-saturated samples), shown in Fig. 7 as a function of w/c ratio, indicate that decreasing w/c ratio caused a decrease

Figure 7 Relationship between porosity and water-to-cement (w/c) ratio.

in porosity. Samples that were cured at high temperatures had lower porosities; this reflected a higher percentage of hydration for early age samples cured at the high temperature. The porosity decreased with increasing percentage of hydration, but the degree of hydration for samples cured at high temperatures is expected eventually, after longer times, to be smaller than for samples cured at the lower temperature (Brunauer and Kantro, 1964).

Permeability. Water permeabilities measured for the same sets of samples (Fig. 8) were found to decrease exponentially with decreasing w/c ratio at a constant curing temperature. Samples cured at high temperatures had higher permeabilities, however. The permeability for the sample with a w/c ratio of 0.35 cured at 27°C could not be calculated exactly because the minimal amount

Figure 8 Relationship between permeability and water-to-cement (w/c) ratio.

of water transported through the specimen was essentially at the detection limit of the apparatus (White et al., 1979).

Pore Size Distribution. Pore size distributions in samples with a w/c ratio of 0.40 cured at 27 and 60°C are shown in Fig. 9. The mercury intrusion porosimetry technique measured pores only below a 7.5- μm radius. The sample cured at 27°C had a peak in the pore size distribution at 75 $\approx$ 140 Å and revealed no pores having radii larger than 4300 Å. The sample cured at 60°C had two peaks, at 75 $\approx$ 140 Å and at 1400 $\approx$ 2300 Å. Note that the values of total pore volumes measured by mercury intrusion porosimetry were 0.190 and 0.135, in comparison with 0.339 and 0.379 for samples cured at 60 and 27°C, respec-

tively, measured from the evaporable water content. The volumes of pores greater than 7.5 μm in radius are reflected in the values calculated from the evaporable water content, not the porosimeter measurements.

The current results showed that total porosity is not necessarily the controlling factor for permeability; rather the pore size distribution and the degree of interconnection of the pores are responsible. Samples with substantial volumes of pores greater than 750 Å in radius (i.e., with a second peak in the pore size distribution measured by mercury porosimetry) had larger permeabilities. This is in general agreement with some recent data of Mehta and Manmohan (1980).

The relationships between permeability, porosity, and pore size distribution are complex, but the present results show the value of adequate characterization of pore size distribution in relation to permeability. Studies of other aspects related to the kinetics of phase changes and the transport of species through seal materials are continuing. These include the relationships between permeability and ionic diffusion of relevant species.

Interfacial Bonding Between Rock and Seal Material. Investigations of the nature and integrity of cement-rock interfacial regions are in progress. These studies are based on the likelihood that an important relationship exists between the structure and morphology of the cement-paste-aggregate (wall rock) interfacial region and the initiation and propagation of microcracks (Langton and Roy, 1980b). Curing conditions in a set of tests included temperatures of 27, 60, and 90°C and pressures of 0.1, 6.9, and 68.9 MPa. The morphology and mode of fracture at the interfacial region formed between portland cement paste matrix and rock depended on both the reactivity of the

Figure 9 Pore size distributions of Hardened cement pastes.

rock and the degree of hydration of the cement. A two-layered zone developed in the interfacial region between nonreactive rock (aggregate) and portland cement paste. The interfacial morphology is characterized by a thin film of silica-containing calcium hydroxide [$\text{Ca}(\text{OH})_2$] from which calcium silicate hydrate (C-S-H) particles appear to be growing. In addition to the C-S-H, larger crystals of $\text{Ca}(\text{OH})_2$ appear to attach the interfacial region to the bulk matrix material and, thereby, the aggregate to the bulk matrix. As the degree of hydration increased, more bulk material became attached to the interfacial region. When the interfacial region was exposed in 6-month runs, it still appeared as a two-layer zone. The effect of elevated pressures was to increase the contact between the matrix and rock surface, and, when combined with elevated temperature, to increase the hydration rate also. Surface roughness of the rock had no major effect on the basic structure of the interface. Future studies are expected to determine the effect of composition on the bonding and interfacial structure.

Characterization of Old and Ancient Hydrated Cementitious Materials

The remarkable longevity of ancient cementitious mortars, plasters, and concrete, which are compositionally similar to their modern counterparts, suggests that the information gained from studying these materials may be applicable to repository seals. Thus old hydrated cementitious building materials provide a potential source of information useful for predicting long-term stability and performance of modern repository seal materials.

Borehole plugging materials quite recent on this scale (approximately 18

yr old) (Scheetz et al., 1979; Wakeley et al., 1981) were characterized first. A summary of the physical and mechanical properties of a plug material is given in Table 4. This material, although relatively weak, maintained its mechanical and chemical integrity. These data and the other characterization results and observations illustrated that the plug had performed adequately over the 18-yr time frame but revealed some deficiencies in the specific materials design (it had a relatively high permeability to gas).

Studies currently are being made of ancient cementitious materials from a variety of sources. A first-phase study was made to develop characterization procedures for ancient building materials (Langton and Roy, 1980a), and to explain chemically and physically the remarkable durability of selected cementitious materials. The specific objectives were to: (1) Search the archaeological, engineering, and materials science literature for pertinent information; (2) obtain representative samples of a variety of old/ancient hydrated building materials; (3) establish procedures for sample characterization; (4) characterize the samples; (5) evaluate the potential for correlations between raw materials and cements; (6) determine and evaluate the interactions between cementing materials and the environments in which they existed; (7) determine and evaluate the nature and extent of interactions between cement matrix (binder) and aggregate; (8) provide information regarding the stabilities of hydrated matrix phases; and (9) provide information applicable to predicting the long-term durability of products containing modern portland cement.

The multimethod analysis used included macroscopic and microscopic methods and petrographic and scanning electron microscopy, combined

Table 4 Physical and Mechanical Properties of Borehole Plug and Permeability Values for Host Rock and Interface

Bulk density	1.45 g/cm ³
Helium density	1.78 g/cm ³
Porosity	18.5%
Compressive strength	2.59 MPa (375 psi)
Solubility	~2 g/l in deionized water at room temperature
Elemental analysis of filtrate	
Cl	575 ppm (gravimetric)
Na ₂ O	310 ppm
O	216 ppm
SiO ₂	139 ppm
CaO	58 ppm
Al	<1 ppm
Mg	<1 ppm
Elemental and XRD analysis of filtrate solids	
Elemental*	
Cl	
Ca	
Na	
Si	
S	
K	
Fe	
X-ray diffraction	
NaCl	
KCl	
CaCO ₃	
Friedel's salt [Ca ₂ Al(OH) ₆][Cl · 2H ₂ O]	
C-S-H	
Permeability	
Salt	2×10^{-6} darcy
Cement	1×10^{-3} darcy
Interface	3×10^{-3} darcy

*Scanning electron microscopy and energy dispersive X-ray analysis

with energy-dispersive X-ray analysis, chemical analysis, X-ray diffraction measurements, and trimethylsilylation (Sagar and Roy, 1979) for identification of silicate fractions. The chemical compositions of the matrixes of the cementitious materials studied in the first phase fell into distinct groups, as shown in Fig. 10. The group of pozzolanic cements in the upper left of the diagram are of particular interest since the oldest ones date to about the second century B.C.

The results of the first-phase study (Langton and Roy, 1980a) confirmed

the remarkable integrity of certain materials and offered preliminary explanations for their longevity. The hypotheses are currently being tested in systematic studies of suites of materials approximately 2000 yr old and older collected from Rome, Cyprus, and Greece.

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Figure 10 Plot of $\Sigma\text{CaO} + \text{MgO}$ vs. $\Sigma\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ for the matrix fractions of selected cementitious building materials and rock specimens. (Data from Langton and Roy, 1980a.)

M. Daimon, M. W. Grutzeck, S. Goto, C. A. Langton, P. H. Licastro, M. Perez, A. Rousan, A. K. Sarkar, B. E. Scheetz, L. D. Wakeley, and E. L. White participated in research. F. L. Burns, Office of Nuclear Waste Isolation, was project manager.

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Field-Test Programs of Borehole Plugs in Southeastern New Mexico

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This paper gives a general overview of the repository-sealing field test effort being conducted by Sandia National Laboratories in support of the Waste Isolation Pilot Plant in southeast New Mexico. Summary descriptions of supporting activities, such as performance assessment and plugging materials development, are included to create the connection between modeling and laboratory activities as they relate to field results. Results of tests on a portion of a 17-year-old plug (Plug 217) recovered from a mine horizon and the Bell Canyon Test, in which a cement plug was emplaced to isolate a naturally pressurized aquifer, are given. Conclusions from these field plugging tests are included.

Introduction

This paper provides an update on the Sandia Borehole Plugging Program (BHP) (Christensen and Hunter, 1979), as reported at the October 1979 National Waste Terminal Storage (NWTS) Information Meeting (Christensen, 1979b) sponsored by the Office of Nuclear Waste Isolation (ONWI) and included in the proceedings of the information meeting (Office of Nuclear Waste Isolation, 1979). As reported by Christensen, the Sandia BHP is specifically designed to support plugging activities for the proposed Waste Isolation Pilot Plant (WIPP) being considered by the

Department of Energy (DOE) for storing defense non-heat-producing transuranic waste. This program will also provide generic information on bedded-salt formations to ONWI for inclusion in the NWTS commercial nuclear waste repository programs. The goal of the Sandia BHP is to provide the plugging technology that will be required at the decommissioning and final closure of the WIPP facility.

At the time of the 1979 meeting, the program and field-test emphasis was on using cementitious plugging materials and modifying existing industrial emplacement techniques as needed to suit repository plugging requirements. These efforts, coupled with supporting laboratory testing, consequence-assessment modeling of wellbores and plugs, and an ONWI-sponsored geochemical program to evaluate long-term interactions between the host rock and the plug were considered adequate to provide the technology required for repository plugging. It is encouraging that, at present, this emphasis is still considered adequate. Development and progress in the BHP from January 1979 through May 1981 disclosed no serious gaps in the program as originally planned, and there is high confidence that progress toward the goal will continue. Cementitious plugging materials are still considered appropriate for repository sealing. Two basic expansive grout formulations—a freshwater mix, designated BCT-1FF, and a brine-based mix, designated BCT-1F—having water-to-cement (w/c)

ratios on the order of 0.3 and permeabilities in the range of 0.1 to 10 μ darcy (Gulick, 1980; Gulick et al., 1980) continue to be the prime candidates for plugging the overlying-underlying formations and the salt horizons, respectively, at the WIPP site. These mixes show evidence of good compatibility with the respective host rocks, and steps are now under way at the U. S. Army Corps of Engineers Waterways Experiment Station (WES) to assess the inclusion of CaSO_4 into the freshwater mixes to provide an enhanced compatibility. The ONWI-sponsored geochemical research programs at both WES (where the principal investigator is Katherine Mather) and the Pennsylvania State University (PSU) Materials Research Laboratory (where the principal investigator is Della Roy) include these mixes and modifications in the long-term geochemical assessment of material interactions. Steven Lambert, in the Sandia WIPP program, developed a theoretical technique for the continuous precipitation and deposition of particulate salt from brine within a wellbore to replace salt removed during drilling. Laboratory-scale demonstration of the process was completed in late 1981, and full-scale field-test demonstrations will follow. Successful demonstration of this salt deposition-replacement technique will provide confidence that the wellbore will eventually be healed by natural redistribution of stress, thus restoring the formation within the salt horizon to near its pre-drilled state. Progress in materials development suggests that the proper materials and techniques will be available when they are required at repository closure.

Field-testing experience with cementitious materials indicates that emplacement techniques routinely used within the oil-field cementing industry will be adequate for repository plugging operations. Any modifi-

cations that may be required are expected to involve only minor changes; no new technology will be required.

Consequence assessment calculations (Department of Energy, 1980) for the WIPP site indicate that even the most severe conditions of regional fluid flows through the repository via unplugged wellbores will not result in significant consequences to the public. Unplugged wellbores in and near a repository will be plugged, however, to develop even greater assurance in the isolation provided.

The proposed WIPP repository will be approximately 2150 ft deep in the Salado bedded-salt formation (Powers et al., 1978). Figure 1 shows a generalized stratigraphy of the site. The primary protection required of a wellbore plug is to minimize possible fluid migration through the repository. Consequently, the field effort is directed at understanding and quantifying the effect of a plug in reducing possible flows in the plugged region.

The first of the field efforts undertaken in 1979 assessed the effectiveness of an existing plug in media similar to those at the WIPP. A potash exploration hole drilled and plugged in 1961 was intercepted at the ore horizon in a working potash mine. Approximately 0.8 m^3 of rock, including the plug (Plug 217) was removed and sawed into nominal 20-cm-thick sections perpendicular to the plug axis. One sample section each was sent to the WES and PSU for analysis. The results of the petrographic analysis (Buck and Boa, 1979; Scheetz et al., 1979) indicated that the plug did set up and was relatively competent with regard to bond strength. The plug had a high water-to-cement (w/c) ratio (approximately 0.7), in contrast to the currently used high-strength expansive grouts with a w/c near 0.3. This difference could account for the permeabilities of the

- HALITE
- ANHYDRITE, GYPSUM, AND SILTSTONE
- SANDSTONE
- SILTSTONE
- DOLOMITE
- LIMESTONE
- ANHYDRITE
- CEMENT GROUT
- BOTTOM OF CASING

plug-formation complex, which were on the order 5 to 50 mdarcy—much higher than the values of 10 μ darcy possible with more recently designed plug mixes (Gulick, 1980). Consequently, it was determined that, even though the relatively long in-place time of the plug should lead to valuable insights on plug performance, the unknowns associated with the original mix preclude confidence in the 1961 technology.

The second field effort in 1979 was the initiation of the Bell Canyon Test (BCT) in late March in the AEC-7 wellbore, located near the proposed WIPP Site in southeast New Mexico. The results of this test are reported by Christensen and Peterson (1981). Excerpts from that report follow.

Background

The Bell Canyon Test was the culmination of prior efforts to develop materials tailored to the WIPP lithology. Previous work in the BHP program centered around cementitious grouts as candidate plug materials because the technology was available and developed, costs were reasonable, and these materials exhibited long-term stability and competency.

Before the BCT, grout development for borehole plugging had progressed to the point that candidate mixes were available (Gulick et al., 1980). Emplacement techniques had been demonstrated in an earlier field test in which another drill hole, ERDA-10, was plugged (Gulick, 1979). It was appropriate then to test a grout mix in situ to determine the level of performance that could be obtained and compare the results with system performance. The Bell Canyon Test objectives were to evaluate in situ the state of the art in borehole plugs and to identify and resolve problems encountered in evaluating a "typical" plug installation in anhydrite.

The concept was to place a plug in contact with a naturally pressurized fluid source in the field and determine the resulting restriction of fluid flow. While simple in concept, the testing was complex in execution and evaluation: trade-offs had to be made between emplacing the shortest possible plug that would allow reasonable fluid flows over a short testing time and using the minimum length that could be physically emplaced as a representative installation. Clearly these are competing effects. The shorter the plug, the higher and faster is the flow under a given pressure differential; hence the time is shorter, and the expense of the test is lower. Conversely, the longer the plug, the more representative it is of a typical plug installation, and the time and expense required to assess its performance increase correspondingly. These details were resolved and presented in the test plan for peer review before the test began (Christensen, 1979a). After the peer reviews, the resulting comments and suggestions were considered, and an operational plan was developed for conducting the test. The Bell Canyon Test evaluated a 2-m-long grout plug 1370 m deep in a 20-cm-diameter borehole and exposed to a 12.4-MPa pressure differential.

Wellbore Preparation

An abandoned exploratory hole [AEC-7, which was drilled by Oak Ridge National Laboratory (ORNL) in April 1974 (Statler, 1980)], located approximately 11 km northeast of the center of the proposed WIPP site, was selected for the BCT. The wellbore configuration at the completion of the ORNL effort consisted of a surface conductor to 15 m, 8 $\frac{5}{8}$ -in.-diameter cemented casing into the Salado Formation to 310 m, and a 7 $\frac{1}{16}$ -in.-diameter open hole to total depth of 1194 m.

Reentry began on Mar. 19, 1979, and the wellbore was cleared to total depth in preparation for drilling to the Bell Canyon high-pressure aquifer. The wellbore was deepened by continuous coring through the lower anhydrite of the Castile Formation into the Delaware Mountain Group until the high-pressure aquifer was intercepted in the Ramsey sands between 1413 and 1426 m. The hole was extended to a total depth of 1435 m. Figure 1 shows the stratigraphy of the AEC-7 wellbore, and Fig. 2 shows the BCT configuration as emplaced. Before the plug was installed, the Bell Canyon aquifer pressure was established at 12.4 MPa at the intended plug location (1370 m)

by a series of three drill-stem tests. Once the high-pressure aquifer was intercepted and the suitability of the wellbore as a test bed for the BCT was established, preparation continued for the emplacement of the plug. During and after the reentry and coring phases, routine geophysical logs and permeability testing of the Salado Formation were conducted to support the BHP and other WIPP-related tasks (Statler, 1980; Peterson, 1981)

Grout Development

The most advanced candidate material currently available for plugging boreholes is high-quality cement grout, which is the focus for the

Figure 2 As-built BCT test bed (not to scale).

long-range development and testing program at WES (Gulick, 1978) and which provided the basis for selecting the BCT plug mix.

In general, desirable properties of plugging grouts are low permeability, low porosity, high mechanical bond strength with the host rock, expansivity, homogeneity, pumpability, and geochemical stability. Lower w/c ratios are correlated with lower permeability and porosity and higher bond strength and strength. The w/c ratio has been reduced by controlling the coarseness of the cement; including super plasticizers and turbulence-inducing compounds, which enhance the fluidity of the mix; using retarders to control set times; and controlling slurry temperature (Gulick et al., 1980).

Previous laboratory experience at WES suggested a grout mixture of Class H cement and a proprietary additive provided by Dowell Division of the Dow Chemical Company. Twenty-four candidate mixtures were formulated and tested by WES for time of efflux, workability, density, and strength under accelerated curing. Dowell further developed this mixture (Table 1), designated BCT-1F, by including a powder dispersant (Gulick, 1980).

After the borehole was cored to intercept the Bell Canyon aquifer, the plug location was selected in the basal Castile anhydrite. The BCT-1F was tested for short-term compatibility with anhydrite core by WES, PSU, ORNL, and Dowell (Gulick, 1980; Grutzeck et al., 1980; Moore et al., 1981).

These investigators found permeabilities of the various grout-anhydrite samples ranging from 10^{-3} to 10^{-6} darcy. The BCT-1F grout samples consistently had permeabilities less than 10^{-6} darcy. Grout-filled anhydrite cores leaked at the interface, and some samples, particularly those cured at ambient temperatures of about 22°C, exhibited a white powdery deposit at the interface (Gulick, 1980). The push-out bond strength was in excess of 2.5 MPa (Gulick, 1978; Grutzeck et al., 1980; Moore et al., 1981).

An alternate freshwater grout, designated BCT-1FF, was also formulated for further testing (Table 1). The w/c ratio was increased to an acceptable viscosity and pumpability. The fresh-water grout had a higher strength and greater expansion than the salt grout (BCT-1F), and its push-out bond strengths were equal to or greater than those of the saltwater

Table 1 Ingredients and Properties of Grout

	BCT-1F	BCT-1FF
Ingredients, wt. %		
Class H cement	50.1	52.2
Expansive additive*	6.7	7.0
Fly ash	16.9	17.6
Salt (NaCl)	6.5	
Dispersant*	0.2	0.2
Defoamer*	0.02	0.02
Water	19.5	23.0
Properties		
Water-to-cement ratio	0.26:1.0	0.30:1.0
Fluid density, g/cm ³	2.04	1.98

*Proprietary additives of the supplier (Dowell).

grout. Permeabilities of the BCT-1FF grout-rock sample ranged from 1 to $15 \mu\text{darcy}$. The grout adhered more tightly to the rock, and there was no observable leakage at the interface (Gulick, 1980). The BCT-1FF mixture was selected for the BCT plug.

One conclusion resulting from the testing of grout-rock samples was that push-out bond-strength tests should not be related to plug permeability. This result has led to the inclusion of permeability testing as a routine part of plug material evaluation. Results of studies to date have been published, and investigations of grout properties are continuing at Sandia, WES, and PSU. Full details of the BCT grout development, selection, and emplacement are given by Gulick (1980).

Instrumentation

Instrumentation has been developed to evaluate the environment in which plugs are placed and to determine the performance of emplaced plugs (Cook, 1979; Cook et al., 1980). Developments to support specific tests include:

- A guarded straddle-packer system to evaluate the permeability of the formation
- A self-contained instrumentation package incorporating a timed-release tracer gas, temperature and pressure measurements, and a packer-release system
- A geophone system to monitor release functions
- Fluid buildup and shut-in pressure measurements with current oil-field systems
- Probes for measuring discrete fluid leaks, fluid electrical conductivity, pressure, and temperature
- A wire-line closed-circuit TV system capable of operating in drill holes to a depth of 1000 m

The instrumentation systems to monitor the migration of tracer gas

and brine through the plugged region were used to evaluate the BCT plug performance. The original plan was to create a pressure differential across the plug by applying the Bell Canyon production zone pressure to the plug bottom, with the upper wellbore fluids evacuated. Upper wellbore fluid production precluded this approach, however, and an "umbrella" packer was used to create a test chamber above the plug (Fig. 2).

As shown in Fig. 2, a packer below the plug, deflated after the cement had cured, ensured that the plug was being loaded by the production zone. Also included below the plug was an instrumentation package containing multiple charges of time-released electronegative tracer gas (sulfur hexafluoride, SF_6). The instrumentation package monitored fluid pressure and temperature below the plug, and the tracer gas allowed for assessment of multiphase flow through the plugged region. Since there were no cable penetrations through the plug, all these functions were controlled by preset timers in the instrument canister (Cook et al., 1980).

Test Description

The test configurations used for evaluating the Bell Canyon plug performance are shown in Fig. 3. The plug was installed to isolate the upper regions of the borehole from the Bell Canyon aquifer, which has a 12.4-MPa shut-in pressure and a production capability of $3.8 \times 10^7 \text{ cm}^3/\text{d}$ (240 standard barrels per day, STB/d). The aquifer temperature and pressure were continuously monitored by the instrumentation package described. Measurements were made of both the volumetric flow and the velocity of fluid flowing from the aquifer through, or around, the plug into the upper wellbore. Because the upper portions of the borehole produce fluid, the umbrella packer was installed

Figure 3 Schematic showing testing techniques. (a) Fluid buildup tracer flow. (b) Shut-in. (c) Neutral. P_H is hydrostatic pressure. Pressure is 0.519/ft depth.

(Fig. 3) to provide an isolated test chamber for measurement purposes. The pressure in the wellbore annulus above this packer was approximately 15.8 MPa.

Since plug performance is evaluated from measurements of fluid intrusion into the test chamber, it is important to identify possible flow paths into the region. As shown schematically in Fig. 4, four distinct fluid charge paths exist from the aquifer through, or around, the plug into the test region. These are the cement plug; the plug-borehole interface region, in which some porous microstructure may exist either as a result of bonding imperfections or chemical reactions; a possible damage region along the borehole wall resulting from drilling and coring operations; and the undisturbed formation surrounding the plug. It is, in fact, the flow occurring along all these paths, defined as the plug-formation system, which must be measured.

Additional possible paths along which fluid can enter or leave the test region also exist. These include flows from above the umbrella packer through the surrounding formation or wellbore damage region and flows occurring along some formation discontinuity leading to a distant source.

Finally, depending on the configuration, test measurements are influenced by leakage from the umbrella packer (including leakage from the packer valves) and attached tubing assembly through joints in the 2-in. tubing string leading to the surface. Flow occurring along these paths must be differentiated from that occurring through the plug-formation system.

In addition to tests to characterize the wellbore in the vicinity of the plug, three specific techniques to evaluate the plug-formation system performance are shown schematically in Fig. 3. These include the fluid

Figure 4 Schematic showing possible fluid charge paths in the test region.

buildup, shut-in, and tracer-flow tests discussed in detail in the following paragraphs. Since standard oil-field technology was used for data acquisition, the measurement sensitivity of these techniques and its associated impact on plug performance assessment is also discussed by Christensen and Peterson (1981).

Data Analysis

The data analysis is intended to characterize (i.e., to determine the permeability, porosity, cross-sectional area, fracture extent, etc.) the flow paths originating below the plug and penetrating into the test region (shown in Fig. 4). Available data include the experimentally measured test-region pressures, water accumulation rates, tracer arrival times, and pressures in the annulus and Bell Canyon aquifer. Additional inferences can be made by using data from laboratory tests of grout and grout anhydrite permeability. Therefore there is a classic problem under a

specified set of boundary conditions in which a number of constants, representing the formation characteristics and flow-path geometries, need to be evaluated. A rigorous derivation of the equations defining the flow through this plug-formation system is given by Christensen and Peterson (1981).

Test Results

System Integrity-Wellbore Characterization Test Results.

Before the BCT grout plug was installed, system-integrity and plug zone characterization tests were performed. The system configuration generally appeared as shown in Fig. 2, with the exception that the inflated bridge plug was positioned at the cement grout plug location and Freon tracer gases were used to preclude "poisoning" the wellbore with the SF_6 used after plug emplacement. Fluid buildup test rates are shown in Fig. 5 for two potential plug locations.

Figure 5 Fluid buildup test data obtained during plug zone characterization studies. Changes in fluid level were determined from pressure changes measured with the Lynes CWL system.

Plug Performance Test

Results. Performance characteristics of the emplaced BCT grout plug were monitored over a 4-month period, beginning Oct. 9, 1979. Results of the fluid buildup, shut-in, and tracer-flow tests are summarized in Tables 2, 3, and 4, respectively. Individual test results are discussed in the following paragraphs, and the overall system performance is described fully.

Fluid Buildup Tests. Five fluid buildup tests were conducted. Data obtained during four of these tests are shown in Fig. 6. The Oct. 19 test was continued for a total of 144 hr, with the fluid rise continuing at roughly the rate shown in the figure. The fluid level was measured with a wire-line tool at 1330 and 1296 m on Dec. 21 and Jan. 11, respectively. These measurements represent the data for the last test shown in Table 2.

The changes in fluid level in the 5-cm diameter tubing (Fig. 6) were determined from measured pressure changes. The relatively rapid fluctuations do not represent actual changes

in fluid level but reflect noise in the pressure-monitoring system.

The permeability-area (kA) products shown in Table 3 were determined from measured inflow rates (Q) in the test region. Inflow rates were evaluated using straight-line approximations of the data shown in Fig. 6. Since fluctuations in the Oct. 9 and 10 data are large in comparison with the average increase in fluid level occurring during the 18-hr test periods, the method of least squares was used to obtain best straight-line fits for these data. Because of the intensity of the fluctuations, we can only state that the data indicate that kA values are less than $2.5 \times 10^{-10} \text{ cm}^4$ (80 μdarcy under the wellbore cross-sectional area assumption).

The Oct. 9 and 10 data definitely indicate the lowest test-chamber inflow rates. Any leakage through, or around, the packer-tubing assembly would result in increased rates. Therefore, of the fluid buildup test results, these are probably most representative of the plug-formation system performance.

Table 2 Summary of Fluid Buildup Test Results

Test initiation date	Test duration, h	Measured test region inflow rate,* cm ³ /d	Flow path permeability area† (kA), 10 ⁻¹⁰ cm ⁴
10/09/79	18	320	0.9 (27 μdarcy)
10/10/79	18	670	1.8 (57 μdarcy)
10/19/79	144	4600	12.0 (385 μdarcy)‡
12/12/79	16	7100	(607 μdarcy)‡
12/21/79	504	3300	(275 μdarcy)‡

*Inflow rate obtained for a 12.4-MPa pressure differential across the 2.0-m-long cement grout plug.

†Numbers in parentheses indicate the permeability for a flow path whose cross-sectional area is taken equal to that of the wellbore.

‡High values are thought to result from leakage into the test region through the tubing packer assembly since they are not supported by shut-in test or tracer-transit data.

Table 3 Summary of Shut-In Test Results

Test initiation date	Test duration, h	Measured test region inflow rate,* cm ³ /d	Flow path permeability area† (kA), 10 ⁻¹⁰ cm ⁴
11/05/79	67	610	1.6 (51 μdarcy)
12/19/79	62	830	2.3 (70 μdarcy)
01/18/80	100	550	1.5 (46 μdarcy)

*Inflow rate obtained for a 12.4-MPa pressure differential across the 2.0-m-long cement grout plug.

†Numbers in parentheses indicate the permeability for a flow path whose cross-sectional area is taken equal to that of the wellbore.

Table 4 Summary of Tracer Flow Test Results

Tracer release	Time until first arrival,* h	Permeability-to-porosity ratio (k/φ), 10 ⁻¹¹ cm ²	Maximum flow channel width (δ), 10 ⁻⁵ cm	Maximum channel flow velocity, m/d
10/09/79	68	2.2	1.5	.6
10/30/79	36	3.3	2.0	1.2
12/12/79	36	3/3	2/0	1.2
01/18/80	No sampling			

*Time until first arrival for a continuous 12.4-MPa pressure differential acting across the 2.0-m-long cement grout plug.

Figure 6 Fluid buildup test data obtained during plug performance evaluation studies. Fluid level changes were derived from pressure changes.

Shut-In Tests. Data obtained during the three shut-in tests, shown in Fig. 7, can be well represented by the simple one-dimensional model and the values of kA shown in Table 3. Results of the shut-in tests were consistent and indicated that the plug-formation system responds as if there were an approximately 50- μ darcy flow path of cross-sectional area equal to that of the wellbore.

During the Dec. 19 test, a significant time lapse occurred between shut-in and the onset of the rapid pressure buildup phase. Also, at late times the pressure continued to increase above the Bell Canyon value. The delayed initial response is thought to be the result of an air bubble trapped in the tubing that extends into the test region below the umbrella packer. A small flow from the annulus region can account for the higher late-time pressure. Both of these effects were modeled (as illustrated in Fig. 7) with the simple one-dimensional formulation. The air bubble was modeled as a 1.1 l void, on the

basis of the field-determined geometry of the test assembly. The product $(kA)_a = 3.3 \times 10^{-11} \text{ cm}^4$ refers to an assumed annular formation disturbed zone surrounding the umbrella packer. Using a cross-section area of this zone equal to the wellbore cross section (325 cm^2), we obtain a value of 10 μ darcy for the disturbed zone, in comparison with 70 μ darcy for the plug zone. Subsequently, the packer-valve-tubing assembly was modified to eliminate the possibility of air entrapment, and the Jan. 18 test was performed for data verification.

It is important to note that there is no evidence of flow from the high-pressure annulus into the test region during the Nov. 5 and Jan. 18 pressure buildup tests. This strongly suggests that, at least in the area where the umbrella packer is positioned, wellbore damage is slight. Assuming a damage area equal to the wellbore area, these shut-in tests are consistent with an equivalent permeability on the order of 10 μ darcy. Note also that the flow observed from the

Figure 7 Shut-in test data obtained during plug performance evaluation studies. The symbols (○, △, □) indicate measured data, and curves show calculated response.

annulus region during the Dec. 19 test could have just as readily occurred through the packer-valve-tubing assembly. Leakage through this assembly is believed to be responsible for the higher flow rates measured during the fluid buildup tests.

Tracer-Flow Tests. A history of the tracer sampling tests is presented in Table 5. The approximately 36-hr time interval between gas release and detection at the top surface of the plug was well established after the Dec. 12 series of tests. Further sampling was, therefore, discontinued.

Tracer release and arrival time measurements are consistent with having flow occur from below the plug into the test region through a channel (i.e., fracture) that is 2.0 m long and 2×10^{-5} cm wide at a velocity of 1.2 m/d. Analysis indicates that larger channel widths would allow significantly higher velocities and correspondingly earlier tracer arrivals. If all flow were to occur through such fractures (e.g., if the wellbore exhibited an onion-skin-type

failure, as illustrated in Fig. 4) and if the individual fracture lengths (l) (measured in the horizontal plane having a depth of the 2.0-m plug vertically) were equal to the wellbore circumference, then approximately 4000 such fractures would be required to produce the measured volumetric flow rate. This suggests that flow through the plug-formation system does not occur through a small number of fractures but rather through a region where the behavior of the microstructure approximates, to a reasonable extent, that of a porous medium.

When interpreted in terms of flow through a classical porous medium, the tracer data indicate a permeability-to-porosity ratio of $k/\phi = 3.3 \times 10^{-11} \text{ cm}^2$ (33 μdarcy , assuming $\phi = 0.01$). If the actual cross-sectional area (A) of the flow path through the plug-formation system (see Fig. 4) is known, the associated permeabilities and porosities cannot be determined. There is evidence that plug permeabilities are small and that flow occurs primarily through a

Table 5 History of Tracer Sampling Tests

Tracer release date	Sampling date	Tracer detected	Remarks*
10/09/79	10/08/79	No	Background check
	10/12/79	Yes	Arrival had occurred in 68 h
	10/18/79	Yes	
	10/27/79	Yes	Wellbore fluid replaced
10/30/79	10/29/79	Trace	Background check
	10/31/79	Trace	
	11/01/79	Yes	Arrival had occurred in 36 h
12/09/79	12/06/79	Trace	Background check
	12/11/79	No	
	12/12/79	No	
	12/13/79	Yes	Arrival had occurred in 36 h
01/18/80			No further tracer samples were taken

*Arrival times represent the tracer transit time, given a continuous 12.4-MPa pressure differential across the 2.0-m cement grout plug. The actual wellbore pressure history is used to determine this value.

permeable microstructure at the plug borehole interface (Gulick, 1980; Grutzeck et al., 1980). Required permeabilities and porosities of such an interface zone (see Fig. 4) are shown in Fig. 8 as a function of flow-zone cross-sectional area.

Conclusions

The field test programs undertaken thus far provide confidence that satisfactory isolation of radioactive waste is technically feasible. Results from Plug 217 testing and the Bell Canyon test show that fluid flow restrictions can be achieved by cementitious plugs. The degree of restriction can be included in transport models to predict radionuclide egress rates through wellbores from the geologic storage horizons. These, in turn, can be used to provide estimates of the amount of radionuclide reentry to the biosphere and the resulting consequences with regard to public health and safety.

Both freshwater and brine-based grouts, suitable for field emplacement, are available now to provide sealing functions if the proper care is exercised in matching physical properties of the local rock. The reduction in fluid flow provided by even limited-length plugs is far in excess of that required by bounding safety assessments for the WIPP.

Field-testing techniques to evaluate in situ plugs have been developed. Although these techniques were generally adequate to evaluate the Bell Canyon plug, some improvements must be made in the system if resolution for lower (less than 50 to 100 μ darcy) permeabilities are needed.

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Figure 8 Relationship between flow zone permeability, porosity, and cross-sectional area, based on one-dimensional analysis of measured data.

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An Overview of Nuclear Waste Disposal in Space

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One option receiving consideration by the Department of Energy (DOE) is the space disposal of certain high-level nuclear wastes. The National Aeronautics and Space Administration is assessing the space disposal option in support of DOE studies on alternatives for nuclear waste management. The space disposal option is viewed as a complement, since total disposal of fuel rods from commercial power plants is not considered to be economically practical with "Space Shuttle" technology. The space disposal of certain high-level wastes may, however, provide reduced calculated and perceived risks. The space disposal option in conjunction with terrestrial disposal may offer a more flexible and lower risk overall waste management system. For the space disposal option to be viable, it must be demonstrated that the overall long-term risks associated with this activity, as a complement to the mined geologic repository, would be significantly less than the long-term risk associated with disposing of all the high-level waste. The long-term risk benefit must be achieved within an acceptable short-term and overall program cost.

This paper briefly describes space disposal alternatives, the space disposal destination, possible waste mixes and forms, systems and typical operations, and energy and cost analysis.

Introduction

The disposal of nuclear wastes, specifically the disposal of high-level wastes (HLW)*, is an issue of crucial importance to the future of nuclear power. Regardless of whether nuclear power will be used in the future, however, a solution for HLW disposal will be needed for wastes that have been accumulating in the United States since 1943 from defense and commercial activities. In particular, there are approximately 2300 t of radioactive spent fuel assemblies that have accumulated in storage ponds at some 71 nuclear reactor sites around the country (Interagency Review Group, 1979). Additional waste will be generated and added to the inventory.

The Department of Energy (DOE) has the responsibility for developing the technology required for managing nuclear wastes in a safe and environmentally acceptable manner. Several alternate strategies have been proposed for dealing with the nuclear wastes (Interagency Review Group, 1979), and several potential technologies have been described, along with their environmental impacts (Department of Energy, 1979). Even though

**The term high-level wastes (HLW), as used here, refers to either intact fuel rod assemblies that are being discarded after having served their useful life in a nuclear reactor (spent fuel) or wastes that remain after the reprocessing of spent fuel and contain the fission products and the unusable actinides.*

the mined repository approach is considered to be the current reference technology in the waste management program, DOE is following the National Environmental Policy Act [Public Law 91-190, Secs. 102(2)(C) and 102(D)] to insure that alternative technologies are given appropriate and careful consideration in the decision-making process for the management of nuclear wastes.

One of the options currently receiving consideration by DOE is space disposal of certain high-level nuclear wastes (Fig. 1). The National Aeronautics and Space Administration (NASA) is assessing the space option in support of DOE studies on alternatives for nuclear waste management and with program guidance and waste technology definition provided by DOE. The space option is viewed not as a replacement for the currently considered terrestrial disposal options but as a complement to them. Any disposal method that leaves radionuclides on or in the earth's surface must consider the long-term integrity of containment systems, the potential release mechanisms, and local public sentiment and perception of risks. The space option may offer the possibility of alleviating some of these concerns by removing from the earth certain long-lived and difficult to confine radionuclides.

Some residual high-level wastes would still require disposal in a geologic site, but its hazard level and required isolation time may be significantly

reduced to aid public acceptance of the geologic sites (Fig. 2). Not only does the space option provide permanent separation of the selected wastes from the human environment, but also it may allow a high confidence level in the quantification of short- and long-term risk. The space option, in conjunction with terrestrial disposal options, may, in fact, allow a more flexible and lower-risk waste management system.

Space Disposal Alternatives

During the last few years, many alternatives for space disposal have been evaluated. (Aerospace Corporation, 1971; Reichert, 1972; NASA/Lewis Research Center, 1972, 1973a, 1973b, 1973c, 1973d, 1974a, 1974b; MacKay, 1973; Perlich, 1975; Burns, 1975a, 1975b, 1978; Burns et al., 1978; Burns and DeField, 1978; Priest et al., 1978; Peoples, 1979; Jet Propulsion Laboratory, 1979; Rochlin, Metlya, and Windham, 1976; Brown et al., 1977; Friedlander et al., 1977a, 1977b; Friedlander and Davis, 1978, 1979; Pardue et al., 1977; Edgecombe et al., 1979; Platt and Schneider, 1974; Ruppe et al., 1979; Salkeld and Beichel, 1979; Natenbruk, 1979). Questions that have been addressed include:

What wastes should be disposed of in space?

What form should the waste take?

Where should the launch site be?

What launch vehicle and upper stages should be used?

How can safety and practical economics be maintained?

Where in space should the waste go?

Figure 3 summarizes the major alternatives that have been and are being considered. A proposed reference space disposal concept is identified in the blocks, and primary alternatives are indicated by asterisks. Consideration has been given to technology that is likely to be available within the next 20 yr.

Space Disposal Destination.

The several space disposal destinations considered in recent years (Burns et al., 1978) (Tables 1 and 2) include injection into the sun, solar system escape, placement on the moon or in lunar orbit, placement in a high earth orbit, and injection into a stable solar orbit. Injection into the sun and solar system escape are likely to demand more energy than is neces-

Figure 1 Space disposal augmentation of the national nuclear waste management program.

Figure 2 Reduction of long-term risk by space disposal.

sary to assure permanent isolation from the Earth. Disposal on or in the lunar surface represents a technically viable concept, but the potential for scientific and public controversy may be high. High earth orbit and lunar orbit require the least energy of the possibilities considered, but the long-term stability of these orbits is a concern. The current reference concept is injection into a circular, 0.85 astronomical unit (AU), solar orbit about halfway between the orbits of Earth and Venus. Orbital calculations indicate that for at least 1 million yr, and probably more, this orbit is stable with respect to the Earth and Venus and would not intersect the orbits of either one (Friedlander and Davis, 1978, 1979) (Fig. 4). The energy required to reach this solar orbit is lower than that required for solar system escape and significantly lower

than that needed to reach the sun's surface.

Waste Mixes for Space Disposal.

With technology that is likely to be available within the next 20 yr, disposal of all nuclear waste (e.g., entire spent fuel rods) in space is impractical because of the high launch rate required, resulting environmental impacts, high energy requirements, and high costs. Thus some waste separation is necessary. Selecting the nuclear waste mix for space disposal involves a number of complex issues, some economic and some technical. Factors involved in waste mix selection are the half-lives of the waste nuclides, their masses and specific activities (these affect launch rates, heat loads, etc.), their transport properties in a terrestrial repository (Text continues on p. 8.)

Figure 3 Major options for space disposal of nuclear waste. The example discussed in the text is enclosed in a box; the primary alternative is indicated by an asterisk (*) and the secondary alternative, by a bullet (•).

Table 1 Major Space Disposal Destinations Being Considered

Major characteristics	High earth orbit	Lunar orbit	Lunar surface (soft landing)	Solar orbit	Solar system escape	Impact the sun
On orbit velocity requirement (ΔV), m/sec	4000	4250	6050	4450	8750	24,000
Nominal subsystem lifetime requirement, d	<1	6	6	180	<1	<1
Typical disposition	55,000 km, circular	21,700 km, circular	Backside surface	0.85-AU orbit at 1° inclination		
Expected number of on orbit propulsive maneuvers	2	5	5	2	1	1

Table 2 Ranking of Space Disposal Options

High earth orbit	Lunar orbit	Lunar surface (soft landing)	Solar orbit	Solar system escape	Impact the sun
Advantages					
Easily rescued	Can be rescued	Can be rescued	Permanent disposal	Permanent disposal	Permanent disposal
Easily recovered	Recoverable	Recoverable	Excellent orbital stability ($>10^7$ yr)	Potential high public acceptance	Operationally simple
Lowest ΔV	Low ΔV	Permanent disposal on celestial body		Operationally simple	
		No orbital stability problem			
Disadvantages					
Orbital stability uncertain	Orbital stability uncertain	Potential for lunar surface contamination	Subsystem lifetime considerable	High ΔV	Very high ΔV
Public controversy	Complex flight profile	Public and scientific controversy	Rescue difficult	Rescue difficult	Small fraction of waste returns to earth
Disposal not permanent		Complex flight profile		Nonrecoverable	
Overall Rank					
5	4	2	1	3	6

Figure 4 Orbital variations of an initially circular orbit at 0.85 AU.

medium, their potential biological effects, the overall net energy analysis, and the total costs. The relative ease or difficulty of performing the separation chemistry, including the level of risk associated with the separation process, will also affect the mix chosen. The optimum nuclear waste mix for space disposal has yet to be determined.

Current studies use the output from the Purex process as the reference HLW mix for commercial nuclear waste since it is the normal process planned for use at commercial fuel-reprocessing facilities. The Purex process currently being considered for space disposal involves recovering 99.9% of the plutonium and uranium from the dissolver solution and solidifying the remaining dissolver (designated PW-4b) for space disposal (Rose et al., 1978). This results in a mix containing the fission products and actinides (including 0.1% plutonium

and 0.1% uranium). The mass of this waste mix is about 40.8 kg/t of heavy metal—only about 3% of the mass of the spent fuel rods. On the basis of projected spent fuel rod accumulations (Yates and Park, 1979), approximately 175 t/yr of reprocessed commercial nuclear waste could be available for space disposal beginning in the early 1990s. Although it appears feasible to use the space option for disposing of these Purex wastes, the mass of waste for space disposal is still large, and consideration needs to be given to additional processes that will selectively separate only the most hazardous radionuclides for disposal in space. Hazards studies involving geologic pathway modeling have shown that the actinides (americium, curium, and neptunium), technetium, and, to a lesser extent, iodine contribute significantly to the long-term risk of geologic disposal. Studies planned over the next few years

should determine the desirability of selectively separating these from the waste stream and disposing of them in space.

Approximately 340,000 t of military nuclear waste exists at the present time. The bulk of this mass, however, is nonradioactive inert material added to the HLW to facilitate tank storage. Depending on the technical and economic feasibility of the processes used for separating the radionuclides from the vast bulk of inerts, the waste reduced for space disposal is estimated to be about 1000 t; this includes fission products, actinides, and some inerts. These concentrated high-level defense wastes will generally be thermally cooler and exhibit lower radioactivity levels than the commercial HLW. As such, they would be more easily handled and disposed of in space than would commercial waste.

Waste Form for Space Disposal.

Waste forms suitable for space disposal should be chosen on the basis of their ability to meet various physical and chemical requirements in conjunction with other engineered protection systems. Parameters considered should include high waste loading, high thermal conductivity, thermochemical stability, resistance to leaching, toughness, applicability to both commercial and defense waste mixes, fabrication, economics, resistance to oxidation, and resistance to thermal shock. The final determination of the best waste form for space disposal has yet to be made, but, in a study at Oak Ridge National Laboratory (ORNL) (Aaron et al., 1979), the iron-nickel-copper-based "cermet" appeared very promising because of its relative high waste loading (~60%), good thermochemical stability, and toughness in comparison with other potential waste forms (Table 3). Cermet is a waste form in which ceramic particles are uniformly dispersed within a metallic

phase. Fabricating the reprocessed commercial nuclear waste (175 t/yr) into a cermet waste form would result in a total of approximately 300 t/yr of waste material for space disposal beginning in the 1990s (60 space disposal flights of 5000 kg each per year). The defense waste in cermet form would add a total of approximately 2500 t (500 5000-kg loads), which could be disposed of over a long time period, perhaps 20 yr or more.

Typical Operations of a Reference Mission

Figures 5 and 6 illustrate both ground and space operations of a space disposal mission— injection of commercial waste into a 0.85-AU solar orbit. The Space Transportation System should eventually include a space shuttle uprated with liquid rocket boosters (replacing the solid rocket boosters) able to deliver about 45,000 kg to low earth orbit (Marshall Space Flight Center, 1979), a reusable cryogenic orbit transfer vehicle for escape from Earth's atmosphere; and an expendable storable propellant vehicle for the solar orbit insertion maneuver. With this equipment, the reference mission can be described as having six major phases:

- Nuclear waste processing and payload fabrication
- Nuclear waste ground transport
- Payload preparation at launch site
- Prelaunch activities
- Space shuttle operations
- Upper stage operations

These phases are described in the following paragraphs.

Typically, spent fuel rods from domestic power plants would be transported to waste processing and payload fabrication sites in conventional rail shipping casks by ground transportation systems. High-level waste containing fission products and actinides, including 0.1% plutonium

Table 3 Potential Forms for Nuclear Waste in Space Disposal*

Factor	ORNL cermet	Idaho Chemical Processing Plant glass ceramic	Sandia National Laboratory titanate ceramic	Boro- silicate glass	Metal matrix (coated particle)	Hot-pressed supercalcine
High waste loading	M	M	M	L	L	H
High thermal conductivity	H	L	L	L	H	L
Resistance to thermal shock	H	H	H	L	H	H
Thermochemical stability (fabri- cation temperature), °C	1450	1100	1100	1100	1000†	1100
Resistance to leaching	H	H	H	H	H	H
Toughness	H	M	M	L	H	M
Applicability to commercial (PW-4b) and defense (Hanford) mixes	H	L	L	L	H	L
Fabrication of waste into desired shape and size	M	L	L	H	M	L
Economics	M	M	M	H	L	M
Resistance to oxidation	L	H	H	H	L	H

*Potential is rated as H, high; M, moderate, or L, low.

†Copper.

Figure 5 Typical ground operations for the space disposal options.

Figure 6 Typical flight operations for space disposal.

and 0.1% uranium, would be made from these spent fuel rods by the Purex process. HLW would be processed into an acceptable form, such as a cermet metal matrix, by calcining and hydrogen reduction; fabricated into a spherical payload shape; loaded into a stainless steel container; and packaged into a flight-weight radiation shield (depleted uranium).

For transportation to the launch site, the shielded waste container would be loaded into a ground transportation shipping cask, which would provide enough shielding and thermal and impact protection for the waste container to meet Nuclear Regulatory Commission and Department of Transportation regulations. A specially designed rail car would be used to transport the cask from the fabrication site to the launch site (e.g., Kennedy Space Center, Florida). At the

launch site, the cask would be placed in a nuclear payload preparation facility (NPPF), where it would be prepared for launch.

The NPPF could store several shielded waste containers, thus buffering delays in operations. Storage would include additional radiation shielding, thermal control, monitoring, and inspection of the waste container.

The nuclear waste payload would be assembled and checked in the NPPF. The space shuttle (Fig. 7) payload would consist of the waste (~5000 kg in cermet form), a reentry vehicle (RV) structurally supporting the waste in the shuttle orbiter's cargo bay, the orbit transfer vehicle (OTV) (Boeing Company, 1979; General Dynamics Convair Div., 1979), for boosting the payload to escape from low earth orbit and inserting it into heliocentric transfer trajectory, and

Figure 7 Shuttle, space vehicle, and nuclear payload configuration.

the solar orbit insertion stage (SOIS) for putting the waste payload into the circular solar orbit. Typically, the SOIS's storable propellant would be loaded at the NPPF to minimize the hazard at the launch pad. The payload would be installed in the orbiter cargo bay at the launch pad, and then the OTV and shuttle propellants would be loaded.

The shuttle would be launched at a 108° south azimuth (to minimize land overflight) to a 300-km circular orbit inclined 38° to the equator. Once in orbit, the OTV, SOIS, RV, and waste payload would be deployed from the orbiter cargo bay and stabilized in a fixed attitude in space. The orbiter would then move away to a safe distance. The waste payload would be transferred mechanically by remote control from the RV and radiation shield to the SOIS, and the OTV would be oriented for its first propulsive maneuver. The RV and radiation shield would then be returned to the orbiter and reinstalled in the cargo bay. Removing the RV and radiation shield in low earth orbit would significantly increase the payload mass that could be delivered to solar orbit. Appropriate safety measures must prevent reentry of the unshielded waste container.

After the OTV, SOIS, and waste payload have passed final checkout, the OTV would be used to escape from low earth orbit and place the SOIS and waste payload on a heliocentric transfer trajectory to achieve a 0.85-AU circular orbit, inclined 1° to the ecliptic plane. Following the heliocentric transfer trajectory, the OTV would be separated from the SOIS and waste payload, retro-thrusted back to low earth orbit, installed in the orbiter, and deorbited to Earth for refurbishment and reuse. The SOIS would insert the waste into the final solar orbit in approximately 160 d.

Reentry Vehicle Concept. The reentry vehicle (RV) has an aerodynamic shape (Fig. 7) to reduce reentry and impact velocities in case of launch accidents. It has a carbon-carbon shell for reentry protection, steel honeycomb impact attenuator, depleted-uranium radiation shield, and the spherical waste payload. The conical forward and cylindrical aft sections provide aerodynamic stability and house various subsystems—flotation system for use if the RV lands in water, avionics for flight operations, attitude-control system, a combination boiler and heat exchanger to provide thermal control of the waste during launch, docking system, and waste payload transfer device.

Risk and Rescue Mission Considerations. Space disposal should present a lower long-term risk to human health than terrestrial disposal, but short-term risks may not be lower. The phases of the space disposal mission that contribute to the short-term risk are (1) the launch to orbit phase, (2) the early deployment phase, while the waste payload is still in earth orbit, and (3) the phase after injection to deep space. Each of these phases is discussed in the following paragraphs.

Catastrophic failures on or near the pad could subject the waste payload to extreme environments. To minimize the risk, we can:

- Eject the reentry system loaded with nuclear waste from the orbiter's cargo bay and out of the adverse environment
- Make the containment system (e.g., container, shielding, and reentry systems) virtually impervious to the hazards
- Use waste forms not easily dispersed (e.g., cermets)
- Apply launch constraints (e.g., wind direction) to reduce the possibility of exposure

If a shuttle subsystem fails (e.g., if one main engine shuts down) later in the boost phase, we can:

- Use intact shuttle aborts—return to launch site, abort to once-around, or abort to orbit
- Develop contingency aborts—either return to land or ditch at sea
- Design the boost trajectory to avoid overland flight (e.g., 38° inclination orbit)

A rescue mission approach would be based for the early deployment phase while the waste payload is still in earth orbit. The earth-orbit rescue mission would consist of retrieving the SOIS and the nuclear waste from orbit in case the OTV failed during the escape burn from low earth orbit. The rescue OTV would rendezvous and dock with the SOIS and continue the mission from the failed orbit. The rescue mission is based on the premise that, with proper control of the OTV launch, its failure would place the space vehicle and payload in an elliptic orbit about Earth. In a payload rescue mission, a rescue OTV would be placed in low earth orbit in the shuttle, transferred by a burn of the OTV to a phase-adjust orbit, and transferred from the phase-adjust orbit at the proper time for rendezvous and docking with the failed space vehicle. The lifetime of the rescue OTV, considering the coast time in the phase-adjust orbit, may be as much as 300 hr, in comparison with about a 50-hr lifetime for the OTV on the original reference mission.

After injection into deep space, the nuclear waste payload could fail to achieve a stable final orbit because of premature shutdown of the OTV engine beyond earth-escape conditions or failure of the SOIS to ignite at solar orbit conditions. Investigators (Friedlander et al., 1977a; 1977b) who addressed the probability of earth reentry under failure conditions recommended the development of a

deep-space rescue mission capability to further reduce the overall risk during this phase of the mission. A deep-space rescue mission capability is defined as the ability to send another propulsion system (i.e., OTV and SOIS) to rendezvous with the failed payload in solar orbit and place it into the desired stable circular 0.85-AU solar orbit.

Because of the potential consequences of accidents, exhaustive analyses of accident environments and methods of safely coping with these events and conditions must be demonstrated. This can only be done over a long period of time as the system concept and design evolves.

Energy and Cost Analysis

Preliminary estimates of the energy required and the cost surcharge needed to support the space disposal of nuclear waste are shown in Table 4; they consider only the space transportation system. Cost estimates include operations associated with the uprated space shuttle launch vehicle, the OTV, and the SOIS. Energy estimates (Rice, 1978) are based solely on energy requirements for the standard space shuttle at a flight rate of 40/yr. The energy requirements and costs associated with spent fuel reprocessing and ground transportation would add to the total, but the Space Transportation System contribution is expected to be dominant. Disposing of the entire spent fuel elements would consume over 20% of their generated electrical energy and require a user surcharge of over 60 mills/kWh—both prohibitive. For the Purex nuclear waste, however, the energy consumed and the cost surcharge would be much lower. The generated electrical energy needed to support the shuttle launches would be less than 1%, and the projected surcharge to electrical users is slightly more than 2 mills/kWh. The space disposal of a few of the selected

Table 4 Estimated Energy and Cost Surcharge Required to Support Space Disposal of Nuclear Wastes

Nuclear waste mix	Waste for space disposal,* t/yr	Shuttle launches per year†	Generated electrical energy needed for shuttle launches,‡ %	Projected surcharge to electrical users,§ mills/kWh
Spent fuel rods	5590	1905	23.8	67.1
Purex mix	175	60	0.75	2.11
Selected radionuclides	8	3	0.04	0.10

*For an average of 4300 t of heavy metal per year in equivalent fuel cycle (commercial nuclear waste).

†For 5000 kg of cermet waste payload per mission and a single uprated shuttle; cermet loading, 58.7%.

‡For 0.51×10^{12} kJ per shuttle flight and 9.5×10^{11} kJ (2.64×10^8 kWh) generated per tonne of heavy metal.

§For a Shuttle-OTV-SOIS cost per flight of \$40 million.

more hazardous radionuclides from the nuclear waste (e.g., actinides, iodine, and technetium) would result in even lower energy consumption and user cost surcharges. These results point out the need for selecting for space disposal only the radionuclides that are the most significant contributors to the long-term risk of geologic disposal.

Closing Remarks

The space option for disposal of certain radioactive nuclear wastes has been studied for some time and is receiving increased attention in recent environmental and policy reports on nuclear waste management. The Department of Energy and NASA are jointly preparing a 4-yr concept definition and evaluation plan for use in further assessment of incentives for space disposal of certain nuclear wastes. This plan will describe the steps required to appropriately assess the desirability of the space option. The major issues addressed in the plan are:

- Selection of space disposal destination

- Design of nuclear waste mix, form, and payload
- System reliability, safety, and safeguards
- Economics
- Environmental impacts
- Relation to terrestrial disposal options
- Possible effects on current and future space program plans
- Effects of advanced technology on feasibility, viability, and the environment
- Political, international, and legal aspects
- Socioeconomic aspects
- Commitment of resources and energy analysis

For the space option to be viable, it must be demonstrated that the overall long-term risks associated with a space disposal program, as a complement to the mined geologic repository, will be significantly less than the long-term risks associated with terrestrial disposal of all high-level waste. This long-term risk reduction must be achievable within an acceptable short-term risk and overall program cost.

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Index

- actinides, 9
 - leaching, 185
 - solubility limits, 188
 - solubility, 171
 - sorption, 225-226
- actinium-227
 - distribution coefficients, 221
 - environmental transport, 240
- age estimation, 42
 - decay products method, 44
 - methods, 43
- Alabama, 28
- alkali metals, leaching, 189
- alluvium, radionuclide migration, 238
- aluminum oxides, sorptive properties, 227
- americium
 - distribution coefficients, 211, 219
 - sorption, 226, 228, 238
- americium-241, distribution coefficients, 221
- americium-241, environmental transport, 240
- americium-243, distribution coefficients, 221
- americium-243, environmental transport, 240
- Anadarko Basin, 31
- anorthite, sorptive properties, 226
- Antelope Shales, 36
- Antrim Shales, 17
- apatite, sorptive properties, 226
- Appalachian Basin, 24-25
- Appalachians, 26
- aquifers, 8, 26, 30, 39
- Ardmore Basin, 31
- argillaceous rocks
 - assessment, 29, 37, 38
 - map of field studies, 17
 - properties, 39
 - radionuclide migration, 238
- argon, 52, 54
- argon-40, 42, 47
- Arizona, 24, 38
- Arkansas, 29, 31
- Arkoma Basin, 31
- Atlantic Coastal Plain, 26-27
- Avery Island, 100, 110, 113
- barium
 - leaching, 187
 - sorption, 228, 241
- Barnett Shales, 30
- basalt, 6
 - hydraulic properties of fractures in, 67
 - radionuclide migration, 221-222
 - sorptive properties, 208-209, 212, 234-236
- Baxter Shales, 33
- Belle Fourche clay, 232
- Belle Fourche Shales, 32
- Belt Series, 37
- bentonite, 17, 32
- Big Horn Basin, 33
- biotite, sorptive properties, 226, 235-236
- Black Mesa Basin, 34-35
- black shales, 17
- Blue Gate Shales, 34
- Blue Ridge Province, 26
- borehole plugs
 - cementitious grout, 357
 - field tests, 354, 358
 - instrumentation for testing, 360
 - longevity, 338, 341
 - mechanical properties, 351
 - permeability, 351
 - physical properties, 351
 - test results, 363-367
 - testing, 362
 - testing techniques, 361
- borehole sealing, 10
- boron, leaching, 187
- borosilicate glass
 - leaching, 177-178, 180, 185, 187, 194, 197-198
 - pH dependence of leaching, 184
 - radiation effects on leaching, 186
 - reactions, 171
 - solubility limits, 188
 - surface profiles, 182
- borosilicate glasses, pH effects, 183
- brine, corrosive effects, 101
- brine flow model, 128
- brine inclusion flow, 128, 131
- brine migration, 110, 112, 127, 129-130
 - experiments, 133
 - model, 113
 - tests, 114
- Burke Formation, 38
- cadmium, sorption, 227
- calcium, leaching, 187

- California, 24
 - Great Valley, 36
- Cambric event, radionuclide migration, 242
- canisters
 - design, 165
 - handling, 298
 - radiation damage, 137
 - transfer, 298
- Capay Shales, 36
- carbon dioxide, 52
- carbon monoxide, 52
- carbon-14, distribution coefficients, 221
- Carlisle Shales, 32
- Cashaqua Shale, 25
- cementitious materials
 - characterization of old, 350
 - compressive strength, 347
 - heat of hydration, 346
 - heat liberation, 345
 - length and volume changes, 344
 - permeability, 348
 - pore size distribution, 349
 - porosity, 348
 - stability, 344
 - temperature effects, 343
 - viscosity, 343
- cements, 10, 354-355
 - evaluation, 340
 - testing, 358
 - testing as grout, 359
- cerium, sorption, 228
- cerium-242, environmental transport, 240
- cesium
 - distribution coefficients, 232-233
 - ion exchange, 230
 - leaching, 187
 - sorption, 208-209, 212-213, 227-228, 237
- cesium-135
 - distribution coefficients, 221
 - environmental transport, 240
- cesium-137
 - distribution coefficients, 221
 - environmental transport, 240
 - leaching, 193
- Chainman Shales, 36
- chlorine release, 138
- chlorine-36, distribution coefficients, 221
- clays
 - ion-exchange processes, 230
 - map by geologic age, 23
 - physical properties, 40
 - sorptive properties, 212
- coal mining, 25
- cobalt, sorption, 227
- Coldwater Shales, 26
- Colorado Plateau, 34, 38
- Colorado, 24, 32, 310
- commercial nuclear reactors,
 - fuel discharge and accumulation, 292
 - computer models, 8-10, 13
- Conasauga Shales, 17
- conceptual reference repository
 - cost, 307
 - description, 287
 - service systems, 306
 - utility and service system, 305
- consequence assessment, 12
- containers
 - chemical reactions, 4
 - corrosion, 8
- Copper Basin, 34
- corundum, sorptive properties, 226
- cost of space disposal, 383
- crystalline rock, 50, 55, 310-311, 323, 327-331, 333, 335
- cubic law of flow, 81
- curium, sorption, 228
- curium-242, distribution coefficients, 221
- curium-244
 - distribution coefficients, 221
 - leaching, 197
- curium-245, environmental transport, 240
- Deep River argillaceous rocks, 17
- Delaware Creek Shales, 31
- deuterium oxide, 132, 133
- Devonian-Mississippian Shales, 22
- disposal site hydrology, 21
- distribution coefficients
 - comparisons, 217
 - data analysis, 245
 - data bank, 220
 - value comparisons, 218
- dome salt
 - brine migration, 110, 115, 127, 130, 131
 - brine migration tests, 114
 - extensometer measurements, 105
 - floor heave measurements, 107
 - heat capacity, 101
 - heat flux measurements, 103
 - heat transfer, 120
 - heater tests, 113
 - mechanical properties, 101
 - moisture, 123, 125-126
 - moisture inflow, 128
 - permeability, 132
 - post-test permeability, 124
 - radionuclide migration, 221-222
 - recrystallization, 109
 - stress measurements, 108
 - synthetic brine inclusions, 116
 - temperature distribution, 120
 - temperature measurements, 103, 117
 - thermal conductivity, 101
 - thermal gradients, 122
 - thermomechanical tests, 100
- Doremus leaching model, 189
- Dunbarton argillaceous rocks, 17

- Earth orbit disposal, 375
- Earth sciences, 3
- Eleana argillite, 17
- Eleana Formation, 24, 36
- electric heater borehole closures, 108
- electric heater tests, 100-101, 110, 121, 134
 - configuration, 113
 - geometry, 102
 - instrumentation, 102
 - stress sensors, 108
 - temperature sensors, 103
- electric heaters, 87, 89
- electrical double-layer model studies, 231
- electron irradiations, 136, 144
- element leaching, 182
 - static test, 179
- element release, 171, 173, 181
- Etchegoin Shales, 36
- europium, ion exchange, 230
- europium, sorption, 227
- europium-154, distribution coefficients, 221
- excavation methods, 5
- excavation technology, 312
- exploratory boreholes, 29
- extensometers, 106

- F-centers, 140, 144
 - absorption, 145-146
 - decay, 151, 154
 - diffusion, 161
 - formation, 160
 - growth, 155
 - growth curves, 148-149
 - interactions, 157-158
- far-field environment, 7, 12
- fission products
 - mass spectrometric analysis, 255
 - migration, 259
- Florence argillaceous rocks, 17
- Florida, 28
- Floyd Shales, 25
- fluid flow
 - in fractured rocks, 76
 - in fractures, 65
 - in granites, 67, 80
- Forbes Formation, 36
- Forest City Basin, 31
- Fort Worth Basin, 30
- fractures
 - effects of loading cycles, 80
 - flow in, 71
 - flow through, 66
 - models, 68-69, 76
 - models of flow in, 81
 - orientation, 314-316
- fuel pools, 296-297
 - fuel rod assemblies, disposal, 370

- Gabon, 256
- gadolinium, sorption, 237
- Galeros Formation, 38
- geologic isolation, 3, 16, 20, 42, 172, 204
- Georgia, 27
- gibbsite, sorptive properties, 235-236
- glass
 - alkali ion removal, 189
 - element depth profile, 181
 - leachate composition effects, 185
 - leaching, 178-179, 198
 - leaching model, 189
 - pH dependence of leaching, 184
 - pH effects, 182
 - radiation effects on leaching, 185
- Goddard Shales, 31
- Grand Canyon, 38
- granites, 6
 - displacements around heaters, 93
 - elasticity, 93
 - fluid flow in fractured, 80
 - fracture map, 74
 - fracture map of Charcoal Black, 79
 - fractures in Charcoal Black, 77
 - hydraulic properties of fractures in, 67
 - permeability of Charcoal Black, 65
 - permeability tests, 71, 75
 - Poisson's ratio, 96
 - radionuclide migration, 221-222, 238
 - sorptive properties, 212, 234
 - strength tests, 73
 - Stripa thermomechanical tests, 88
 - structural continuity, 310
 - thermal expansion, 93, 97-98
 - thermomechanical tests, 87, 90-92
 - Young's modulus, 96
- Great Basin of Nevada and Utah, 35
- Great Divide Basin, 33
- Great Plains, 22, 30
- Great Valley of California, 36
- Green River Basin, 34
- Green River Formation, 24, 34
- groundwater, 5, 7-8, 10-11, 19, 21, 25, 32, 37, 39, 42
 - age estimation, 63
 - chemical composition, 226
 - dating, 42, 44, 48, 58
 - Eh, 184
 - electric conductivity, 53
 - flow in crystalline rock, 323
 - gas analysis, 51, 53
 - gas composition, 52, 54
 - gases, 55
 - helium content, 50, 53, 56-57, 62
 - ion-exchange processes, 230
 - pH, 184
 - piezometric map, 50
 - radionuclide migration, 175, 203, 214, 223, 225
 - residence time, 55

- tracers, 210
- velocity, 43
- Gulf Coast, 22, 28
- Hakati Shales, 38
- halite crystals, 111
- Hanford Site, 9
- Hanna Basin, 33
- heat-transfer analyses, 120
- helium, 52, 54-57
 - in groundwater, 50
- helium-3, 47
- helium-4, 42, 45, 48
- hematite, sorptive properties, 235-236
- Hench leaching model, 189
- Henry Basin, 34-35
- high-level waste disposal, 3, 16, 171, 370
 - in space, 377
- high-level wastes, simulation, 102
- hydraulic conductivity, 42
 - methods of measuring, 62
 - tests, 58-60
 - tracer techniques, 60
- hydrogen release, 137
- hydrogen, 52, 54
- hydrocarbon resources, 25
- IAEA leach tests, 176
- Idaho, 24, 34
- Illinois Basin, 24-25
- illite, 32
- iodine, sorption, 241
- iodine-129
 - distribution coefficients, 221
 - environmental transport, 240
- Iowa, 31
- isotope dating, 42, 48
- Jain-Lidiard theory, 136, 159-160, 162
- Kaiparowits Basin, 34-35
- Kansas, 30-31
- kaolinite, sorptive properties, 235-236
- Kiowa Shales, 32
- Kirtland Shales, 35
- Kreyenhagen Shales, 36
- krypton-83, 46
- krypton-84, 46
- krypton-85, distribution coefficients, 221
- krypton-86, 46
- Kwagunt Formation, 38
- laminar flow, 66
- Laramie Basin, 33
- leach testing methods, 175
- leach tests, 177-178
- leachate composition, 185
- leaching models, 189
- leaching studies, 174
- lead
 - isotope ratio, 258
 - migration at Oklo, 272
- lead-210
 - distribution coefficients, 221
 - environmental transport, 240
- Lewis Shales, 33, 35
- limestone, sorptive
 - properties, 208-209, 212-213
- Louisiana, 28-29, 100, 110
- low-level transuranic wastes,
 - disposal, 288
 - handling, 298
 - terminal storage, 287
 - underground handling, 303
- low-level wastes, annual
 - repository requirements, 294
- lunar disposal, 375
- Mancos Shales, 24, 34-35
- Maquoketa Shales, 17
- marbles, hydraulic properties
 - of fractures in, 67
- Marias River Shales, 32
- Marietta Basin, 31
- Markley Formation, 36
- Maryland, 27
- mass transport, 8-9
- Masuk Shales, 34
- Materials Characterization
 - Center, 173
- McClure Shales, 36
- Media Shales, 36
- metamorphic rocks, 42
 - crystalline, 49, 51, 53, 56
 - exploratory wells, 59
 - groundwater residence time, 55
 - helium content, 57
 - hydraulic conductivity, 58-60, 62
 - porosity of crystalline, 55
 - water in crystalline, 50
- Michigan Basin, 24-25
- microcline, sorptive properties, 226
- mineral resources, 33
- mines
 - damage zone assessment, 317-319, 323
 - damage zone contour, 320
 - fracture orientation studies, 333
 - stresses, 321
- mining technology, 310, 312
- Mississippi, 28-29
- Missourian Shales, 30
- modified IAEA leach test, 176
- molybdenum, leaching, 187
- molybdenum-93, distribution
 - coefficients, 222
- Montana, 32
- Montana Disturbed Belt, 38
- montmorillonite, 29, 32
 - sorptive properties, 213, 232, 235-236
- Mowry Shales, 32
- mudstones, 16
- National Aeronautics and Space
 - Administration, 371

- National Waste Terminal Storage Program, 287
- near-field environment, 4, 12
- Nebraska, 32
- neodymium, abundance at Oklo, 270, 273, 276-277
- neodymium, retention at Oklo, 255
- neodymium-143, isotope ratio at Oklo, 260
- neodymium-144, isotope ratio at Oklo, 260
- neon-21, 45
- neon-22, 45
- neptunium, sorption, 226, 228, 234, 241
- neptunium-237
 - distribution coefficients, 222
 - environmental transport, 240
 - release from PNL-76-68 glass, 186
- neptunium-239, distribution coefficients, 222
- neptunium dioxide, solubility limits, 188
- Nevada, 24, 36
 - Great Basin, 35
- Nevada Test Site, 9, 36
- New Albany Shales, 17
- New Madrid seismic zone, 25
- New Madrid zone, 28
- New Mexico, 354
- New York, 24
- New York shales, 22
- nickel-59
 - distribution coefficients, 221
 - environmental transport, 240
- nickel-63
 - distribution coefficients, 221
 - environmental transport, 240
- niobium-93, distribution coefficients, 221
- nitrogen, 52, 54
- noble gases, radiogenic, 44, 46
- nontronite, sorptive properties, 235-236
- North Carolina, 27
- North Dakota, 32
- Nortonville Shales, 36
- nuclear fuels
 - heat flux, 134
 - power levels, 134
- Ohio, 24-25
- Ohio shales, 22
- Oklahoma, 30-31
- Oklo reactors, 9, 18, 255
 - characteristics, 256
 - chemical environment, 258
 - criticality, 258
 - element equilibrium, 277
 - element transport, 270-271, 274, 278
 - fission product abundance, 273
 - geologic setting, 256-257
 - lead transport, 272
 - lithology, 259
 - nuclear material composition, 260
 - nuclear parameters, 263-264
 - operating parameters, 262
 - oxide oxidation and solubility, 276
 - physical environment, 258
 - radionuclide migration, 243
 - ruthenium isotope ratio, 266-268
 - ruthenium transport, 275
 - technetium-99 production, 265
 - technetium-ruthenium fractionation, 269
- optical absorption, 136
- Optical Electron Radiation Facility, 142
- oxygen, 52, 54
- Pacific Northwest, 37
- palladium-107
 - distribution coefficients, 221
 - environmental transport, 240
- Pennsylvania, 25
- Pennsylvania shales, 22
- permeability testing, equipment, 326
- Piceance Basin, 34
- Piedmont, 27
- Pierre Shale, 17, 24, 32
- Pilot Shales, 36
- Pioneer Shales, 38
- pitchblende, 257
- plugging materials, 338, 354-355
 - ingredients, 359
 - instrumentation for testing, 360
 - testing, 358, 362
 - tests, 357
- plutonium dioxide, solubility limits, 188
- plutonium
 - desorption, 235
 - distribution coefficient, 211-212
 - isotope ratios at Oklo, 278
 - sorption, 208-209, 228, 234-237
- plutonium-238
 - distribution coefficients, 222
 - environmental transport, 240
- plutonium-239
 - distribution coefficients, 222
 - environmental transport, 240
 - leaching, 197
 - release from spent fuel, 194
 - sorption, 236
- plutonium-240
 - distribution coefficients, 222
 - environmental transport, 240
 - leaching, 197
 - release from spent fuel, 194
- plutonium-241
 - distribution coefficients, 222
 - environmental transport, 240
- plutonium-242
 - environmental transport, 240
- PNL-76-68 glass
 - leaching, 180, 187, 196-197
 - Np-237 release, 186
 - radiation effects on leaching, 186
 - solubility limits, 188
 - surface profiles, 183

- Poisson's ratio, in granites, 96
 Porters Creek Clays, 17, 22, 28-29
 potassium-40, 47
 potassium chlorides, liquid
 inclusions, 112
 Prichard Formation, 38
 protactinium-231
 distribution coefficients, 221
 environmental transport, 240
 Purcell Anticlinorium, 38
- quartz, sorptive properties, 226
- radiation damage studies, 136
 radiation effect measurements, 141
 radiation effects, 136
 radiation hazards, reduction by
 space disposal, 373
 radionuclide migration, 7-9, 11-12, 111, 175,
 205, 215, 221, 238, 241-243, 280
 data bank, 220
 ion-exchange processes, 229
 at Oklo, 259
 oxidation-reduction in, 233
 retardation processes, 224
 radionuclide release, 174-175
 radionuclides
 batch sorption studies, 207
 column sorption tests, 214
 data bank on sorption, 220
 desorption, 203, 223
 distribution coefficient, 203,
 206, 216, 229
 electric double layer sorption
 model, 231
 laboratory sorption-desorption, 207
 retardation, 246
 retardation studies priorities, 239
 sorption, 203, 206, 215-217, 223,
 225, 227, 243, 245
 radium, sorption, 241
 radium-226
 distribution coefficients, 221
 environmental transport, 240
 rare earths, sorption, 225-226
 Reef Ridge Shales, 36
 repository design, 5
 repository failure analysis, 12
 repository host rocks, 20
 repository openings, 4
 repository performance, 3, 6, 11, 13
 repository site criteria, 19-20
 repository site mineral
 resources, 22
 repository site selection, 39, 165
 repository site studies, 100
 repository temperature, 4
 Revett Formation, 38
 rock mechanics, 6
 rock salt, absorption
 spectra, 143, 145
 rock salt
 colloid content, 163
 colloid formation, 147, 152, 154-158
 colloid growth, 150-151
 colloids, 164
 F-center decay, 152, 154
 F-center diffusion, 161
 F-centers, 147-149
 irradiated, 165
 luminescence, 143
 micrograph, 159
 radiation damage, 136-140, 160, 162
 sample data, 141
 sample preparation, 140
 temperature gradients, 129
 Rock Springs Uplift, 33
 rocks
 chemical reactions, 4, 11
 cubic law of flow, 81
 damage from blasting, 313, 317-318
 fluid flow in fractured, 65, 76
 fracture index of crystalline,
 327-331
 fracture orientation in crystalline,
 333
 fracture orientations, 314-316
 fractures in crystalline, 323
 geology of mine in crystalline, 311
 hydraulic conductivity, 42
 hydraulic properties, 66, 75
 load cycle effects, 80
 metamorphic, 42, 49-60
 mining in crystalline, 310
 mining technology for crystalline, 312
 models of fractures, 68
 permeability of crystalline, 322,
 331, 335
 permeability of fractured, 65
 permeability testing of crystalline,
 325-326
 permeability variation with pressure,
 332
 permeability-pressure profiles, 334
 radionuclide migration, 203, 215, 246
 sorptive properties, 8-9, 227-228
 stress displacement, 70
 stresses in crystalline, 321
 structural continuities, 313-314
 tests on fractured, 71
 Rocky Mountains, 24, 33
 Rocky Mountains Region, 37
 ruthenium
 abundance at Oklo, 277
 fractionation at Oklo, 269
 isotope ratio at Oklo, 266-268
 migration at Oklo, 270-271,
 275-276, 279
 retention at Oklo, 255
 ruthenium-99, abundance at Oklo, 273
 geochemistry at Oklo, 265
 ruthenium-101, abundance at Oklo, 273
 ruthenium-102, abundance at Oklo, 273

- Sacramento Basin, 36-37
 Salina Basin, 31
 salt
 corrosive effects, 101
 deuterium oxide content, 132
 temperature field, 121
 temperature gradients, 123
 thermal properties, 121
 temperature profiles, 118-119
 salt crystals, brine migration, 111
 salt deposits, 6
 brine migration, 112
 mining, 304
 plugging, 355
 radionuclide migration, 221-222
 repository development in, 302
 stratigraphy, 356
 thermomechanical tests, 100
 waste disposal in, 288, 299
 salt mines, 101
 brine inclusions, 113
 brine migration, 110, 127
 floor expansion, 107
 floor heaves, 107
 heat flux, 106
 heater tests, 113
 moisture collection system, 117
 moisture collection, 123, 126, 130-131
 permeability testing, 124, 132
 stress tests, 108
 temperature measurement, 104-105, 117
 temperature profiles, 106
 thermal gradients, 122
 samarium-151
 distribution coefficients, 221
 environmental transport, 240
 San Joaquin Basin, 36-37
 San Joaquin Shales, 36
 San Joaquin Valley, 37
 San Juan Basin, 34-35
 saprolite, 49
 Savannah River Plant, 42, 48
 Savannah River Plant,
 geologic profile, 49
 sealing materials, 10, 338
 bonding, 347, 349
 compressive strength, 347
 evaluation, 340
 longevity, 339
 permeability, 347
 stability, 344
 sedimentary basins, map, 23
 sediments, radionuclide migration, 203
 seismic activity, 21, 28, 33, 37
 selenium-79
 distribution coefficients, 222
 environmental transport, 240
 shaft plugs, longevity, 338
 shales
 assessment, 22, 24-25, 28, 30-37
 black, 26
 faults, 20
 gas-bearing, 26
 hydrology, 21
 lithology, 21
 map by geologic age, 23
 mineral resources, 22
 physical properties, 40
 properties, 18-19
 sorptive properties, 212, 234
 structure, 20
 Shepard Formation, 38
 silica, sorptive properties,
 233
 silicon, leaching, 187
 simulated waste canisters, 101
 single-pass, continuous-flow
 leach tests, 177
 Skull Creek Shales, 32
 Snowslip Formation, 38
 sodium
 leach rates, 189
 leaching, 187
 sodium chlorides
 absorption spectra, 145, 147
 colloid absorption, 148
 colloid growth, 151, 153
 colloids, 157
 color centers, 139
 F-center diffusion, 161
 F-centers, 140, 153, 157
 liquid inclusions, 112
 radiation damage, 136, 140, 160
 radiation effects, 138-139
 radioinduced color, 144
 sample preparation, 140
 sodium metal colloids, 136, 139, 144,
 147, 154-156, 158, 163-164
 absorption, 145-146
 growth, 151
 growth curves, 150
 interactions, 157
 nucleation, 160
 soils, sorptive properties, 212
 solar orbit disposal, 375
 solar system escape disposal, 375
 South Carolina, 27, 42
 hydrology, 48
 South Dakota, 32
 space missions
 hazards and risks for waste
 disposal, 382
 for waste disposal, 389
 space shuttle
 high-level waste disposal, 370
 waste disposal configuration, 381
 space
 cost of waste disposal in, 383
 waste disposal, 370-373
 waste disposal options, 376
 waste forms for disposal in, 379
 spent fuel casks
 cooling, 296
 decontamination, 297
 washing, 296

- spent fuels
 - accumulation at commercial reactors, 292
 - Cs-137 leaching, 193
 - disposal, 288
 - disposal in space, 370
 - leach test parameters, 191
 - leachate composition effects, 193
 - leaching, 177, 190, 194, 196-198
 - oxygen effects on leaching, 192
 - packaging, 293, 297
 - plutonium release rate, 194
 - reactions, 171
 - receiving system, 293
 - simulation, 102
 - storage, 297
 - temperature effects on leaching, 192
 - terminal storage, 287
 - underground handling, 303
- Spokane Formation, 38
- static leach tests, 176
- Steele Shales, 33
- Stripa mine, 71, 87
 - electric heaters, 91
 - tests, 88
- strontium, distribution coefficients, 219
- strontium, ion exchange, 230
 - leaching, 187
 - sorption, 208-209, 227-228, 237
- strontium-90,
 - distribution coefficients, 221
 - environmental transport, 240
- sun impact disposal, 375
- surface waters, 21
- Sweden, 87
- synthetic brine inclusions, 116
- technetium
 - abundance at Oklo, 277
 - fractionation at Oklo, 269
 - ion exchange, 230
 - migration at Oklo, 270-271, 276, 279
 - retention at Oklo, 255
 - sorption, 234, 241
- technetium-99
 - abundance at Oklo, 273
 - distribution coefficients, 222
 - environmental transport, 240
 - geochemistry at Oklo, 265
- Tennessee, 39
- terminal waste storage, schedule, 308
- Texas, 28-29
- thermomechanical properties,
 - temperature dependence, 90
- thermomechanical stresses, 87
 - measurement, 92
 - prediction, 90
- thermomechanical test equipment, 94
- thermomechanical tests, 97, 100
- thermomechanical tests control
 - system, 95
- thorium, 56-57
- thorium-230
 - distribution coefficients, 221
 - environmental transport, 240
- thorium-232, 45
- tin-126
 - distribution coefficients, 222
 - environmental transport, 240
- transition metals, sorption, 225
- transuranic wastes
 - disposal of low-level, 288
 - handling of low-level, 298
 - terminal storage of low-level, 287
 - underground handling of low-level, 303
- tritium, 9, 60
 - distribution coefficients, 221
- Tropic Shales, 35
- tuff
 - radionuclide migration, 221-222, 238
 - sorptive properties, 211-212
- tunnel-boring machines, 32
- Tununk Shales, 34-35
- Uinta Basin, 34
- ultrasonic pulse testing, 317, 319
 - equipment, 318
- Upper Ordovician Shales, 22
- uraninite, 257
- uraninites
 - fission products, 255
 - radionuclide migration, 280
- uranium, 9, 56-57
 - ion exchange, 230
 - isotope ratio at Oklo, 260, 278
 - isotope ratio, 258
 - leaching, 193, 196-197
 - mineralization at Oklo, 257
 - sorption, 226, 228, 237-238
- uranium-233
 - distribution coefficients, 222
 - environmental transport, 240
- uranium-234
 - distribution coefficients, 222
 - environmental transport, 240
- uranium-235, 45
 - distribution coefficients, 222
 - environmental transport, 240
 - isotope ratio at Oklo, 261
- uranium-236, environmental
 - transport, 240
- uranium-238, 45
 - distribution coefficients, 222
 - environmental transport, 240
 - isotope ratio at Oklo, 261
- uranium dioxide
 - chemistry, 190
 - dissolution, 195
 - models for reactions, 194
 - oxidation, 195
 - solubility limits, 194, 197
- Utah, 24, 36
 - Great Basin, 35

- Val Verde Basin, 30
- vermiculite, sorptive properties, 235-236
- Virginia, 27

- Wadesboro argillaceous rocks, 17
- Waltman Shales, 34
- Washakie Basin, 33-34
- waste disposal, 136
 - conceptual description, 287
 - density of spent fuel in, 291
 - energy and cost analysis for space, 383
 - forms for space, 379
 - natural analogs, 255
 - plan of salt deposit, 288
 - radiation damage, 137
 - radionuclide migration, 204-205, 243
 - ranking of space options, 376
 - risks for space, 382
 - rock mechanics, 65, 87
 - in salt deposits, 299
 - in space, 370-371, 378
 - schedule, 308
 - thermal output, 87
- waste drums
 - decontamination, 300
 - handling, 300
- waste facilities, plans, 288
- waste glasses, composition, 179
- waste interaction system, 172
- waste isolation, 1, 3, 14, 19
- Waste Isolation Pilot Plant
 - sealing, 355
 - stratigraphy, 356
- waste leaching, 173-174
- waste package, 5, 14
- waste repositories, 163
 - annual requirement for low-level, 294
 - capacity, 291
 - conceptual description, 287
 - cost, 307
 - decommissioning, 307
 - design, 300-301
 - development sequence, 302
 - natural analogs, 255
 - plugging, 355
 - radiation doses, 137
 - receipt rate, 291
 - sealing, 338, 354
 - service systems, 306
 - siting, 65
 - underground facilities, 304
 - utility and service systems, 305
 - ventilation, 303
- waste retrieval, 111, 291
- waste, space destinations for, 375
- Waste/Rock Interactions
 - Technology Program, 204
- wastes
 - chemical reactions, 4
 - dissolution, 7
 - radiolysis, 171
 - risk reduction by space disposal, 373
 - solubility, 8
- water, chemical reactions, 11
- water vapor, 54
- water wells, 61
 - gas analysis, 51
 - gas composition, 52
- Wind River Basin, 33-34
- Woodford Shales, 30-31
- WRIT Program, 203, 239, 244
- Wyoming, 24, 32

- xenon-131, 46
- xenon-132, 46
- xenon-134, 46
- xenon-136, 46

- Yazoo Clays, 17, 29
- Young's modulus, in granite, 96

- zinc, leaching, 187
- zirconium-93
 - distribution coefficients, 221
 - environmental transport, 240

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