

1. INTRODUCTION

1.1 PURPOSE OF REPORT AND LIMITATIONS

The purpose of this report is to present analogue studies and literature reviews designed to provide qualitative and quantitative information to test and provide added confidence in process models abstracted for performance assessment (PA) and model predictions pertinent to PA. This report provides updates to studies presented in the *Yucca Mountain Site Description* (CRWMS M&O 2000 [151945], Section 13) and new examples gleaned from the literature, along with results of quantitative studies conducted specifically for the Yucca Mountain Site Characterization Project (YMP). The intent of the natural analogue studies was to collect corroborative evidence from analogues to demonstrate additional understanding of processes expected to occur during postclosure at a potential Yucca Mountain repository. The report focuses on key processes by providing observations and analyses of natural and anthropogenic (human-induced) systems to improve understanding and confidence in the operation of these processes under conditions similar to those that could occur in a nuclear waste repository. The process models include those that represent both engineered and natural barrier processes. A second purpose of this report is to document the various applications of natural analogues to geologic repository programs, focusing primarily on the way analogues have been used by the YMP. This report is limited to providing support for PA in a confirmatory manner and to providing corroborative inputs for process modeling activities. Section 1.7 discusses additional limitations of this report.

Key topics for this report are analogues to emplacement drift degradation, waste form degradation, waste package degradation, degradation of other materials proposed for the engineered barrier, seepage into drifts, radionuclide flow and transport in the unsaturated zone (UZ), analogues to coupled thermal-hydrologic-mechanical-chemical processes, saturated zone (SZ) transport, impact of radionuclide release on the biosphere, and potentially disruptive events. Results of these studies will be used to corroborate estimates of the magnitude and limitation of operative processes in order to build realism into conceptual and numerical process models used as a foundation for PA in the representative case of postclosure safety.

1.2 DEFINITION OF ANALOGUE

Natural analogues refer to either natural or anthropogenic systems in which processes similar to those expected to occur in a nuclear waste repository are thought to have occurred over long time periods (decades to millenia) and large spatial scales (up to tens of kilometers). Analogues provide an important temporal and spatial dimension to the understanding of processes not accessible to laboratory experiments that may take place in a nuclear waste repository and surrounding area. The use of analogy has been endorsed by the international nuclear waste community as a means of demonstrating confidence in the operation of systems, components, and processes related to nuclear waste disposal (e.g., publications of the International Atomic Energy Agency [IAEA] and the European Community's Natural Analogue Working Group). "The role of a natural analogue should ... be to confirm: (a) that the process is in fact something which can or will occur in practice as well as in theory, and in nature as well as in the laboratory; (b) where, when, and under what conditions it can occur; (c) that the effects of the process are

those envisaged in the model; and (d) that the magnitude of the effects in terms of scale and time are similar to those predicted for a similar set of conditions” (Chapman and Smellie 1986 [124323], p. 167).

1.3 ROLE OF NATURAL ANALOGUES IN PROCESS MODELS AND PERFORMANCE ASSESSMENT

Natural analogues may be applied in a quantitative or a qualitative manner, depending upon the purpose to which they are applied and upon the specific analogue. They can provide descriptive information about the occurrence of various processes, or they may be able to constrain the bounds of those processes. Natural analogues allow testing of the pertinence of individual processes over geologic time and space scales, assessing the relative importance of various processes, and gauging the effects of process coupling. For some processes (e.g., those that are thermally coupled), natural analogues may be the only means of providing the required understanding of long-term and large-scale behavior needed to provide scientific confidence in process models for input to total system performance assessment (TSPA). Analogue investigations may determine the conditions under which the processes occur, the effects of the processes, and the magnitude and duration of the processes.

Analogue information may also provide a body of data for testing codes and for validation of conceptual and numerical models. Natural analogue information may also be used to build confidence in databases themselves. Because natural analogues can be used to evaluate the validity of extrapolating from temporally limited field-scale experiments to longer time scales, or to add confidence when extrapolating from laboratory and intermediate-scale experiments to tests at larger spatial scales, they are uniquely suited to building confidence in process models. In this manner, they are used as a means of model validation, or confidence-building. Each of the Process Model Reports (PMRs) that support Site Recommendation (SR) includes a section on “validation” that in many cases utilizes natural analogue information.

Less commonly, natural analogues may be used to assist and support the selection of scenarios and to establish the probability of occurrence of selected scenarios. Natural analogues do not reduce uncertainty *per se*; that is, the uncertainty bounds on a given parameter value may remain unchanged. However, natural analogues can build confidence that the bounds are set appropriately. Because some uncertainties are greater in natural analogues than at the site being characterized, information from natural analogues should only be used in conjunction with other information to evaluate consistency with laboratory and field data.

Comparison of model predictions with the results of natural analogue investigations will in general only permit confirmation that the model takes into account the relevant processes in appropriate ways. Validation of a predictive model by such comparison provides reasonable assurance that the model reflects future behavior. This is the level of confidence required by 66 FR ([156671], p. 55804), which states, in §63.101(a): “Demonstrating compliance will involve the use of complex predictive models that are supported by limited data from field and laboratory tests, site-specific monitoring, and natural analogue studies that may be supplemented by prevalent expert judgment.”

1.4 ROLE OF NATURAL ANALOGUES IN LICENSE APPLICATION

The National Research Council endorsed the use of natural analogues as “natural test cases, geological settings in which naturally occurring radioactive materials have been subjected to environmental forces for millions of years” (National Research Council 1990 [100061], p. 27). The Council’s report indicates that natural analogues are essential for validating performance assessment models of geologic repositories over thousands or millions of years, as well as forming the basis for communicating the safety of a deep geologic repository in terms the public can understand. The Nuclear Waste Technical Review Board concurred in these recommendations (NWTRB 1990 [126162], p. xiii).

In 66 FR ([156671], p. 55804, Section 63.101(a)(2)), the Nuclear Regulatory Commission (NRC) has identified natural analogues as one way of demonstrating compliance with the reasonable expectation that postclosure performance objectives will be met. As summarized in Section 1 of this report, the NRC also specifies natural analogues as one method to provide the technical basis for models in (66 FR [156671], p. 55804).

The content requirements for the license application (66 FR [156671], p. 55798, Section 63.21(c)(15)) specify natural analogue studies as one of the measures used to support analyses and models that are used to assess performance of a geologic repository. In addition, the technical criteria for a license application (66 FR [156671], p. 55804) specify the use of natural analogue information as part of the demonstration of compliance with the performance objectives of the disposal regulations. Further, the demonstration of the concept of multiple barriers and the performance of complex engineered structures must include information from natural and archaeologic analogs (66 FR [156671], p. 55805, Section 63.102(h)). The importance of natural analogs in supporting performance assessment models is again included in the requirements for performance assessment (66 FR [156671], p. 55807, Section 63.114(g)).

Ten agreements from the DOE-NRC technical exchanges and management meetings on key technical issues (KTIs) include mention of analogues or information from analogue studies as necessary to address the agreement item. As shown in Table 1-1, two KTI agreement items are at least partially addressed by information in this report. A cross reference to this table is found in the sections of this report that could provide information related to these KTIs.

1.5 CRITERIA FOR SELECTION OF ANALOGUES USED IN MODEL VALIDATION

As pointed out by Percy and Murphy (1991 [157563]), the 10,000-year period required for high-level waste isolation is a difficult period to approximate with natural analogues. For instance, most ore deposits are on the order of a million to a billion years in age, whereas anthropogenic sites (i.e., human made) are generally on the order of a few thousand years or less. To be most helpful in terms of long-term processes relevant to a high-level waste repository, it would be useful to find analogues with ages on the order of 1,000 to 1 million years.

Because no single site will be a perfect analogue to all ongoing and anticipated processes at Yucca Mountain, focus is placed on identifying sites having analogous processes rather than total system analogues. Nevertheless, it is still worthwhile to attempt to match as many features and

characteristics as possible when identifying suitable analogue sites. An ideal analogue site to long-term radionuclide transport at Yucca Mountain would have to satisfy the following conditions: (1) a known source term, (2) a similar set of radionuclides, (3) well-characterized with site data, (4) similar geologic conditions, (5) observable long-term conditions, (6) identifiable boundaries of the system, and (7) a clear-cut process that can be decoupled from other processes. It is most useful if the analogue has been in place for at least thousands of years, so that the results of long-term behavior are observable.

In addition to using natural analogues for long-term predictions, models must be able to explain and match the transport times and pathways from contaminated sites that provide anthropogenic analogues, such as Hanford, Washington; the Idaho National Engineering and Environmental Laboratory (INEEL); and the Nevada Test Site (NTS). Anthropogenic analogue sites are a challenge to constrain in models, because they often contain more than one contaminated source, (sometimes with poorly identified source terms), have a complex mixture of radionuclides and other contaminants, and often occur in highly heterogeneous formations.

With respect to choosing different geochemical transport analogues, Chapman and Smellie (1986 [124323], p. 168) state the following:

The essentials to bear in mind when selecting analogues are as follows: (1) The process involved should be clear-cut. Other processes which may have been involved in the geochemical system should be identifiable and amenable to quantitative assessment as well, so that their effects can be accountable. (2) The chemical analogy should be good. It is not always possible to study the behavior of a mineral system, chemical element or isotope identical to that whose behaviour requires assessing. The limitations of this should be fully understood. (3) The magnitude of the various physicochemical parameters involved (P, T, Eh, concentration, etc.) should be determinable, preferably by independent means. (4) The boundaries of the system should be identifiable (whether it is open or closed, and consequently how much material has been involved in the process being studied). (5) The time-scale of the process must be measurable, since this factor is of the greatest significance for a natural analogue.

Care must be taken in selection of an appropriate analogue to represent correctly the process of interest. For example, all uranium deposits are not categorically good analogues for stability of a nuclear waste repository. Uranium deposits indicate the long-term stability of some geologic environments, but some of the same ore deposits could be used to make arguments for massive transport of radioactive materials over large distances by natural processes. Care must also be exercised to exclude those analogues for which initial and/or boundary conditions are poorly known and where important data, such as the source term, are poorly constrained and may not be obtainable. A given site will usually only be analogous to some portion of a repository or to a subset of processes that will occur in a repository. Furthermore, additional processes will have occurred that are not characteristic of the repository. Therefore, choices must be made to select the processes of greatest relevance and the ability to isolate them for study. The long-term nature of analogues introduces some limitations and uncertainties, but analogues can still be used effectively if appropriate selection criteria are determined and applied.

In the early 1990s, the U.S. Department of Energy (DOE)/YMP convened a panel of international experts in natural analogues to provide guidance in selection and use of natural analogues for implementation by the YMP. The Natural Analogue Review Group (NARG) report recommended that natural analogues be process-oriented and “should address the issues resulting from the perturbation of a natural system (the geologic site) by the introduction of a technological system (the repository)” (DOE 1995 [124789], p. 2). The NARG was explicit in stating that “one should clearly discriminate such studies from those which, following the classical approach of earth sciences, are based on the comparative study of geological sites or situations. In particular, all investigations normally part of site characterization, even when considering comparisons with similar remote sites, such as (paleo)hydrology, etc., should not be considered as natural analogue studies” (DOE 1995 [124789], p. 2). The YMP has abandoned that approach and now defines analogues in a more all-encompassing sense in order to avoid the narrower definition.

1.6 SCOPE AND ORGANIZATION OF REPORT

This report considers a broad range of analogues that encompass both the engineered barriers and natural system components of a geological repository at Yucca Mountain. In each section, the conceptual basis for the process model is provided as a framework for discussion of relevant analogue studies and examples. Next, examples of analogue studies relevant to the operative processes in the conceptual models are presented. This is followed by an assessment of the applicability of the information or conclusions derived from the analogue. The current repository design approach (Section 2) and configuration of engineered barriers (Section 5) are provided as the basis against which to identify relevant analogues for those systems. Section 3 presents analogues related to drift stability. Section 4 provides qualitative corroboration of waste form degradation processes. Section 6 presents examples of analogues for waste package corrosion processes. Section 7 addresses analogues for engineered barrier components and processes. Section 8 illustrates seepage into underground openings at sites with varying degrees of analogy. Section 9 addresses unsaturated zone (UZ) flow processes, but is primarily concerned with Part I of a modeling study using INEEL data. Part I of that study describes a flow model that was calibrated using INEEL data and YMP modeling methods. The calibration parameter values were then used in Part II of the study, which is described in Section 10 in a model of radionuclide transport at INEEL. Section 10 also includes results to date of the Peña Blanca field study and literature examples of analogues related to UZ transport. Section 11 presents analogues related to coupled processes, includes an extensive literature search for geothermal analogues, and summarizes experimental work on drillcore from Yellowstone National Park. In addition, Section 11 presents the results of a field and modeling study for the Paiute Ridge coupled processes analogue site and a literature study of thermal-hydrologic-mechanical (THM) processes. Section 12 presents an analysis of uranium mill tailing data relevant to saturated zone (SZ) transport and includes literature examples from selected sites. Section 13 uses parameters measured after the Chernobyl nuclear accident to arrive at Biosphere Dose Conversion Factors (BDCFs) that can be compared to those applied in the Yucca Mountain Biosphere Process Model. Section 14 provides examples of the ways in which analogues have been used to support conceptual models for volcanism and seismic hazard assessments and process models. Finally, Section 15 discusses how the analogue information is applied, both for illustrative purposes and in performance assessments. The ways in which other countries have used analogues in performance assessment are summarized. The specific needs for analogue information requested

by YMP performance assessment are listed, and each of the analogues covered in the report is mapped to its use in either conceptual model development, provision of data, or model validation. In a few cases, topics are identified that could potentially increase confidence with the use of natural analogues.

1.7 QUALITY ASSURANCE

This report provides corroborating information for the modeling of natural and engineered barrier performance at Yucca Mountain. This report was developed in accordance with AP-3.11Q, *Technical Reports*. Other applicable DOE Administrative Procedures (APs) and YMP-LBNL Quality Implementing Procedures (QIPs) are identified in the Technical Work Plan (TWP) *Natural Analogue Studies for License Application* (BSC 2001 [157535]). The Activity Evaluation in the TWP (BSC 2001 [157535], Attachment I) graded the natural analogue work as being non-Q and not subject to control under the DOE Office of Civilian Radioactive Waste Management (OCRWM) Quality Assurance Requirements and Description (QARD) (DOE 2000 [149540]). All procedures followed were current revisions at the time of implementation.

The data collected under this study is corroborative and will not be used directly by Performance Assessment (PA) for licensing. This report will be used to support PA in a confirmatory manner only. The TWP stipulates that all data generated by this work will be unqualified. However, data that have been collected have been submitted to the YMP Technical Data Management System (TDMS) in accordance with AP-SIII.3Q, *Submittal and Incorporation of Data to the Technical Data Management System*. The TWP also exempts the natural analogue work from following AP-SI.1Q, *Software Management*. Procedures that were followed during the course of the work, including AP-SIII.1Q, *Scientific Notebooks*, and AP-12.1Q, *Control of Measuring and Test Equipment and Calibration Standards* are listed on the TWP. Scientific notebooks are used to provide traceability to sample collection, data analysis, calculations, and modeling studies.

Input for this report consisted of a combination of existing information from natural analogue sites reported in the literature and data collected for the YMP. Literature data not developed by the YMP are available for review through the Technical Information Center (TIC); data collected by project personnel are available in TDMS; scientific notebooks (with relevant page numbers) used in preparation of this report are listed in Table 1-2 and are available from the Records Information System (RIS). Software referenced in this report is listed in Table 1-3. More detailed discussion of software usage is provided in relevant scientific notebooks. Finally, this document was developed to meet the deliverable criteria listed in Section 5 of the TWP (BSC 2001 [157535]).

Table 1-1. KTI Agreements Addressed in This Report

Agreement Number	Text of Agreement	Section of This Report
KIA0204	Document that the ASHPPLUME model, as used in the DOE performance assessment, has been compared with an analogue igneous system. (Eruptive AC-2). DOE agreed and will deliver calculation CAL-WIS-MD-000011 that will document a comparison of the ASHPPLUME code results to observed data from the 1995 Cerro Negro eruption. This will be available to the NRC in January 2001. DOE will consider Cerro Negro as an analogue and document that in Eruptive Processes AMR (ANL-MGR-GS-000002). This will be available to the NRC in FY2002 (Eruptive AC-2).	14.3
KUZ0407 ¹	Provide documentation of the results obtained from the Natural Analogues modeling study. The study was to apply conceptual models and numerical approaches developed from Yucca Mountain to natural analogue sites with observations of seepage into drifts, drift stability, radionuclide transport, geothermal effects, and preservation of artifacts. DOE will provide documentation of the results obtained from the Natural Analogues modeling study. The study was to apply conceptual models and numerical approaches developed from Yucca Mountain to natural analogue sites with observations of seepage into drifts, drift stability, radionuclide transport, geothermal effects, and preservation of artifacts. This will be documented in the Natural Analogues for the Unsaturated Zone AMR (ANL-NBS-HS-000007) expected to be available to NRC FY 2002.	3.2–3.4, 6.2, 8.2–8.4, 10.3–10.5, 11.2–11.5

¹The Natural Analogue Synthesis Report replaces the AMR in the provision of documentation stated in KUZ 0407

Table 1-2. Scientific Notebooks

LBNL Scientific Notebook ID	YMP M&O Scientific Notebook ID	Responsible Individual	Page Numbers	Citation
YMP-LBNL-AMS-NA-1	SN-LBNL-SCI-108-V1	Simmons, A.	83–87, 124–127, 139–144	Simmons 2002 [157544]
YMP-LBNL-AMS-NA-2	SN-LBNL-SCI-108-V2	Simmons, A.	6–23	Simmons 2002 [157578]
YMP-LBNL-AMS-NA-AU-2	SN-LBNL-SCI-186-V1	Unger, A.	55–63	Simmons 2002 [157578]
YMP-LBNL-DSM-ELS PD-2	SN-LBNL-SCI-190-V2	Dobson, P.	79–80	Simmons 2002 [157578]
YMP-LBNL-AMS-NA PD-1B	SN-LBNL-SCI-185-V1	Dobson, P.	7-1	Simmons 2002 [157578]
YMP-LBNL-AMS-NA PD-photos	SN-LBNL-SCI-185-V1	Dobson, P.	Roll 17 Images 2 and 4	Simmons 2002 [157578]
N/A	SN-LANL-SCI-237-V1	Murrell, M.	16	Simmons 2002 [157578]
N/A	SN-LANL-SCI-215-V1	Lichtner, P.	6–32, 56–59, 63, 69–76, 89–94, 100–104, 107, 110–112, 117–118, 128, 130–131	Simmons 2002 [157578]
N/A	SN-LANL-SCI-234-V1	Lichtner, P.	16, 20, 22–24, 26–33, 61–68, 75–76, 83, 88–90	Simmons 2002 [157578]

Table 1-3. Software Codes Referenced in Text

Software Name	Version Number	Software Tracking Number	Software Reference by Section
ASHPLUME	V 1.4LV	10022-1.4LV-00	14.3
ASHPLUME	V 2.0	10022-2.0-00	14.3
CXTFIT	V 2.1	N/A ²	10.3.2.1, 11.4.7.1
DRKBA	V 3.3	10071-3.3-00	14.4
EQ3/6	V 7.2b	UCRL-MA-110662	11.2.12.1, 11.3.5
FEHM	2.0	10031-2.00-00	10.3.1, 10.3.6.1, 10.3.6.3, 10.3.6.5
FLOTRAN	1.0	N/A	10.3.1, 10.3.6.1, 10.3.6.3, 10.3.6.4, 11.4.7, 11.4.7.1, 11.4.7.2,
iTOUGH2 ¹	V 4.0	N/A	9.3.3, 9.3.5, 9.3.6, 9.3.7, 9.5
Mathematica	V 4.1	N/A	10.3.6.4
TOUGH2	V 1.4	10007-1.4-01	11.3.5
TOUGHREACT	V 2.2	10154-2.2-00	11.3.5
TOUGHREACT	V 2.3	10396-2.3-00	11.3.5
UDEC	V 2.0	B00000000-01717-1200-30004	14.4

NOTE: ¹ iTOUGH2 with EOS9 and EOS7r modules

² N/A signifies that the code is unqualified and it is currently not tracked by the Software Configuration Management System.

2. REPOSITORY DESIGN SELECTION FOR SITE RECOMMENDATION AND RELATION TO APPLICABLE ANALOGUES

2.1 INTRODUCTION

Studies of natural and anthropogenic systems can improve understanding and confidence in the variables affecting the evaluation and operation of a selected repository design. The selection of appropriate analogues to build confidence in repository design parameters should focus on the variables affecting operational parameters rather than on a specific design for a potential Yucca Mountain repository. The current design approach is flexible in that a wide range of thermal operating modes is being examined. The flexible design approach is presented in Section 2.2. The range of potential thermal operating modes is described on the basis of three evaluated scenarios in Section 2.3, while Section 2.4 presents design methods by which the thermal goals can be achieved. Section 2.5 provides a basis for evaluating analogues to repository materials and processes that are discussed in subsequent chapters.

2.2 FLEXIBILITY IN DESIGN

Refining the design and operating mode of the potential monitored geologic repository at Yucca Mountain has been an ongoing process since inception of the YMP. This iterative design process has been focused on improving the understanding of how design features contribute to the performance of a potential repository and to the uncertainty in that performance.

A primary design aspect has been the thermal load that will be generated by the repository. Previous design concepts have considered higher-temperature operating modes, in which the rock surrounding emplacement drifts exceeds the boiling point of water. More recently, to maintain flexibility in design, the design process has evolved to examine the effects on the repository over a wider range of thermal conditions. A flexible approach to design was introduced in the *Yucca Mountain Science and Engineering Report* (S&ER) (DOE 2001 [153849], Section 2.1.3). The design has flexible operating modes that can be adapted to accommodate a waste stream with potentially evolving thermal characteristics.

2.3 OBJECTIVES OF THERMAL OPERATING MODES

The current design concepts range from a lower-temperature operating mode to a higher-temperature operating mode. For the lower-temperature mode, the objective is to keep the waste package surface temperature below 85°C (DOE 2001 [153849], Section 2.1.2.3). In the higher-temperature mode, the wall rock of the drift is above boiling temperature but the temperature is controlled to prevent boiling fronts from coalescing in the rock pillars between the emplacement drifts. Strategies that have been considered with regard to selecting the operating mode of the repository are presented below.

2.3.1 Manage Boiling Fronts within the Rock Pillars

The higher end of the thermal operating mode, presented in the *Supplemental Science and Performance Analyses* (SSPA) (BSC 2001 [155950], Table 2-1), assumes an average waste package maximum temperature of ~160°C. This mode preserves the capability of the rock mass

to drain percolation flux through the repository horizon by preventing the boiling fronts from coalescing in the rock pillars between the emplacement drifts. In this mode, the close spacing of waste packages with thermally blended spent fuel inventories achieves a relatively uniform distribution of rock temperatures along the drift, limiting potentially complex thermal-mechanical effects resulting from a varying thermal gradient along the drift axis. This operating mode would also meet a design requirement established to maintain the integrity of the waste package cladding by not exceeding a temperature of 350°C, the temperature at which the cladding loses its integrity.

2.3.2 Maintain Drift-Wall Temperatures Below Boiling

One lower-temperature objective is to keep all the rock in the repository below the boiling point of water to reduce uncertainties associated with coupled thermal-hydrologic-chemical-mechanical processes driven by the boiling of water (BSC 2001 [155950], Section 2.3.2). In the higher-temperature operating mode described in the S&ER, the rock temperatures within the first several meters outside the emplacement drifts exceed the boiling point of water for about a thousand years.

2.3.3 Reduce Uncertainty in Corrosion Rates

The lower-temperature end of the range of thermal operating modes was defined by considering the potential for reducing uncertainty in the rate of localized corrosion of Alloy 22 waste package material. At temperatures below about 85°C or relative humidity (RH) below 50 percent, the susceptibility of Alloy 22 to crevice corrosion is very low (DOE 2001 [153849], Section 2.1.5, Figure 2-a). Operating the repository so that the temperature or relative humidity is below this window of crevice corrosion susceptibility may increase confidence that corrosion will not significantly reduce waste package service life.

2.4 MANAGING THERMAL OPERATING MODES

The temperature and relative humidity under which a repository would be operated for any specified underground layout can be managed either singularly or through various combinations of several operational parameters (DOE 2001 [153849], Section 2.1.4) such as by:

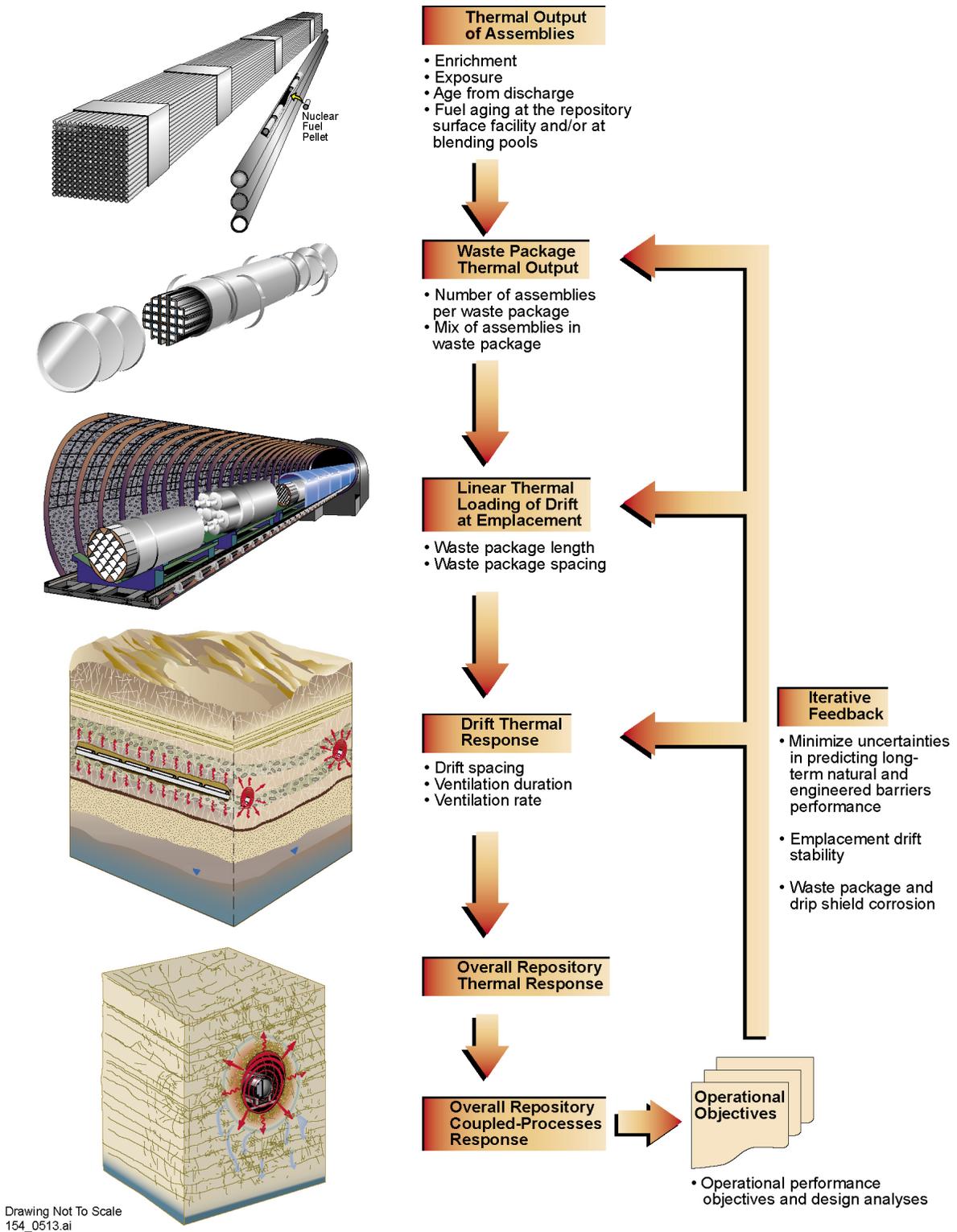
- Varying the thermal load resulting from the repository by managing the thermal output of the waste packages
- Managing drift ventilation prior to repository closure
- Varying the distance between waste packages in emplacement drifts.

Figure 2-1 illustrates the variables affecting the thermal performance of the repository, from waste forms to emplacement drifts.

2.5 APPLICATION TO NATURAL ANALOGUES

Because of the flexible design approach, analogues must be considered in terms of repository design variables rather than attempting to match a specific design. The important variables are

temperature of drift walls, presence or absence of a boiling front, dimensions and spacing of drifts, absence of backfill, and ventilation. These variables affect drift stability (addressed in Section 3), waste package and drip shield corrosion (discussed in Sections 5 and 6, respectively), processes operative within the engineered barrier system (addressed in Section 7), and thermally coupled processes affecting the host rock at the drift and mountain scales (covered in Section 11).



Source: DOE 2001 [153849], Figure 2-8.

Figure 2-1. Variables Affecting the Thermal Performance of the Repository

3. REPOSITORY DRIFT STABILITY ANALOGUES

3.1 INTRODUCTION

Section 2 provided background information on the current flexible design for a potential repository at Yucca Mountain against which to discuss analogues for drift stability. The proposed emplacement drift diameter is 5.5 m (18 ft) (DOE 2001 [153849], Section 2.3.1.1). The ability of underground openings to remain open and stable depends on a number of variables, including: (1) rock strength; (2) the size, shape, and orientation of the opening; (3) orientation, length, and frequency of fracturing; (4) effectiveness of ground support, and (5) loading conditions. There are no exact analogues to the openings that would be created for a potential repository at Yucca Mountain, but numerous examples demonstrate that both natural and man-made underground openings can exist for thousands of years in a wide variety of geologic settings, even with minimal or no engineering. Analogue information is available for natural underground openings (Section 3.2) and man-made excavations (Section 3.3). An analogue demonstrating thermal effects on underground openings is presented in Section 3.4. Effects of ground shaking on underground openings are mentioned in Section 3.4 and discussed in more detail in Section 14. Information found in Section 3.2, 3.3, and 3.4 may help to support arguments associated with Key Technical Issue (KTI) KUZ0407 listed in Table 1-1.

3.2 NATURAL UNDERGROUND OPENINGS

Caves represent examples of natural underground openings. They are abundant, and in many cases, it can be demonstrated that they have remained open for very long spans of time. The oldest documented examples noted in this study are from the limestone formations of the Guadalupe Mountains in New Mexico. Alunite is a mineral that forms on the floor of caves. Undisturbed, uncovered alunite collected from the cave floors has been dated at 4.0–3.9 million years (m.y.) for the Big Room at Carlsbad Caverns and at 6.0 to 5.7 m.y. for the upper level of the nearby Lechuguilla Cave. Alunite from other nearby caves yields ages as old as 11.3 m.y. (Polyak et al. 1998 [156159], p. 1919). Sections of the cave floors have blocks that appear to have fallen from the ceiling; however, none of the dated caves has been closed by rockfall, demonstrating the stability of most of these openings over millions of years. Because these settings are common, they demonstrate stability for most of the openings for millions of years. Many of these openings are as large or larger than those proposed for Yucca Mountain (Figure 3-1).

The San Antonio Mountain Cave in northern New Mexico is an example of a different geologic setting in which an opening has remained open over a long period of time. This cave is a lava tube in basalt from 3.4–3.9 million years ago (Ma) (Rogers et al. 2000 [154320], pp. 89–93). The cave is more than 170 m long and generally several meters wide. In some places, the ceiling is over 12 m high. The large size of the openings combined with abundant cooling fractures has resulted in fallen blocks (generally less than $\frac{3}{4}$ m in length and width) that cover about 30% of the cave's floor. Several spots preserve a long record (up to 1 m.y.) of sedimentation, more than 400 cm thick, with no collapse (Rogers et al. 2000 [154320], Figure 5). Davis (1990 [144461], p. 338) notes that similar cave sediments in Europe date back 1.5 Ma, which suggests that long-term stability of caves is a common feature.

Most lava tubes are a few thousand to a few hundred thousand years in age. They are commonly ellipsoidal to circular in cross section and several meters in diameter. Some of the most extensive lava tubes are in the Undara region of Australia, where 190,000-year-old tubes reach 100 km in length (Undara Experience 2001 [157515]). Figure 3-2a shows the interior of a lava tube in the Undara region (with a person included in the photo for scale). Lava tubes are also common in Hawaii (Figure 3-2b) and in the Cascade Range of California, Oregon, and Washington, in lava that is modern to a few thousand years in age. Most lava tubes exhibit areas of collapse where the roof is thin, but large sections of open tunnel persist for long periods of time.

The maximum length of time that caves have stood open is usually not known, but the age dates of datable biologic or archeologic materials found in many caves indicate that the caves have remained open for extended periods of habitation without collapse. Some packrat middens found in caves are thousands to tens of thousands of years old, and Davis (1990 [144461], p. 341) reports that over 1,000 middens have been studied in caverns and rock shelters of the western United States. Stuckless (2000 [151957], p. 4-6) reports on several caves in limestone that contain paintings that have been dated at 11,000 to 32,000 years old.

Kebara Cave in Mt. Carmel, Israel, is a very large opening (26 m long and 20 m wide, with a ceiling up to 18 m high), and sediments accumulated on the floor of the cave yield ages as old as 50,000 years (Bar-Yosef et al. 1996 [157419], p. 305). Although the main portion of the cave shows no sign of collapse, a terrace in front of the cave entrance was formed by collapse sometime after 30,000 years ago (Bar-Yosef et al. 1996 [157419], p. 298). However, even this collapsed section must have stood open for more than 20,000 years, because this section was the entrance from before 50,000 until 30,000 years ago.

3.3 ANTHROPOGENIC OPENINGS

Anthropogenic, or man-made, underground openings do not provide as long a history as the natural ones, but they may provide a closer analogy to a mined geologic repository. Here too, there are abundant examples that exhibit considerable stability for hundreds to thousands of years even with minimal engineering. The oldest examples are the Neolithic flint mines of northern Europe and England. These were mined into chalk deposits in 3,000 to 4,000 B.C. At one site in England, shafts that are 6 to 14 m deep access galleries that are 4 to 24 m in length and are still open today (Crawford 1979 [157420], pp. 8–32).

Around 1,500 B.C., Egyptians began excavating tombs on the west bank of the Nile River, across from Luxor. Over 100 tombs were excavated in bedded and jointed limestone (Figure 3-3). The tombs were generally a few meters in length and width and about 2 m in height. Many have pillars that were left for support in the larger rooms. Most of the tombs have incurred some water damage to plaster and paintings on the walls and ceilings, but none seems to have suffered collapse (Simmons 2002 [157578], SN-LBNL-SCI-108-V2, p. 7).

Mining of metallic ores has produced subterranean openings in a variety of rock types and often in intensely altered or fractured rock. Unfortunately, many of the oldest examples have been mined continuously or reopened in more modern times to mine remaining lower-grade ore. The Laurion mines, about 40 km south of Athens, Greece (Figure 3-4), were first mined about 2,000 to 1,500 B.C., but were mined most actively from 600 to 300 B.C. (Shepherd 1993 [157425], p.

75). These silver and lead mines are in a gently dipping sequence of mica schists and marble, with sulfides occurring along the contacts. Shafts 1.25–1.4 m by 1.5–1.9 m were sunk up to 111 m deep (Shepherd 1993 [157425], p. 17). Underground workings were 140 km in length; tunnels averaged 1 m in width and 1.75 m in height (Shepherd 1993 [157425], pp. 17–18). Ore zones were mined out by underhand stoping, which left large cavities a couple of meters high and a few meters in diameter. Pillars of inferior ore-grade rock supported these cavities. Removal of rock from these pillars was punishable by death (Shepherd 1993 [157425], p. 25).

Bronze-age mining of metal also occurred at the Great Orme Copper Mine in Wales. Charcoal recovered from the early workings dates at 1,000 to 2,000 B.C. In 1849, miners broke into a cavern nearly 40 m long, which contained stone hammers, most likely from the Bronze Age. The cavern, mined into limestone, had stood open for nearly 4,000 years (Llandudno Museum 1998 [157526]).

Underground mining was common during the Roman Empire, and the size and state of preservation of the mines not destroyed by subsequent mining are fairly similar. Shepherd (1993 [157425]) and Davies (1935 [157421]) present locations and descriptions for most of these mines. In addition to mining for metals, the Romans created large tunnels to transport water. For instance, the aqueduct at Tresmines, Portugal, is 60 m wide, 80 m high and 480 m long; at Corta das Coras, the tunnel is 100 m wide, 100 m high, and 350 m long (Shepherd 1993 [157425], p. 17).

Buddhist monks carved temples into caves in the fractured Deccan basalts of west-central India, from approximately the second century B.C. until the tenth century A.D., with most excavated in the late fifth or early sixth century A.D. (Behl 1998 [156213], pp. 27, 39). There are 31 caves at Ajanta, India, carved along a 550 m long, horseshoe-shaped gorge of the Waghora River. Each temple originally had steps carved into the rock leading up to it, but only Cave #16 still has a vestige of steps. The monsoonal climate has destroyed the exterior stone structures exposed to the elements, but subterranean openings have been well preserved in spite of the climatic effects. Similar Buddhist caves, from the sixth through the tenth centuries A.D., are preserved at Ellora and from the ninth century A.D. (Jain caves) at Sittanavasal, India (Behl 1998 [156213], p. 39).

The cross-sectional dimensions of most of the temples at Ajanta are larger than those proposed for a mined geologic repository. For example, Cave #10 is 30.5 m × 12.2 m. Cave #2 has a verandah of 14.10 m × 2.36 m, a main hall of 14.73 m × 14.5 m, and a shrine of 4.27 m × 3.35 m. Cave #16 has a verandah of 19.8 m × 3.25 m and a main hall of 22.25 m on a side with a height of 4.6 m. In spite of these large sizes, there is no reported collapse. As in the case of the Egyptian tombs, most of the Ajanta paintings appear to have suffered some water damage and vandalism (Behl 1998 [156213], pp. 234–236).

During the second through eleventh centuries A.D., the Christians of Cappadocia, Turkey, excavated underground cities and churches. One of these cities, Derinkuyu, covered approximately 4 km² and had an estimated 15,000 to 20,000 inhabitants (Toprak et al. 1994 [157429], p. 54) during much of the first millennium A.D. As of 1994, eight levels of ancient habitation had been discovered. Access to the underground cities was by way of narrow passageways that could be closed by rolling a 1.5 m diameter millstone across the opening

(Figure 3-5). The excavated rooms were generally several meters across and more than 10 m long.

The geology of Cappadocia (Toprak et al. 1994 [157429], pp. 8–11) is similar to that of southern Nevada (Sawyer et al. 1994 [100075]). In both regions, the late Tertiary section is composed of a thick sequence of silicic volcanic rocks. At Yucca Mountain, the host rock for the potential repository is a densely welded, quartz latite ash-flow tuff that formed about 11.6 Ma, whereas the underground cities of Cappadocia are situated in a partially welded, rhyolite ash-flow tuff that formed about 4 to 9 Ma. The difference in welding at Yucca Mountain and the underground cities of Cappadocia results in markedly different fracture density and engineering properties. Fracture density, which is a major variable contributing to underground collapse, is much lower in the underground cities. Ground support, which would be carefully engineered at Yucca Mountain, was never used in the underground cities. Thus, the fact that there has been no collapse in the underground cities of Cappadocia during the past 1,500 to 1,800 years suggests that excavations in tuff should be stable for long periods of time if undisturbed. Stability of unsupported openings would be favored in tuffs of a low degree of welding and fracturing.

Churches were excavated into the tuff north of the underground cities at Goreme, in Cappadocia, during the ninth to thirteenth centuries A.D. (Toprak et al. 1994 [157429], p. 53). All but one of these show no evidence of collapse. The exception is a collapse of a cliff face that exposes part of the inside of one church. The interior portions of the church are still in excellent condition, and their painted walls and ceilings within are well preserved except for spallation and vandalism (Stuckless 2000 [151957], p. 22).

Some of the underground openings excavated into the tuffs of Cappadocia are still used as dwellings. There are at least two other places where underground excavations are still used as dwellings. In Tunisia, 20 to 40 km south of the city of Gabes, ten underground villages, some of which date back nine centuries, are excavated in limestone (Golany 1983 [157422], pp. 5–6). The limestone is composed of poorly indurated layers approximately 2 m thick, which are easily mined out, along with better indurated layers of similar thickness. Room sizes are typically 2 to 2.5 m on a side, with flat ceilings that may have a supporting column in the center. Similarly, in northern China, thick deposits of slightly indurated loess exist, which could be easily excavated. However, its internal structure is such that loess can form vertical cliffs as much as 30 m in height. The underground dwellings accommodate more than 10 million people, who farm the land above their houses (Golany 1983 [157422], p. 13).

Although all the examples given so far either lack ground support or utilize only unmined pillars, examples do exist of wooden ground support. Around the beginning of the second century A.D., the Roman Emperor Hadrian mandated the use of wooden supports in all mines (Shepherd 1993 [157425], p. 25). Shepherd (1993 [157425], p. 26) provides a discussion of some examples, but does not comment on the stability of openings that were shored up. Tombs in China provide a different kind of example. Sixteen emperors from the Ming Dynasty (1368 to 1644 A.D.) were buried in tombs excavated in rock near Beijing. The earliest of the tombs has 32 sandalwood pillars 1.17 m in diameter; all are still intact and sturdy (Golany 1989 [157423], pp. 21–22).

3.4 UNDERGROUND OPENINGS AFFECTED BY TEMPERATURE

The foregoing descriptions show that both natural and manmade underground openings maintain stability well in an undisturbed setting. In fact, many of the examples given, as well as several mines not discussed, have probably been subjected to significant seismic shaking. Further discussion of seismic effects on underground openings is provided in Section 14.

The stability of underground openings can also be affected by temperature. An example of thermal stresses causing rockfall around rock bolts in a heated area occurred at Linwood Mining Company's limestone excavations (Simmons 2002 [157578], SN-LBNL-SCI-108-V2, pp. 7, 8). Linwood has excavated limestone adjacent to the Mississippi River downstream from Moline, Illinois, since World War I for processing in a kiln. The mine started as a surface quarrying operation, but as excavation progressed, the mine was converted to an underground room and pillar operation. The elevation of the underground workings is lower than the Mississippi River.

The company started venting the kiln exhaust underground in 1971 as part of a solution for controlling dust emissions from the kiln (Simmons 2002 [157578], SN-LBNL-SCI-108-V2, pp. 7, 8). To do this, a 96-acre portion of the mine was nominally mined with 30 ft × 30 ft pillars 21 ft high. This portion was walled off from the active workings. Exhaust from the kiln is vented to these workings at 400°F (204°C), leaving the dust behind for later collection.

The mining company adds bolts and mesh when a karstic depression is encountered, but otherwise the mine is essentially unsupported. Perhaps for this reason, steel-bar rock bolts were placed near the entry of the exhaust. After some period of venting, the rock near the exhaust vent broke out, leaving the bolts that had been emplaced in the rock, with the bottom 5 feet or so of the bolts surrounded by air. It was suggested that the surrounding rock had probably fallen out because heat was transferred up the rock bolt faster than it was transferred through the rock, which resulted in a thermal stress that caused failure for a rock with an unconfined compressive strength of 18,000 psi (~125 MPa) (Simmons 2002 [157578], SN-LBNL-SCI-108-V2, pp. 7, 8).

3.5 SUMMARY

In Section 3, numerous examples are provided of the stability of natural and man-made underground openings for millennia or longer under undisturbed conditions. However, an inherent bias is reflected in the studies because of the difficulty of determining the relative percent of openings that remain versus those that have collapsed. It is more difficult to evaluate the cause of collapse of such openings, whether by human interference or natural causes. The ability of underground openings to remain open and stable under ambient conditions depends on a number of variables, including: (1) rock strength; (2) the size, shape, and orientation of the opening; (3) orientation, length, and frequency of fracturing; and (4) effectiveness of ground support. Radiometric dating of cave floor minerals at Carlsbad Caverns and Lechuguilla Cave indicates that natural openings larger than those proposed for repository drifts at Yucca Mountain have remained open for millions of years. Collapse of the roof of an opening tends to occur where the fracture density is high and the overburden is thin, as is the case with some lava tubes. Factors that contribute to the size of a block falling are fracture spacing, which in turn depends on rock type and texture, and the size and shape of the opening.

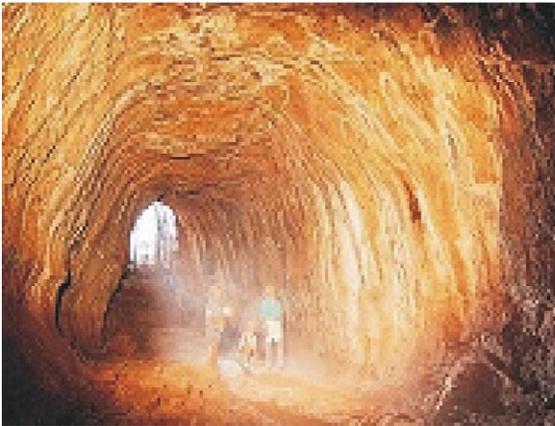
The oldest examples of stable man-made openings are Neolithic flint mines dating from 4,000 to 3,000 B.C. However, numerous Roman mines and some aqueducts remain intact that tended to have been constructed of a similar size and now exhibit the same state of preservation. These and other examples demonstrate that both natural and man-made underground openings can exist for thousands of years in a wide variety of geologic settings, even with minimal or no engineering.



NOTE: Areas such as this have no obvious roof blocks on the floor of the cavern or holes in the ceiling from which blocks might have fallen.

Source: Simmons 2002 [157578], SN-LBNL-SCI-108-V2, p. 6.

Figure 3-1. Photograph of Fairyland in Carlsbad Caverns, New Mexico



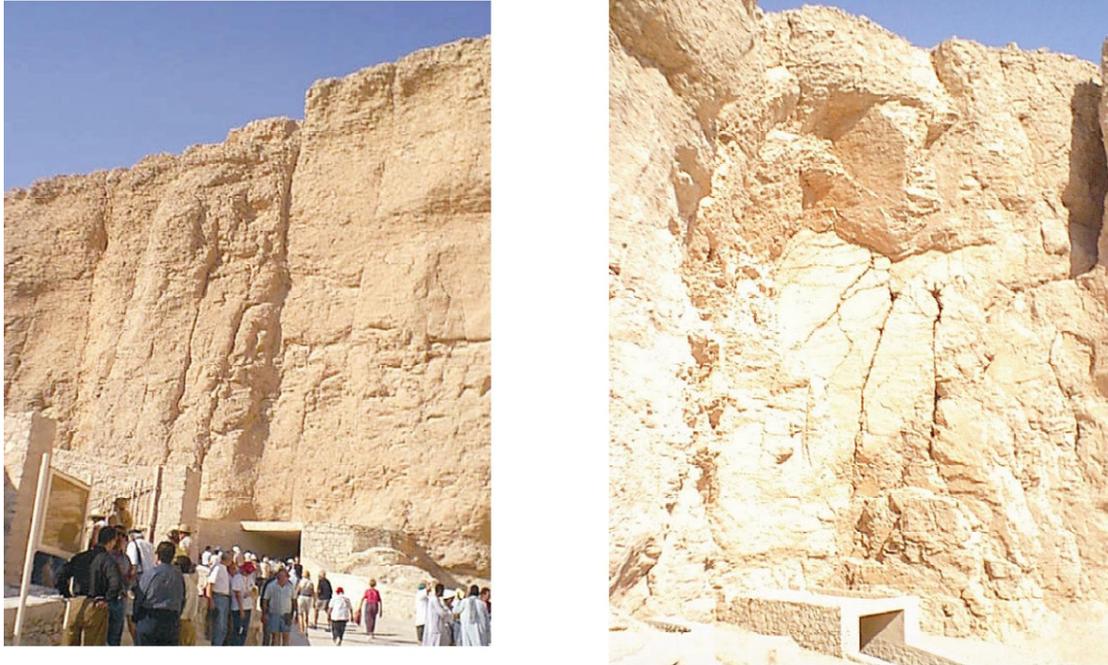
(a)



(b)

Source: (a) Undara Experience 2001 [157515] and (b) USGS 2000 [157517].

Figure 3-2. Photographs of (a) Lava Tube in Undara, Australia, and (b) Nahuku Lava Tube in Hawaii



Source: Simmons 2002 [157578], SN-LBNL-SCI-108-V2, p. 6.

Figure 3-3. Photographs of the Nubian Limestone That Hosts the Tombs in the Valley of the Kings, Egypt



NOTE: The roof is formed by mica schist and the floor by marble. Ground support appears to be modern because older reports make no mention of either wood or cement.

Source: Gill 2001 [157516].

Figure 3-4. Mined Out Cavern in the Laurion Mines, Greece



NOTE: The millstone is about 1.5 m in diameter.

Source: Stuckless 2000 [151957], Figure 13.

Figure 3-5. Photograph of a Room in the Underground City of Kaymakli, Turkey

4. ANALOGUES TO WASTE FORM DEGRADATION

4.1 INTRODUCTION

Many variations of waste form types may be emplaced within a potential repository at Yucca Mountain. However, most of the waste will be spent fuel in the form of UO_2 , with the remaining 10% or so being encapsulated in borosilicate glass resulting from vitrification of defense high-level nuclear waste. These waste forms are thermodynamically unstable under wet, oxidizing conditions (DOE 2001 [153849], 4.2.6.1). For this reason, quantification of the degradation modes and dissolution rates that determine the source term for performance assessment is extremely important.

Analogue studies may contribute to understanding long-term waste form degradation processes through the record left behind in secondary minerals and groundwater. Many of the published analogue studies of waste form degradation focus on dissolution of uranium under reducing groundwater conditions. This is because most of the geologic waste disposal configurations of other nations involve saturated, reducing conditions. Sketches of the most important and well-studied of these analogue sites were provided in Section 13 of the *Yucca Mountain Site Description* (CRWMS M&O 2000 [151945]). As a whole, the sites with reducing groundwater chemistry have limited applicability to conditions that would be expected to occur at a potential Yucca Mountain repository, which is located in an unsaturated oxidizing environment. However, in some instances, information from these analogue studies can still provide valuable insights into the processes of waste form degradation. Section 4 relies to the extent possible on information derived from oxidizing environments, but relevant information from examples in reducing environments is included to illustrate general principles of waste form dissolution and potential criticality.

Section 4.2 provides a conceptual basis for waste form degradation. Section 4.3 discusses analogues relevant to spent-fuel dissolution rates. Section 4.4 addresses the formation of secondary minerals that may immobilize uranium and fission products. Section 4.5 briefly covers radiolysis and Section 4.6 briefly covers nuclear criticality of the waste form. Section 4.7 summarizes studies of analogues to glass waste forms. Section 4.8 is a summary of the topics discussed.

4.2 WASTE FORM DEGRADATION—CONCEPTUAL BASIS

4.2.1 Overview of Conceptual Basis

Radionuclide release from the waste forms that would be emplaced at Yucca Mountain is a three-step process requiring: (1) degradation of the waste forms, (2) mobilization of the radionuclides from the degraded waste forms, and (3) transport of the radionuclides away from the waste forms (DOE 2001 [153849], 4.2.6.1). Water strongly influences all three processes.

As described in the S&ER (DOE 2001 [153849], 4.2.6.1) radionuclide release begins after breach of the waste package and the ingress of air. If the breach is early, the waste may still be

highly radioactive and physically hot. The thermal output of hot waste packages, particularly from commercial spent fuel, will limit groundwater access at early times. When water enters the package, the rate of water inflow and evaporation will determine when and if water accumulates. During this period, gamma radiolysis (radiation-induced decomposition) of the humid air within the package may cause production of nitric acid, which could condense into any accumulated water. If the breach is late, radiation levels and heat will be much lower, and evaporation and radiolytic acid production will be less important. During either period, water may enter the package either as water vapor or as liquid. The dissolved constituents in the groundwater entering the package may have a significant effect on in-package chemistry only if evaporation has concentrated them by orders of magnitude. This is unlikely to occur unless the waste package is breached only at the top and large amounts of water enter and evaporate within the package. During the latter period, there is no water transport of groundwater species or radionuclides out of the package.

If the package overflows, or if holes in the bottom allow flow-through, fresh water will dilute the groundwater components, and water-based radionuclide releases may begin. The release of radionuclides does not begin until after the breach of the cladding (for spent fuel). Chemistry within the package is important because it influences the rate of degradation of the package and waste forms (including cladding), and it determines the mobility of radionuclides as dissolved or colloidal species. Films of stagnant, concentrated, acidified groundwater are considered the worst possible scenario for degradation, because they do not inhibit oxygen and carbon dioxide transport and may support localized corrosion of the cladding and waste. Such films, however, do not support significant mobilization and transport of radionuclides and are only possible at times when there is an exact balance of water inflow and evaporation.

As stated previously, most of the many waste form types that may be emplaced within a repository are thermodynamically unstable under wet, oxidizing conditions (DOE 2001 [153849], 4.2.6.1). Uranium dioxide fuels will oxidize and hydrate, and glass waste forms will react with water to form clays, zeolites, and oxides. The rate of these reactions, however, will in most cases be quite slow and may be limited by the rate that reactants such as oxygen and water can be transported to the waste form surface. Although a few radionuclides such as cesium and iodine may concentrate between the fuel and cladding during reactor operation, most of the radionuclides will be incorporated within the various waste forms and cannot be released from the waste package until the waste forms degrade.

Once the waste forms degrade, radionuclides as dissolved species and suspended particles may be mobilized by advection or diffusion. Larger particles settle out of solution, or are filtered out by trapping in small openings. Only after gross failure of the package will these larger particles fall or wash out of the package. Particles in the colloid size range, however, can remain suspended and may travel significant distances. The concentration of radionuclides associated with colloids is limited by the colloid concentration and radionuclide carrying capacity of the colloids (DOE 2001 [153849], Section 4.2.6.1). The concentration of dissolved species is limited by the elemental solubility of the radionuclide within the local environment.

4.2.2 Spent Fuel Dissolution in an Oxidizing Environment

Many laboratory studies attempt to measure parameters that can be used to determine the rate of spent fuel dissolution under repository disposal conditions. These studies use either spent fuel itself, uranium dioxide (as an analogue for spent fuel), or uraninite as a natural analogue. Although the uraninite structure can accommodate some degree of oxidation, in highly oxidizing aqueous environments uraninite is unstable and decomposes (Finch and Ewing 1992 [113030], p. 133). Secondary uranyl (U^{+6})-bearing phases precipitate on the surface of the corroding uraninite, and a rind of corrosion products forms. The impurities often contained in uraninite affect its thermodynamic properties, the rate of uraninite alteration, and the composition of the corrosion products (Finch and Ewing 1991 [105591], p. 392). Studies that have examined the dissolution of uraninites under oxidizing conditions found that the dissolution rate was diminished by the presence of thorium, lead, and rare-earth-element impurities in the uraninite (Finch and Ewing 1992 [113030], p. 133). Compared to uraninite, spent fuel has a lower content of these impurities (Finch and Ewing 1992 [127908], p. 466) and on this basis might be considered to dissolve more rapidly.

Most of the uranium released to solution during the dissolution of UO_2 combines with ions in water to form secondary alteration phases. Both natural and experimental uranium systems display a paragenetic sequence of mineral phase formation that is characterized by the following general trend (Stout and Leider 1997 [100419], Section 2.1.3.5):

$UO_2 \Rightarrow$ uranyl oxide hydrates \Rightarrow alkali and alkaline-earth uranyl oxide hydrates \Rightarrow uranyl silicates \Rightarrow alkali- and alkaline earth uranyl silicates + palygorskite clay.

Specifically, mineralization in the experimentally determined paragenetic sequence of alteration phases is:

$UO_2 \Rightarrow$ dehydrated schoepite ($UO_3 \cdot 2H_2O$) \Rightarrow compreignacite $K_2(UO_2)_6O_4(OH)_6 \cdot 8H_2O$ + becquerelite ($Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$) \Rightarrow soddyite ($(UO_2)_2SiO_4 \cdot 2H_2O$) \Rightarrow boltwoodite ($K(H_3O)(UO_2)SiO_4$) + uranophane ($Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$) + palygorskite clay (Wronkiewicz et al. 1996 [102047], p. 94).

Thus, the uranyl oxide hydrates are common initial corrosion products of uraninite during weathering. In the presence of dissolved silica, these early phases alter to uranyl silicates, most commonly soddyite and uranophane. The phases that form depend on the chemical composition of the waters with which the uraninite is in contact, which in turn depends on the mineralogy of the surrounding host rocks and the oxidation potential of the hydrologic environment. The experimentally determined mineral sequence appears to be controlled by precipitation kinetics and is nearly identical to secondary uranium phases observed during the weathering of naturally occurring uraninite under oxidizing conditions, such as that which occurs at the Nopal I uranium deposit, Peña Blanca, Mexico (Wronkiewicz et al. 1996 [102047], Figure 7). In laboratory UO_2 tests and in the natural uranium deposits at Nopal I, the alkali- and alkaline-earth uranyl silicates represent the long-term solubility-limiting phases for uranium (Stout and Leider 1997 [100419], Section 2.1.3.5). Furthermore, at Nopal I, uranium concentrations in groundwater and seepage waters ranged from 170 parts per trillion (ppt) to 6 parts per billion (ppb) (Pickett and Murphy 1999 [110009], Table 2). The upper part of this range is similar to concentrations seen in filtered

samples from spent fuel dissolution experiments (Stout and Leider 1997 [100419], p. 2.1.3.5-4). This added similarity increases confidence that the experiments and the natural analogue reactions may simulate the long-term reaction progress of spent UO₂ fuel following potential disposal at Yucca Mountain.

Uraninite usually contains radiogenic lead that has in-grown through time (Finch and Ewing 1992 [127908], p. 466). As a result, the early-formed Pb-poor uranyl oxide hydrates alter incongruently to uranyl silicates plus radiogenic-Pb-enriched uranyl oxide hydrates, such as curite (Pb₂U₅O₁₇ · 4H₂O), that may serve to limit the mobility of uranium in nature (Finch and Ewing 1992 [127908], p. 466). Curite may also play an important role in the formation of uranyl phosphates, which are significantly less soluble than the uranyl silicates and control uranium solubility in many groundwaters associated with altered uranium ore (Finch and Ewing 1992 [127908], p. 465). In the absence of lead, schoepite and becquerelite are the common initial corrosion products. The reaction path for the alteration of lead-free uraninite results in the formation of uranyl silicates. Thus, the long-term oxidation behavior for ancient, lead-bearing uraninite is different from that of young, lead-free uraninite, which is more similar to spent fuel. Because the presence of lead effectively reduces the mobility of uranium in oxidizing waters, the concentration of uranium in groundwaters associated with oxidized uranium ore deposits will depend in part on the age of the primary uraninite (Finch and Ewing 1992 [113030], p. 133).

In summary, the paragenesis of uraninite alteration phases depends on the age of the primary uraninite, the mineralogy of surrounding host rocks, and on groundwater composition, pH, and redox potential. In a general oversimplification, the progression of phases of uraninite alteration, in the absence of radiogenic lead in-growth, will be to uranyl silicates, culminating in uranophane in an oxidizing environment. Numerous compositional variations are caused by trace elements present in the system. The composition of schoepite is often used to represent an alteration product in models of spent fuel alteration, but this is an oversimplification, based on observations in nature. As shown by Finch and Ewing (1992 [113030], p. 144), the formation of intermediate-phase schoepite may be favored early during the corrosion of uraninite. Schoepite is not, however, a long-term solubility-limiting phase for oxidized uranium in natural groundwaters containing dissolved silica or carbonate (e.g., the type of groundwaters at Yucca Mountain).

Despite the analogy between uraninite and spent fuel, there are important differences between the two. For one thing, spent fuel is artificially enriched in ²³⁵U and contains nuclear fission products that are not present in uraninite; in contrast, uraninite contains a higher proportion of nonradiogenic trace element impurities. Also, the thermal history of spent fuel, unlike that of natural uraninite, may cause lattice and structural crystallization defects in the spent fuel that are not present in the uraninite. In addition, geologically old uraninite contains in-grown radiogenic lead, which would not be found in younger uraninite or in spent fuel. Section 4.3 presents the general dissolution path of uraninite, and by analogy spent fuel, under oxidizing conditions.

4.3 ANALOGUE STUDIES RELATED TO WASTE FORM DISSOLUTION RATES

The remaining issues of most relevance to the behavior of spent fuel in a repository that could be addressed by natural analogues are dissolution and radionuclide release (Section 4.3),

radionuclide retardation by secondary alteration products (Section 4.4), radiolysis (Section 4.5), and criticality (Section 4.6).

4.3.1 Fission-Product Tracer Method

Rates of UO_2 dissolution can be quantified by measuring the amount of fission product released from the uraninite and using this as a tracer. Concentrations of this tracer in the rock or in the groundwater in the vicinity of the uraninite are proportional to the dissolution rate, assuming that the tracer is released from the uraninite only by dissolution (Curtis 1996 [157497]; Curtis et al. 1994 [105270]; 1999 [110987]). The tracers used for this method are ^{99}Tc in rock, or its stable daughter ^{99}Ru , when technetium has decayed to insignificant amounts, and ^{129}I in groundwater. There are several uncertainties in the modeling and assumptions made in this approach, but some consistency is apparent in the results obtained from different uranium orebodies when using the same isotopic system. For example, using the ^{99}Tc tracer at Oklo, Gabon, and at Cigar Lake, Canada, provided average release rates of 1.5×10^{-6} per year and 1.1×10^{-6} per year, respectively (Curtis 1996 [157497], p. 145). However, different rates are obtained when using ^{129}I as a tracer. Applying this tracer at Cigar Lake provided release rates of between 9×10^{-9} and 3×10^{-10} per year, which are 2 to 4 orders of magnitude less than the values obtained using the ^{99}Tc tracer.

Curtis et al. (1994 [105270]) used measurements of ^{99}Tc , ^{129}I , ^{239}Pu , and U concentrations in rock from uranium deposits at Cigar Lake and Koongarra to estimate radionuclide release rates from uranium minerals. At Koongarra, Australia, release rates appear to have been faster (10^{-7} per year; Curtis et al. 1994 [105270], p. 2234) than at Cigar Lake, where model-dependent release constants from the uraninite bearing rocks were $<5 \times 10^{-8}$ per year (Curtis et al. 1994 [105270], p. 2234), producing small deficiencies of ^{99}Tc , and larger ones of ^{129}I . The inferred differences in radionuclide release rates are consistent with expected differences in uranium mineral degradation rates produced by the differing hydrogeochemical environments at the two sites. In the Cigar Lake ore zone, low uraninite solubility in a reducing environment and small water flux through impermeable rock would inhibit the rate of uraninite degradation and thus the rate of radionuclide release. At Koongarra, higher mineral solubilities induced by higher oxidation potentials, higher aqueous concentrations of carbonate and phosphate, and greater water fluxes would be expected to produce higher rates of uranium mineral degradation. Curtis et al. (1999 [110987], p. 284) note that the consistency of $^{239}\text{Pu}/\text{U}$ and $^{99}\text{Tc}/\text{U}$ ratios in bulk rock suggests that the redistribution processes observed at Cigar Lake are highly localized and do not result in large-scale losses or gains of these nuclear products from the deposit as a whole. The fission product tracer method could be applied to water samples collected at Peña Blanca (Section 10.4). While this method clearly has potential for quantifying UO_2 dissolution under natural conditions, the method has yet to be refined and differences between results for the two tracers explained. Besides this fission product tracer method, there is no other technique for quantifying directly long-term uraninite dissolution rates in natural analogue studies.

4.3.2 Dissolution of Oklo Uraninite

Application of the fission-product tracer method has not been reported for Oklo, but Oklo provides a unique record of uranium and fission-product retention. Because parts of the Oklo orebody achieved nuclear criticality as a result of highly enriched concentrations of ^{235}U , Oklo

uraninite contains significant quantities of fission products or their stable daughters, directly equivalent to those present in spent fuel. In this regard, Oklo is unlike any other known uranium deposit. A photograph of one of the reactor zones is shown in Figure 4-1.

There are, however, some differences between Oklo uraninite and spent fuel. For one thing, Oklo contains lower concentrations of fission products than does spent fuel. Also the temperature of reaction (400° to 600°C; for a discussion of temperatures, see Zetterström 2000 ([157501], p. 13) and power density were somewhat lower than in a reactor, and the duration of criticality at Oklo (on the order of 0.1 to 0.8 Ma; Louvat and Davies 1998 [125914], p. 140) was much longer than the lifetime of reactor fuel. Recognizing these differences, several large-scale analogue investigations have taken place at Oklo, and much relevant information has been obtained, including semiquantitative information on the fate of radionuclides contained in the orebody.

These analogue investigations (e.g., Louvat and Davies 1998 [125914]; Gauthier-Lafaye et al. 2000 [157499]) have revealed that when the Oklo reactor zones were cooling after periods of criticality, some dissolution of the uraninite and elemental remobilization occurred. However, the limited extent of this remobilization is indicated by the fact that more than 90% of the uranium “fuel” has remained in the same spatial configuration since criticality (Miller et al. 2000 [156684], p. 81). This implies that uranium has been almost fully retained within the uraninite minerals. The disposition of some performance assessment-relevant elements and other elements in the reactor zones at Oklo is provided in Table 4-1. The transuranic elements neptunium, plutonium, and americium were all formed *in situ* within the uraninite during criticality, and their stable daughters have also been retained due to their compatibility with the crystal chemical structure of their host or in inclusions in the uraninite. Other radiogenic elements, which were less compatible with the uraninite host (e.g., Cs, Rb, Sr, Ba) have been partially or totally lost by diffusion from the uraninite. Some elements (e.g., Tc, Ru, Rh, Pd), however, migrated only short distances and were totally retained within the clay matrix enclosing the reactors. Data for other elements indicate clear deficiencies in the noble gases, halides, and lead (possibly resulting from volatilization) and suggest that some minor loss from the system has occurred for other elements.

Because the reactions ended nearly two billion years ago, the short-lived radionuclides have decayed to more stable daughter nuclides. Analysis of the behavior of these short-lived radionuclides is problematic. According to Brookins (1978 [133930], p. 309), Pu, Np, and Am were likely retained within the reactor, while Bi and Pb would have been redistributed locally without substantial migration (Brookins 1978 [133930], p. 309). Most geochemical observations at Oklo support these predictions to varying degrees. Curtis et al. (1989 [100438], p. 57) conclude that the retention of fission products is related to their partitioning into uraninite or secondary mineral assemblages. Those fission products that partitioned into the secondary mineral assemblages were largely lost over time, pointing to the importance of small uraninite grains in controlling the chemical microenvironment.

It is important to note that most of the observed uraninite alteration at Oklo occurred under hydrothermal conditions. Little uraninite-groundwater interaction has taken place at present-day ambient temperatures, except at the shallow Bangombé reactor zone (Smellie et al. 1993 [126645], p. 144). In summary, the Oklo natural analogue investigations indicate that the kinetics of UO₂ dissolution, either as uraninite or spent fuel, are exceedingly low under reducing conditions expected in the near field of some repositories. While dissolution rates cannot be

quantified readily from natural analogue data, the abundance of naturally occurring uraninite that is nearly 2 billion years old at Oklo indicates its stability in the natural environment.

4.4 ANALOGUE STUDIES RELATED TO IMMOBILIZATION BY SECONDARY MINERALS

Laboratory experiments have shown that UO_2 dissolution is accompanied by the formation of secondary phases on the fuel surface and that these corrosion products can passivate further dissolution (Wronkiewicz et al. 1996 [102047], p. 79). At the temperature and time scales of laboratory experiments, these phases are amorphous. However, natural sites where uraninite accumulations occur and where dissolution has taken place over long time periods could provide insights into the structure and mineralogy of the secondary passivating phases, and indicate whether they have been able to prevent further mobilization of radionuclides.

4.4.1 Shinkolobwe, Zaire

The 1,800 Ma Shinkolobwe uranium orebody in Zaire (at the time of study) was the subject of a comprehensive investigation regarding the corrosion products of uraninite (Finch and Ewing 1991 [105591]). The Shinkolobwe deposit weathers under oxidizing conditions in a monsoonal-type environment where rainfall is above 1 m per year, thus providing more aggressive hydrochemical conditions than might be expected at a repository. At Shinkolobwe, the uraninite is coarsely crystalline and lacks many of the impurities, such as thorium and rare earth elements, found in other uranium deposits. This lack of impurities led Finch and Ewing (1991 [105591], p. 391) to suggest that the thermodynamic stability of the Shinkolobwe uraninite might closely approximate spent fuel.

The deposit has been exposed at the surface since the Tertiary (< 60 million years), and extensive weathering has altered or replaced much of the original uraninite. Uranium (VI) mineralization occurs along fracture zones where meteoric waters have penetrated up to 80 m deep or more. Uraninite crystals at Shinkolobwe are commonly surrounded by dense rinds of alteration minerals, mostly uranyl oxyhydroxides, as well as uranyl silicates and rutherfordine, a uranyl carbonate (UO_2CO_3). Uranyl phosphates are also common within fractures throughout the host rocks, but are rare or absent from corrosion rinds.

Uranyl minerals comprising the corrosion rinds that surround many uraninite crystals undergo continuous alteration. This alteration occurs through repeated interaction with carbonate- and Si-bearing groundwater combined with periodic dehydration of (especially) schoepite and metaschoepite (Finch and Ewing 1991 [105591], p. 396). Such alteration occurs along small (approx. 0.1 to 1 mm) veins within the corrosion rinds. There is a general decrease in grain size as alteration proceeds, most commonly along veins. Schoepite, however, is not observed to re-precipitate where in contact with dehydrated schoepite (Finch and Ewing 1991 [105591], p. 396). Thus, while the formation of schoepite early during the corrosion of uraninite may be favored, schoepite is not a long-term solubility-limiting phase for oxidized uranium in natural groundwaters containing dissolved silica or carbonate (e.g., the type of groundwaters at Yucca Mountain).

Over 50 secondary uranyl phases were identified from the alteration of the uraninite. It was concluded that uraninite transforms to Pb-U oxide hydrates and then to uranyl silicates if sufficient silica is present in the system. Alteration of Proterozoic (~2400 to 700 Ma) uranium deposits such as Shinkolobwe introduce the important Pb-bearing phases, such as curite, which play a role in development of other stable phases in the system. Because of the very young age of repository spent fuel, radiogenic lead would not be present at Yucca Mountain for helping to immobilize spent-fuel elements.

4.4.2 Secondary Phases of Uranium Found at Nopal I, Peña Blanca

See Section 10.4 for a description of the Nopal I site. At Nopal I, uraninite occurs in rhyolite tuff in a semi-arid environment, where it has been exposed to oxidizing groundwater conditions with nearly neutral pH. Uranium was initially deposited as uraninite at Nopal I approximately 8 Ma (Pearcy et al 1994 [100486], p. 729). Geologic, petrographic, and geochemical analyses indicate that primary uraninite at Nopal I has been almost entirely altered to hydrated oxides and silicates containing uranium in the oxidized (uranyl) form. Because of its young geologic age, the deposit is low in radiogenic lead. The sequence of formation of uranyl minerals by alteration of uraninite at Nopal I is shown in Figure 4-2 and is similar in many geologically young uranium deposits located in oxidizing environments.

Leslie et al. (1993 [101714]) and Pearcy et al. (1994 [100486]) compared the alteration of uraninite at Nopal I to laboratory experiments of degradation of spent nuclear fuel potentially to be disposed of at Yucca Mountain, Nevada. They found that uraninite from the Nopal I deposit should be a good natural analogue to spent nuclear fuel because long-term experiments on spent fuel show alteration parageneses, intergrowths, and morphologies that are very similar to those observed at Nopal I (Wronkiewicz et al. 1996 [102047]). Oxidation of the uraninite at Nopal I has produced an ordered suite of minerals, first forming schoepite, a uranyl oxyhydroxide, followed by hydrated uranyl silicates, such as soddyite (Figure 4-2). Consistent with a high calcium abundance in Nopal I groundwater, the dominant secondary uranium phase is uranophane, a hydrated calcium uranyl silicate. Because of the abundance of calcite at Yucca Mountain, uranophane would be a potential secondary phase there as well. In comparison, laboratory experiments find that the general trend is to form mixed uranium oxides, followed by uranyl oxyhydroxides, and finally uranium silicates, mostly uranophane with lesser amounts of soddyite (Wronkiewicz et al. 1996 [102047], p. 92). In addition, uraninite at Nopal I has a low trace-element component (average of 3 wt%) that compares well with that of spent nuclear fuel (typically < 5 wt% (Pearcy et al. 1994 [100486], p. 730)). The young age of the Nopal I deposit is another similarity to Yucca Mountain with respect to the absence of Pb-bearing secondary phases.

4.4.3 Secondary Phases at Okélobondo

In the first detailed study of the Okélobondo natural fission reactor in Gabon, which corresponds to the southern extension of the Oklo deposit (Figure 4-3), Jensen and Ewing (2001 [157500]) presented a history of uraninite alteration at that site showing complex mineralogical and textural relationships. The Okélobondo reactor is the deepest of the 16 natural reactors (Figure 4-3). It is situated at the base of a 2.5 m deep synform in the FA sandstone of the Francevillian Series. The Okélobondo reactor zone (RZOKE) developed at the interface between overlying brecciated

high-grade uranium-mineralized FA sandstone and underlying bitumen-rich black shale of the FB Formation. RZOKE is relatively small (2.7 m wide and > 4 m long) and contains a ~ 55 cm thick reactor core (Jensen and Ewing 2001 [157500], p. 32).

Criticality in RZOKE was facilitated by fixation and reduction of oxidized uranium by liquid bitumen and precipitation of uraninite into a dense microfracture network in the FA sandstone. The brecciation of the host rock may have been increased by overpressure created by the accumulation of hydrocarbon gases during diagenetic maturation of oil introduced into the FA sandstone. Chemical analyses and model estimates suggest that the ore grade at criticality at RZOKE was on the order of 20 wt% uranium. Operation of the reactor caused extensive dissolution of the FA sandstone and hydrothermal alteration of the black shale of the FB Formation. The sandstone dissolution was the major process that led to formation of the 2.5 m deep reactor synform and the high uranium concentrations (≤ 90 vol% uraninite) in the core of RZOKE (Jensen and Ewing 2001 [157500], p. 59).

The mineral assemblage of RZOKE is comparable to that reported in the other Oklo reactor zones, in that uraninite and Si-rich illite are the major phases in the reactor core, while chlorite and illite are the major phases in the so-called *argile de pile* (reactor clays forming a halo around the reactor zone). Galena (PbS) is also a major phase in the reactor zone. Minor coffinite (USiO₄) and (U,Zr) silicates were also observed in addition to several accessory phases: e.g., titanium oxides, La-bearing monazite, sulfides of Cu, Fe, Co, Ni, and Zn, and ruthenium arsenides. The minor and trace elements include Th, Zr, Al, P, Ce, and Nd that seldom exceed concentrations of 0.1 oxide wt% (Jensen and Ewing 2001 [157500], p. 59). Figure 4-4 shows galena, illite, and zircon embedded in a matrix of (U,Zr)-silicate in the center of the RZOKE reactor core.

The accessory (U,Zr)-silicate, phosphates, and ruthenium arsenides (\pm Pb, Co, Ni, and S) were of particular importance in secondary retardation of the fissiogenic isotopes (Jensen and Ewing 2001 [157500], p. 59). The (U,Zr)-silicate contains elevated concentrations of ZrO₂, ThO₂, Ce₂O₃, and Nd₂O₃ as compared with the “unaltered” uraninite. This result suggests that the fissiogenic ⁹⁰Sr, Zr, Ce, and Nd, as well as the Th precursors, were efficiently retarded by the (U,Zr)-silicate during their migration in the reactor zone. Lanthanide element fission products may also have been retained in rare La-bearing monazite observed in the *argile de pile* of RZOKE. Ruthenium arsenides incorporated fissiogenic Ru, probably including ⁹⁹Ru, the radiogenic daughter of ⁹⁹Tc.

The presence of lead-uranyl sulfate hydroxide hydrate, anglesite, partial dissolution of uraninite and galena, and the rapid oxidation of pyrite are evidence of a later shift toward oxidative alteration conditions in and around the reactor zone. Hence, the slightly oxidizing deep groundwaters at Okélobondo may have already reacted with the Okélobondo reactor zone.

4.5 RADIOLYSIS

Radiolysis is hydrolysis caused by radiation and results in production of charged species (hydrogen and hydroxide ions) that may react to form more mobile species. Radiolysis can affect both the waste form and the waste package. Because the waste canister is thinner than in previous designs (CRWMS M&O 1999 [107292], Table 5-4), it is not self-shielded, so radiation levels at the outside surface of the canister would be higher. However, it is not certain that

radiolysis will be a problem. The effects of radiolysis in the Oklo ore deposit were discussed by Curtis and Gancarz (1983 [124785]). They calculated the alpha- and beta-particle doses in the critical reaction zones during criticality and the energy provided to the fluid phase by these particles. This energy caused radiolysis of water and the production of reductants (H_2) and oxidants (O_2). The effect of these reductants and oxidants on the transport of radionuclides within and outside the reactors has been difficult to quantify. Iron is most reduced in the samples that show the greatest ^{235}U depletion. Curtis and Gancarz (1983 [124785], p. 36) suggested that the reduction of iron in the reactor zones and oxidation of U (IV) in uraninite was contemporaneous with the nuclear reactions and not a later supergene phenomenon of secondary enrichment. Curtis and Gancarz (1983 [124785], p. 36) suggested that radiolysis of water resulted in the reduction of Fe (III) in the reactor zones and the oxidation of uranium. Furthermore, the authors suggested that the oxidized uranium was transported out of the critical reaction zones and precipitated through reduction processes in the host rocks immediately outside the zones. The reduction processes likely involved organics or sulfides present in the host rocks. However, if the host rocks around the natural reactor cores had not contained species capable of reducing the oxidized uranium transported out of the cores, the uranium could have been transported much further from the critical reaction zones. The important point is that, even with intensive radiolysis, very little (only several percent) of the uranium in the natural reactors was mobilized (Naudet 1978 [126123], p. 590).

Jensen and Ewing (2001 [157500], p. 59) noted a migration of Ce from reactor core to rim at Okélobondo and suggested that this resulted from radiolysis taking place during reactor operation. Cerium, particularly, showed indication of redistribution in the reactor zone, when compared with Nd, in the uraninite rim. Because Ce^{3+} can be oxidized to Ce^{4+} , the difference in the behavior of Ce as compared with Nd, results from oxidative alteration. The different concentration of Ce in the uraninite rims, as compared with their cores across the reactor zone, was produced during reactor operation, perhaps as a result of radiolysis.

4.6 CRITICALITY

The uranium deposit at Oklo, which was the site of naturally occurring neutron-induced fission reactions over 2,000 Ma, was used as a basis for reviewing conditions and scenarios that might lead to nuclear criticality within and outside waste packages in the Swedish waste disposal configuration (Oversby 1996 [100485]). The Swedish concept involves disposal in deep granite with chemically reducing groundwaters, so the specific conditions are not relevant to those of oxidizing environments. Yet in either oxidizing or reducing conditions, the combination of simultaneous factors and probabilities required for criticality to occur seems very unlikely. For criticality to occur, sufficient ^{239}Pu and/or ^{235}U would need to accumulate together with enough water to allow for moderation of neutron energies. This would achieve a state where neutron-induced fission reactions could be sustained at a rate significantly above the natural rate of spontaneous fission. The chemical and physical conditions required to achieve nuclear criticality at Oklo were used by Oversby (1996 [100485]) to estimate the amounts of spent fuel uranium that would need to be assembled in a favorable geometry in order to produce a similar reactive situation in a geologic repository. The amounts of uranium that must be transported and redeposited to reach a critical configuration are extremely large in relation to those that could be transported under any reasonably achievable conditions, even under oxidizing conditions. In addition, transport and redeposition scenarios often require opposite chemical characteristics.

Oversby (1996 [100485], p. vii) concluded that the likelihood of achieving a critical condition caused by accumulation of a critical mass of uranium outside the canisters after disposal is nil, provided that space in the canisters is filled by low solubility materials that prevent entry of sufficient water to mobilize uranium. Criticality caused by plutonium outside the canister could be ruled out because it requires a series of processes, each of which has an increasingly small probability. Criticality caused by uranium outside the canister would require dissolution and transport of uranium under oxidizing conditions and deposition of uranium under reducing conditions. There is no credible mechanism to achieve both oxidizing and reducing conditions in the near-field repository host rock in the long term, after decay of the majority of alpha-active isotopes. Thus, the conditional probabilities required to achieve criticality caused by uranium make the likelihood that criticality would occur vanishingly low.

4.7 NUCLEAR WASTE GLASS ANALOGUES

Among the natural volcanic glasses, basalt glasses are compositionally the most similar to nuclear waste glasses (Lutze et al. 1987 [125923], p. 142). However, there are still substantial compositional differences. Basalt glass and nuclear waste glass are similar in silica content, alteration products, alteration layer morphologies, and alteration rates in laboratory experiments (Grambow et al. 1986 [119228]; Arai et al. 1989 [123814]; Cowan and Ewing 1989 [124396]). Basalt glass alteration has been studied in a number of environments including ocean-floor, subglacial, hydrothermal and surface conditions (Grambow et al. 1986 [119228]; Jercinovic et al. 1986 [125289]; Byers et al. 1987 [121857]; Jercinovic and Ewing 1987 [144605]; Arai et al. 1989 [123814]; Cowan and Ewing 1989 [124396]). Inferred alteration rates, as calculated from alteration rinds, range from 0.001 μm (micrometers)/1,000 years to 30 μm /1,000 years (Arai et al. 1989 [123814], p. 73).

Malow and Ewing (1981 [126058]) compared the thermal and chemical stabilities of two borosilicate glasses and one glass ceramic to those of three rhyolitic glasses through a variety of laboratory tests and observations of natural weathering. They concluded that natural glasses are much more stable than waste-form glasses as a result of higher silica contents in the natural glasses (74% versus 28 to 50% in waste-form glasses). Tektites (nonvolcanic glass of extraterrestrial or impact origin) range in age from $\sim 10^5$ years to 35 Ma and rarely show signs of alteration, dehydration, or devitrification (Lutze et al. 1987 [125923], p. 148). Their great durability may be a result of their high silica and alumina ($\sim 30\%$) contents and their low ($<4\%$) alkali contents (Lutze et al. 1987 [125923], p. 152).

The compositions of the glasses utilized in natural analogue studies differ somewhat from borosilicate glasses, and this makes a simple analogy dubious for quantitative purposes. High silica and alumina contents, along with low alkali contents and low water contents, are favorable for long-term preservation. The dissolution rates measured on natural glasses are variable, but always very slow. However, natural analogues cannot be used to provide a quantitative estimate for the time at which devitrification will begin, or the rate at which it will proceed in the repository environment. Natural glass studies do suggest that the rate of devitrification is too slow for the process to be significant in the repository. These studies have not, however, considered the effect of radiation. It might be possible to obtain relevant data on the radiation-induced effects on glass durability by examining glasses that contain uranium oxides as colorants, such as the "vaseline glass" produced in Germany and Bohemia in the 1800s (Miller et

al. 2000 [156684], pp. 75–76). In all cases, the differences in chemistry between borosilicate glass and natural and archeological glasses need to be considered when interpreting analogue data. The qualitative evidence from analogues on natural and archeological glasses has added to confidence that the glass degradation processes are well understood and has provided upper bounding limits to the degradation rates.

4.8 SUMMARY AND CONCLUSIONS

The analogue sites located in chemically oxidizing environments are better analogues to conditions expected to occur at Yucca Mountain than the more numerous sites located in reducing environments. However, some examples from reducing environments may be appropriate analogues for processes that would occur under repository conditions in either type of chemical environment. Hence, both types of conditions were considered in studying the processes relevant to waste form degradation. From the evidence presented in this section, the main points are the following:

- The uranium alteration paragenesis sequence at Peña Blanca is a good analogue to alteration of uranium oxide spent fuel. The reaction path of alteration of spent fuel at Yucca Mountain will be similar to that of geologically young, Pb-free uraninite, with schoepite and becquerelite forming as intermediate products followed by uranyl silicates.
- Measurement of the concentration of fission products as tracers in rock and groundwater surrounding uraninite provides a satisfactory approach to estimating natural dissolution rates. This approach was tested at Cigar Lake and Koongarra under reducing and oxidizing conditions, respectively, and the dissolution rate at Koongarra was found to be more rapid. Use of the fission-product tracer method has not been reported for Oklo, but other lines of evidence indicate that dissolution has been slight under reducing conditions at Oklo over the past approximately 2 billion years. Whether deep oxidizing waters at Okélobondo have increased the dissolution of uraninite as well as created an oxidized suite of minerals is something that could be tested.
- Secondary mineral formation was responsible for incorporating uranium at Shinkolobwe, where 50 secondary uranium-bearing phases could be identified. Because of the great age of the Shinkolobwe uranium deposit, radiogenic lead-bearing phases played a role in sequestering uranium. Lead would not play a role in secondary mineralization of younger deposits, nor would it be present in spent fuel at Yucca Mountain. Other secondary phases, particularly (U,Zr) silicates, formed stable phases at Okélobondo. Presumably radiogenic lead was also present at Okélobondo, because of its approximately 2-billion-year age.
- It is uncertain whether radiolysis will be a potential problem around waste packages in the current design scenario (in which waste packages are not self-shielded). Under radiolysis conditions occurring at the time of reactor criticality at Oklo, only several percent of uranium was estimated to have been mobilized for transport from its original site, under far more extreme conditions than those anticipated at Yucca Mountain. Likewise at Okélobondo, radiolysis effects at the time of reactor operation appear to have been confined to rare earth element migration from mineral core to rim. Because liquid water in

contact with spent fuel is required for radiolysis to occur, the problem seems unlikely under either higher- or lower-temperature operating modes for a potential repository at Yucca Mountain.

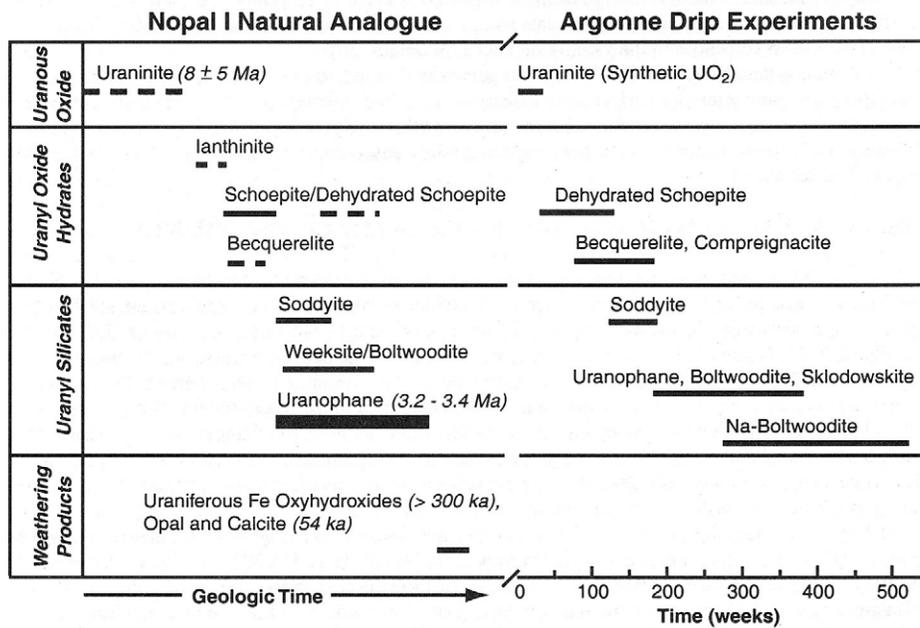
- Criticality of spent fuel can be triggered by changes in pH as well as by reducing conditions. In the study examined, however, criticality was viewed from the standpoint of redox conditions. Criticality of spent fuel, either within waste packages or by reconcentration of uranium outside of the package, has a very low likelihood, because the probability of certain processes required to achieve critical conditions occurring simultaneously or sequentially renders certain conditions mutually exclusive.
- Although natural glasses are somewhat different in composition from borosilicate nuclear waste glass, studies of natural glass alteration indicate that glass waste forms will be stable in a repository environment at Yucca Mountain. Higher stability is favored by higher silica and alumina content and by lower alkali and water content of the glass. Analogue studies have not considered radiation effects on glass over long time periods to confirm experimental results showing that radiation has little effect on glass waste stability.



NOTE: Vegetable matter in lower center is in foreground. Man standing in lower right-center for scale.

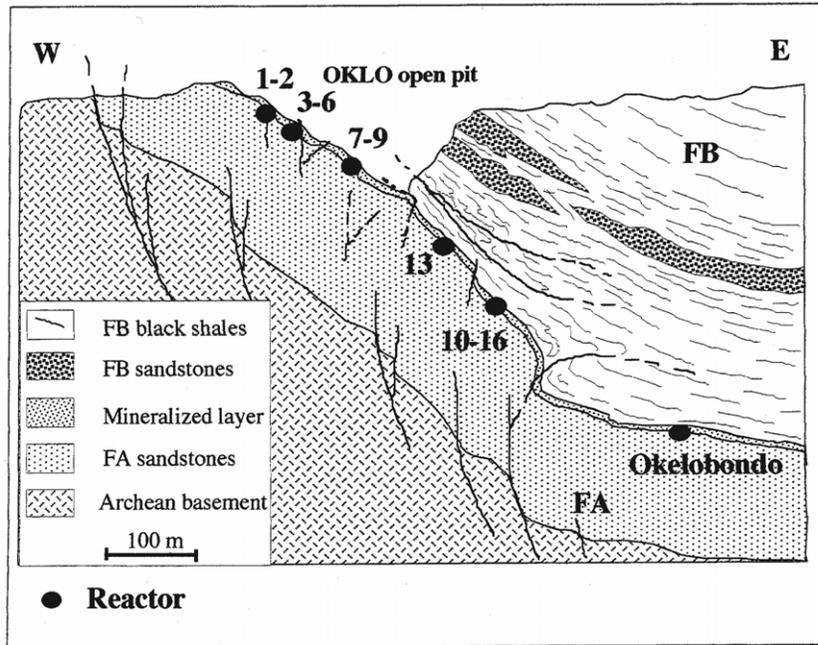
Source: Blanc 1996 [157498], p. III).

Figure 4-1. Photo of a Reactor Zone at the Oklo Natural Fission Reactor, Gabon



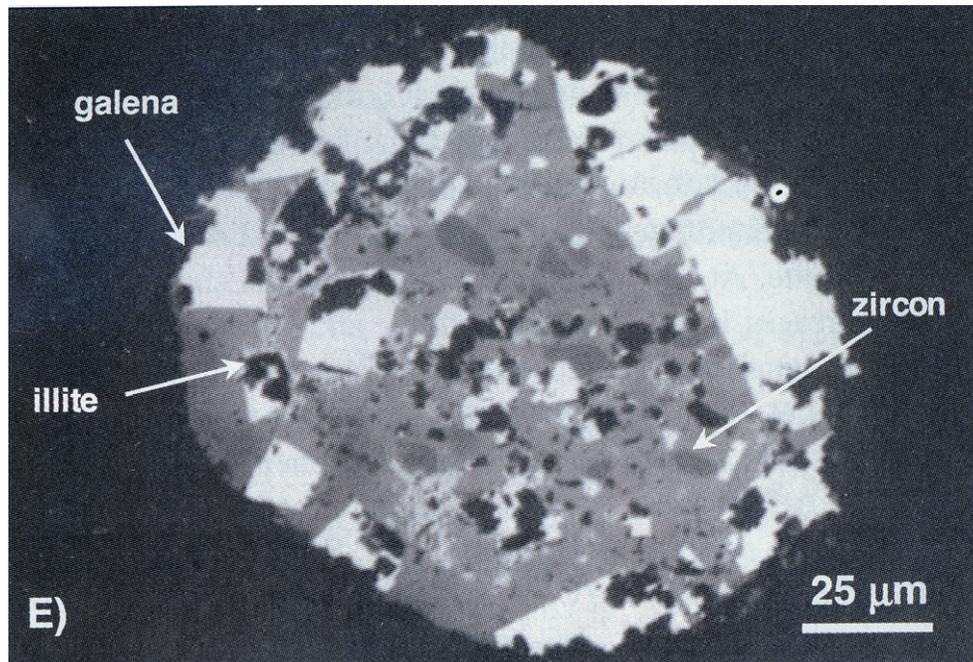
Source: Modified from Murphy 2000 [157487], Figure 1.

Figure 4-2. Sequence of Formation of Uranyl Minerals by Alteration of Uraninite



Source: Gauthier-Lafaye 1996 [157542], Figure 4.

Figure 4-3. Schematic Cross Section Showing Depth of Okélobondo Natural Fission Reactor in Relation to other Oklo Reactors



NOTE: The (U,Zr)-Silicate is the medium gray colored matrix mineral in which the other minerals are encased.

Source: Jensen and Ewing 2001 [157500], Figure 11e.

Figure 4-4. Aggregate of (U,Zr)-Silicate, Zircon, Galena, and Illite in the Center of the Okélobondo Reactor Core (RZOKE)

Table 4-1. Elemental Distribution within Uraninite, Inclusions, and Clays for Elements in the Reactor Zones at Oklo

Element	Uraninite	Inclusions	Clays	Migration
Cs				X
Rb				X
Sr				X
Ba				X
Mo		X		X
Tc		X	X	
Ru		X	X	?
Rh		X	X	?
Pd		X	X	?
Y	X		X	
Nb	?	?		
Zr	X	X	X	
Te		X		
REE	X		X	
Ce		X		
Pb	X	X		X
Bi		X		
Th	X		X	
U	X		X	
Np	?	X		
Pu	X		X	

NOTE: REE-rare earth elements

Source: Miller et al. 2000 [156684], Table 4.2 (summarized from Blanc 1996 [157498]).