Waste Forms Technology and Performance: Final Report

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Waste Forms Technology and Performance

FINAL REPORT

Committee on Waste Forms Technology and Performance

Nuclear and Radiation Studies Board
Division of Earth and Life Studies

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Preface

Nuclear waste forms are at the center of a successful strategy for the cleanup and isolation of radioactive waste from the environment. Initially, the radioactivity is entirely contained in the waste form, which is the first barrier to the release of radionuclides, making an important contribution to the performance of the disposal system. Realizing that much of its work lies ahead, the Department of Energy's Office of Environmental Management (DOE-EM) recognized the potential importance of new waste forms that could offer enhanced performance and more efficient production and requested this study by the National Research Council.

The history of nuclear waste form development and evaluation stretches back more than 30 years. During that time there have been new ideas about the types of materials that could be used; innovations in the technologies for the production of these materials; new strategies for evaluating their performance in a geologic repository; and substantial advances in the relevant fields of materials science, geochemistry, processing technologies, and computational simulations. In this report, we attempt to summarize the advances in waste form science with the parallel advances in related fields.

Several important messages emerged from this study, including the following:

- *The evaluation of waste form performance requires careful consideration of the near-field disposal environment.* Only by matching the disposal environment to a waste form material's properties can repository performance be optimized.

- *Different materials respond to their disposal environments in different ways*. “One shoe does not fit all.” One waste form may not be appropriate for all disposal environments. As an example, the optimal disposal environments for spent nuclear fuel and vitrified waste may be different.
- *There have been important advances in processing technologies, some for other industrial applications*. These new or modified technologies may find important applications in waste form production for nuclear applications.
- *It is important to recognize the limits of current modeling*. Unless the mechanisms of waste form degradation are understood, modeling results are best used for comparing options as opposed to determining quantitative values of risk.

We hope that this report stimulates renewed effort in this field and that the recommendations of the committee enable DOE-EM to progress efficiently in its remediation efforts.

Milt Levenson (Chair)
Rod Ewing (Vice Chair)

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The successful completion of this report would not have been possible without the cooperation and assistance of a large number of organizations and individuals. The committee is especially grateful to the following individuals and organizations for providing logistical support, advice, and information for this study:

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Speakers at the November 2009 Workshop of Waste Forms Technology and Performance (see Appendix B): Bruce Begg (ANSTO), Claude Degueldre (Paul Sheerer Institute), Fred Glasser (Univ. Aberdeen), Berndt Grambow (SUBATECH), David Kosson (Vanderbilt Univ.), Werner Lutze (Catholic Univ.), Rod McCullum (NEI), Ian Pegg (Catholic Univ.), Mark Peters (ANL), Kath Smith (ANSTO), Carl Steefel (LBNL), Sergey Stefanovsky (SIA Radon), Peter Swift (SNL), Etienne Vernaz (CEA), and Bill Weber (PNNL)

The committee extends special thanks to the National Research Council staff who supported the work of this committee. Study director Daniela Strickland initiated the committee's activities, made the arrangements for most of the site visits, and organized the international workshop on waste forms. Her early work for the committee shaped the content of the report. Shaunteé Whetstone handled the logistics for the committee's meetings and site visits with great skill and attention to the needs of the committee. Kevin Crowley stepped in as the study director for the second half of the study period, even as he continued as the director of the Nuclear and Radiation Studies Board. Kevin provided essential guidance to the committee and worked tirelessly to assemble the final report. Kevin's advice and questions to the committee greatly improved the content of the report, and without Kevin's extraordinary effort, the report could not have been finished in a timely manner.

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise in accordance with procedures approved by the National Research Council's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards of objectivity, evidence, and responsiveness to the study charge. The content of the review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their participation in the review of this report:

David Clarke, Harvard University
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Barry Scheetz, Pennsylvania State University

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the report's conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by Edwin Przybylowicz, Eastman Kodak Company (*retired*). Appointed by the Division on Earth and Life Studies, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the National Research Council.

Contents

Appendixes

Executive Summary

The Department of Energy's Office of Environmental Management (DOE-EM) is responsible for cleaning up radioactive waste and environmental contamination resulting from five decades of nuclear weapons production and testing. A major focus of this program involves the retrieval, processing, and immobilization of waste into stable, solid *waste forms* for disposal. This report, which was requested by DOE-EM, examines requirements for waste form technology and performance in the cleanup program. It is intended to provide information to DOE-EM to support improvements in methods for processing waste and selecting and fabricating waste forms. The complete study task is shown in Box 2.1 in Chapter 2. This report focuses on waste forms and processing technologies for high-level radioactive waste, DOE's most expensive and arguably most difficult cleanup challenge.

The following key messages emerged from this study:

- Two characteristics of waste forms govern their performance in disposal systems: (1) capacity for immobilizing radioactive or hazardous constituents and (2) durability.
- U.S. laws, regulations, and other government directives and agreements under which DOE-EM operates are not all technically based, and none establishes specific requirements for waste form performance in disposal systems. The lack of waste form-specific performance requirements gives DOE-EM flexibility in selecting waste

forms for immobilizing its waste in consultation with regulators and other stakeholders.

- Scientific and technical considerations have underpinned some DOE-EM waste form selection decisions in the past. Looking forward, DOE-EM has substantial opportunities to use advances in waste form science and technology to guide future selection decisions.
- Waste form tests are used to ensure waste form production consistency, elucidate waste form release mechanisms, and measure waste form release rates. There is a need to demonstrate the application of current tests to new waste forms if they are to be used in the DOE-EM cleanup program.
- Models of waste form performance are used to estimate the long-term (10^3-10^6 years) behavior of waste forms in the near-field environment of disposal systems. There could be significant benefits in providing more realistic safety and risk-informed analyses by improving existing models to capture the full complexity of waste form–near-field interactions.
- Opportunities exist to develop more efficient waste form production methods and new waste form materials to reduce costs, expedite schedules, and reduce risks in the DOE-EM cleanup program.
- Decisions on waste form development, testing, and selection are best made in a risk-informed systems context by considering, for example, how the waste form will be produced; what disposal environment it will be emplaced in; and how the waste form will function with other barriers in the multi-barrier disposal system to protect public health.
- There is time during the remaining decades of the cleanup program to incorporate advances in scientific understanding of waste form properties and behavior and waste form production technology to achieve significant improvements in cleanup operations. DOE-EM should enhance its capabilities for identifying, developing where appropriate, and utilizing state-of-the-art science and technology on waste forms, waste form production processes, and waste form performance.

These key messages are presented in 10 findings and 1 recommendation in the next chapter.

1

Findings and Recommendations

The task statement for this study (Box 2.1 in Chapter 2) calls on the National Academies to provide "Findings and recommendations . . . to assist DOE in making decisions for improving current methods for processing radioactive wastes and for selecting and fabricating waste forms for disposal." Findings and recommendations are provided in this chapter. Support for these findings and recommendations can be found in Chapters 2-9.

The task statement specifically enjoins the committee that carried out this study (Appendix A) from making "recommendations on applications of particular production methods or waste forms to specific EM waste streams." Although the committee has not made recommendations on specific applications, it has identified *potential opportunities* for applying waste forms and production methods to DOE-EM waste streams. The committee has focused on waste forms and production methods for high-level radioactive waste (HLW) streams because they represent the highest-cost and highest-risk waste streams in the DOE-EM cleanup program (see Chapter 2). The committee recognizes that DOE-EM decisions to adopt any of these committee-identified opportunities involve policy, regulatory, and technical considerations, the former two of which are well outside the scope of this study.

Findings to address the five study charges shown in Box 2.1 in Chapter 2 are given below and are followed by two overarching findings and one overarching recommendation.

FINDING ON STUDY CHARGE 1

Identify and describe essential characteristics of waste forms that will govern their performance within relevant disposal systems. This study will focus on disposal systems associated with high-cost waste streams such as high-level tank waste and calcine but include some consideration of low-level and transuranic waste disposal.

FINDING: Two essential characteristics of waste forms govern their performance in disposal systems: (1) capacity for immobilizing radioactive or hazardous constituents; and (2) durability.

The role of waste forms in disposal systems is discussed in Chapters 6 and 7. The primary role of a waste form is to immobilize radioactive and hazardous constituents in a stable, solid matrix for disposal. The waste form and other engineered barriers in the disposal system, if present, work in concert to isolate the waste. The near-field environment[1] of the disposal system establishes the physical and chemical bounds within which the waste form performs its sequestering function.

The capacity of a waste form for immobilizing radioactive and hazardous constituents depends on intrinsic properties of the material, as discussed in Chapter 3. Some materials have the capacity to chemically incorporate radioactive and hazardous constituents at atomic scales. Other materials have the capacity to encapsulate constituents by physically surrounding and isolating them.

Durability is a measure of the physical and chemical resistance of a waste form material to alteration and the associated release of contained radioactive and hazardous constituents. The durability of a waste form material depends on its intrinsic properties as well as the physical and chemical conditions in the disposal facility into which it is emplaced. Waste forms perform optimally in a disposal environment when they are matched with the appropriate physical and chemical conditions that foster long-term stability. An important implication of this fact is that the suitability of a waste form for disposal depends crucially on the characteristics of the disposal facility into which it will be emplaced.

FINDING ON STUDY CHARGE 2

Identify and describe the scientific, technical, regulatory, and legal factors that underpin requirements for waste form performance.

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[1] The *near-field environment* is generally taken to include the engineered barriers in a disposal facility (e.g., waste canisters) as well as the host geologic media in contact with or near these barriers whose properties have been affected by the presence of the facility.

> **FINDING ON REGULATORY AND LEGAL FACTORS: U.S. laws, regulations, and other government directives and agreements under which DOE-EM operates are not all based on technical factors, and none establishes specific requirements for waste form performance in disposal systems. Performance requirements have been established for disposal systems as a whole to meet human health-protection standards; however, waste forms are just one of several engineered barriers in such systems and do not have any subsystem performance requirements. The lack of waste form-specific performance requirements gives DOE-EM flexibility in selecting waste forms for immobilization and disposal of waste in consultation with regulators and other agreement stakeholders.**

Regulatory and legal requirements are described in Chapter 8. There are well-established regulatory requirements for assessing the long-term performance of disposal systems to meet human health-protection standards; for example, DOE Order G 430.5 for disposal of low-level radioactive waste; Title 40 Part 191 of the Code of Federal Regulations for disposal of defense transuranic waste in the Waste Isolation Pilot Plant in New Mexico; and Title 10 Part 63 of the Code of Federal Regulations for disposal of spent nuclear fuel and HLW at Yucca Mountain, Nevada. Not all of these requirements have a technical basis, and none establishes specific requirements for waste form performance.

There are also established technical criteria for waste acceptance in current and planned disposal facilities; for example, the Waste Acceptance System Requirements Document (WASRD) for HLW and spent nuclear fuel managed by DOE's Office of Civilian Radioactive Waste Management.[2] Some of these criteria establish requirements for specific characteristics of the waste form in terms of physical or chemical characteristics, but they do not establish requirements for waste form performance.

DOE has signed agreements with two states (Washington and South Carolina) that specify the types of waste forms that will be used for immobilizing the low-activity waste (LAW) fraction of HLW at those sites: Saltstone for LAW immobilization at the Savannah River Site and borosilicate glass, or another waste form that is "as good as glass" (see Sidebar 8.1 in Chapter 8), for immobilizing LAW that will be produced in the Waste Treatment Plant at the Hanford Site. DOE has also selected waste forms for immobilizing sodium-bearing waste and HLW calcine at the Idaho Site.

The lack of waste form performance requirements gives DOE flexibility in selecting waste forms for immobilization and disposal of waste in con-

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[2] This office was being subsumed into DOE's Office of Nuclear Energy when the present report was being finalized.

sultation with its regulators and other Agreement stakeholders. Moreover, the ability of DOE to modify its Agreements (again in consultation with its regulators and stakeholders) is evident from the numerous past modifications to reflect scope and schedule changes. The established flexibility in such Agreements provides DOE-EM with the opportunity to pursue optimization of its overall waste management system, including the consideration of new waste forms and processing methods to reduce costs and risks and increase efficiencies. Of course, such alterations have to be supported by scientifically sound analyses.

The Resource Conservation and Recovery Act (RCRA) requirements for disposal of hazardous waste, which DOE has agreed to follow under Order 5400.1, could reduce DOE-EM's flexibility to pursue optimization of its overall waste management system, especially for disposal of Hanford HLW/LAW and Idaho HLW. Vitrified HLW from Savannah River and West Valley currently qualify for disposal because they meet the Environmental Protection Agency's (EPA's) Best Demonstrated Available Technology (BDAT) requirements. However, it is not clear whether immobilized Hanford HLW/LAW and Idaho HLW would also satisfy RCRA requirements under a BDAT rationale. DOE-EM will need to consult with its regulators (EPA and states hosting the disposal facilities for these waste streams) to clarify this issue.

> **FINDING ON SCIENTIFIC AND TECHNICAL FACTORS: Scientific and technical considerations have underpinned some waste form selection decisions in the past. Looking forward, DOE-EM has substantial opportunities to use advances that have occurred in waste form science and technology because these original decisions were made to guide future waste form selection decisions.**

Scientific and technical requirements for waste form performance are described in Chapters 5 and 8. Borosilicate glass was selected for immobilization of defense HLW in the 1980s based on the industrial simplicity of the process, extensive experience in Europe, adequate waste loading, acceptable processing rates processing costs, durability, and a number of other factors. It was judged that borosilicate glass would provide acceptable performance in any of the several geologically diverse repository host rocks (salt, basalt, granite, tuff, and clay) then under consideration (see Section 8.3.3 in Chapter 8).

Advances in science and technology can inform future waste form selection decisions that could reduce costs, expedite schedules, reduce risks, and improve stakeholder acceptance. The absence of specific waste form performance requirements means that a risk-informed, adaptive repository program should readily accommodate new waste forms through the iterative process of modifying the repository design and updating performance assessment, as discussed in Chapter 7.

Reliance on solubility controls on the release of radionuclides, independent of the waste form, could also aid in evaluating strategies for the future development of advanced waste forms. As an example, a radionuclide released from a glass might arrive at a low concentration because of the low solubility product of secondary phases. This is often the case for actinides. In this case, it does not matter what the waste form is (assuming that it meets other waste acceptance criteria) because the concentrations in solution are controlled by secondary phases. In the case where the calculated releases from a disposal system meet safety criteria because of radioelement solubility limits, then the motivation for developing advanced waste forms would be based more on factors such as waste loading and ease of processing rather than durability.

FINDING ON STUDY CHARGE 3

Identify and describe state-of-the-art tests and models of waste forms used to predict their performance for time periods appropriate to their disposal system.

FINDING ON TESTS: Waste form tests are used for three purposes: (1) to ensure waste form production consistency; (2) to elucidate waste form release mechanisms; and (3) to measure waste form release rates under a range of conditions. Information on release mechanisms and rates can be used to model waste form behavior in near-field environments over time scales of interest for disposal (10^3-10^6 years). Tests have been developed and qualified for some waste form materials. There is a need to demonstrate the application of current tests to new waste forms if they are to be used in the DOE-EM cleanup program.

Waste form tests have several purposes, as discussed in Chapter 5. Tests can be used to identify ranges of processing variables that result in acceptable waste forms (production consistency testing). Tests, combined with experimental studies, can also be used to determine mechanisms of release of radioactive and hazardous constituents from waste form materials over short (days to months) time scales. Once release mechanisms are determined, tests can be used to measure waste form release rates over short time scales. The release mechanisms and rates can be used in modeling studies to estimate long-term (10^3-10^6 year) waste form performance in specific disposal environments.

A suite of waste form tests have been developed; these are described in Chapter 5. These tests are material-specific, and no single test can be used to elucidate waste form durability in a given material. Tests to determine release behavior and measure release rates have been developed and qualified for borosilicate glass, glass-ceramic, and some crystalline ceramic materials. However, these tests have not been qualified for some other classes of waste form materials, including non-silicate glasses, hydroceramics, and geopolymers. Additional work will be needed to determine the suitability of existing tests for these materials if DOE-EM intends to use them in its cleanup program.

> **FINDING ON MODELS: Models of waste form performance are used to estimate the long-term (10^3-10^6 years) behavior of waste forms in the near-field environment of disposal systems. There is a need to improve these models to capture the full complexity of waste form–near-field interactions.**

Models of waste form and disposal system performance are described in Chapter 7. Models can be useful for predicting waste form performance in disposal systems when they are based on an adequate scientific understanding of waste form–near-field interactions and reactive transport in those systems. Most critically, valid estimates of waste form performance cannot be made in the absence of knowledge about the near-field environment of the disposal system.

Many of the current models that are being used in the United States to model waste form behavior in disposal systems are based on ad hoc simplifications specific to the proposed repository at Yucca Mountain, Nevada. Other national programs have developed a substantial capability for modeling the long-term behavior of some types of waste forms based on fundamental principles; for example, the GLAMOR program in Europe is a cooperative effort of several researchers, including researchers from the United States, to elucidate the mechanisms controlling long-term durability of vitrified high-level waste.

U.S. regulations have adopted risk-based health standards for assessing the long-term safety of geological disposal using performance assessment (PA) models. PA modeling of waste forms containing radioactive waste can only be meaningfully accomplished within the context of PA modeling of the entire waste disposal system, in which health-risk consequences are the appropriate basis for evaluations. There could be significant benefits in providing more realistic and risk-informed safety analyses by improving these models to capture the full complexity of waste form–near-field interactions, including the durability of waste forms as well as waste form interactions with other engineered and natural barriers in the near-field environment.

Additional R&D on waste form–near-field interactions and reactive transport would likely improve quantitative modeling capabilities for estimating long-term waste form performance in different disposal environments. Having such an improved modeling capability could allow DOE-EM to take credit for waste form performance in future disposal system performance assessments. In addition, study of relevant natural analogue materials, where available, could also provide additional lines of evidence and arguments to increase confidence in waste form performance over 10^3-10^6 year time scales.

FINDING ON STUDY CHARGE 4

Identify and describe potential modifications of waste form production methods that may lead to more efficient production of waste forms that meet their performance requirements.

FINDING: Opportunities exist to adapt more efficient waste form production methods to DOE-EM waste streams to reduce costs, expedite schedules, and reduce risks.

Waste form production methods are described in the committee's interim report (see Appendix C) and in Chapter 4 of this report. The committee identified three opportunities for more efficient production of waste forms in its interim report:

- Fluidized bed steam reforming for conditioning waste feed streams and processing HLW and associated waste streams.
- Cold crucible induction melters as substitutes for Joule-heated melters for processing HLW and LAW.
- Hot isostatic pressing for processing waste streams that are difficult or inefficient to process by other methods.

These identified opportunities are just examples; there are probably many other good ideas that have not yet been investigated.

Chapter 4 of this report provides a more complete discussion of processing technologies and their potential applicability to DOE-EM waste streams. Chapter 9 describes some recent advances in computational science and recently emerging tools in computational fluid dynamics that have applicability in the DOE-EM cleanup program.

FINDING ON STUDY CHARGE 5

Identify and describe potential new waste forms that may offer enhanced performance or lead to more efficient production.

FINDING: Opportunities exist to develop new waste forms for immobilizing DOE-EM waste streams to reduce costs, expedite schedules, and reduce risks.

As discussed in Chapter 3, there are a wide range of waste form materials that could potentially be used in the DOE-EM cleanup program: single-phase (homogeneous) glasses, glass-ceramic materials, crystalline ceramics, metals, cements, geopolymers, hydroceramics, and ceramicretes. The baseline technology for immobilization of HLW in the cleanup program is single-phase borosilicate glass. Other waste form materials are potentially suitable for HLW immobilization:

- Other types of glass (e.g., iron phosphate glass) might be useful for immobilizing waste streams with constituents that are sparingly soluble or chemically incompatible with borosilicate glasses (e.g., phosphate and sulfate).
- Crystalline ceramic waste forms produced by fluidized bed steam reforming have good radionuclide retention properties and waste loadings comparable to, or greater than, borosilicate glass. This waste form material is also potentially useful for immobilizing LAW.

Examples of other opportunities are identified in Chapter 9 of this report for immobilizing actinides and/or fission products in

- Glass-ceramic materials
- Crystalline ceramics (e.g., pyrochlore, murataite, garnet, and apatite)
- Metal-organic frameworks
- Mesoporous materials

Additional research and development work will be required to apply these materials in the DOE-EM cleanup program.

No single waste form is suitable for all EM waste streams or suitable for all disposal environments. Consequently, DOE-EM would benefit from having a “toolbox” of waste forms available for different waste streams and disposal environments. However, compatibility of the waste form with its intended disposal environment is not the only important consideration when making a selection decision, as explained in the following overarching finding.

OVERARCHING FINDINGS AND RECOMMENDATION

OVERARCHING FINDING 1: Waste forms are a central component of the DOE-EM waste management system whose ultimate goal is

to protect public health. Consequently, waste form development and selection decisions are best made in a risk-informed systems context by considering, for example: how the waste form will be produced; what disposal environment it will be emplaced in; and how the waste form will function with other barriers in the multi-barrier disposal system to protect public health.

DOE-EM asked the National Academies to examine "requirements for waste form technology and performance in the context of the disposal system in which the waste form will be emplaced" (see Box 2.1 in Chapter 2). The phrase "in the context of the disposal system in which the waste form will be emplaced" explicitly recognizes that waste form requirements do not exist in isolation of the overall DOE-EM waste management system (Figure 7.1). Consequently, decisions on waste form development and selection are best made in a systems context. Additionally, because the ultimate goal of disposal is to protect public health, such development and selection decisions are best made (to the extent practical) on public health risk considerations.

To illustrate this point, consider the selection of a waste form for immobilizing HLW containing technetium-99. As noted in Chapter 6, technetium-99 is soluble in groundwater under oxidizing conditions and can therefore be mobile in the environment. Consequently, an important consideration in selecting a waste form for immobilizing HLW is its capacity to sequester technetium-99, for example by chemical incorporation (Chapter 3), to reduce the mobility of this radionuclide after disposal. However, there are other systems considerations that are equally important in this selection decision, for example:

- *Is the process for making the waste form compatible with the waste stream?* One might select a durable waste form such as borosilicate glass for immobilizing a HLW stream. However, the process for making glass (vitrification) can drive technetium and other volatile radionuclides into off-gas streams, which creates secondary waste that can be difficult to manage.
- *Is the waste form suitable for its intended disposal environment?* As noted in Chapter 6, the long-term durability of a waste form depends on the physical and chemical conditions in the disposal environment in which it is emplaced. Borosilicate glass waste forms are durable in many, but certainly not all, disposal environments. Disposal of borosilicate glass in an environment that is undersaturated in silica, for instance, could result in accelerated degradation and release of technetium-99.
- *Will the waste form function with other barriers in the disposal facility to protect public health?* As discussed in Chapter 6, the

> waste form is not the only barrier to release of radioactive and hazardous constituents from a disposal facility. Such facilities typically have a number of other engineered and natural barriers that could delay and/or attenuate releases. Determining the public health risks of such releases requires a careful assessment of repository performance.

This example illustrates the importance of understanding the interactions among the various elements of the waste management system when making waste form selection decisions. Critical factors can be overlooked, and suboptimal decisions can be made, when waste form selections are considered in isolation of other system components.

OVERARCHING FINDING 2: Because the currently scheduled DOE-EM cleanup program will not be completed for several decades, there is time to advance and apply scientific understanding of waste form properties and behavior. Materials, processing technologies, and computational methods are under constant development; these developments could lead to improvements in current DOE-EM cleanup operations as well as new and innovative applications in future cleanup and nuclear fuel cycle programs.

As the committee observed in its interim report (see Appendix C), the DOE-EM cleanup program is successfully processing waste and producing waste forms at several sites (see also Chapter 2 of this report). For example, DOE-EM has completed HLW immobilization at the West Valley site, but residual liquid and sludge heels remain in the tanks. DOE-EM is also retrieving HLW from tanks at the Savannah River Site, separating it into high-activity waste (HAW) and LAW streams, and processing these waste streams into HLW glass for disposal in a future geologic repository and LAW Saltstone for near-surface onsite disposal. DOE-EM is also building facilities to process and immobilize HLW at the Hanford Site in Washington.

As the cleanup program continues DOE-EM will have opportunities to incorporate emerging developments in science and technology on waste forms and waste form production technologies into its baseline approaches. As noted in Chapters 3, 4, and 9, waste form-relevant science and technology are advancing rapidly along several fronts—for example, materials science research and development, chemical and materials processing in industry, waste management in advanced nuclear fuel cycle programs, and management of special nuclear materials in national security applications. These advances could lead to the development of

- Waste form materials designed for higher waste loadings or for improved performance in specific disposal environments.
- Waste processing technologies that can handle large volumes of highly radioactive wastes, operate at high throughputs, and/or produce high-quality waste forms.
- Advanced analytical and computational techniques that can be used to understand and quantitatively model interactions between waste forms and near-field environments of disposal facilities.

The committee's interim report (see Appendix C) and this final report provide only snapshots of these advances.

Computational techniques for materials discovery and design have longer-term applications in the DOE-EM cleanup program. Computational simulations can be used to investigate new waste form compositions or structure types and to focus experimental efforts on critical chemical systems and conditions.

Incorporating new science and technology need not (and should not) halt the progress that is currently being made in the cleanup program. In fact, if done wisely, the incorporation of new science and technology can improve the cleanup program by increasing efficiencies, reducing lifecycle costs and risks, and advancing scientific understanding of and stakeholder confidence in waste form behavior in different disposal environments. In short, scientific advances, both now and in the future, offer the potential for more effective solutions to DOE-EM's waste management challenges.

> **OVERARCHING RECOMMENDATION: DOE-EM should enhance its capabilities for identifying, developing where appropriate, and utilizing state-of-the-art science and technology on waste forms, waste form production processes, and waste form performance.**

To take full advantage of future scientific and technological advances, DOE-EM will need to identify, develop where needed, and incorporate where appropriate state-of-the-art science and technology on waste forms, waste form production processes, and waste form performance. This will require:

- Active engagement with governmental, academic, and industrial organizations that are researching, developing, and implementing these technologies.
- Development and/or expansion of intellectual capital, both within DOE-EM and in external contractor staff, to identify and transfer this knowledge and technology into the cleanup program.
- Appropriate resources to support these capabilities.

Such engagement can take a variety of forms: For example, DOE-EM could collaborate or partner with the DOE Office of Science and Office of Nuclear Energy to identify and, where appropriate, fill knowledge gaps on waste forms, waste form production, and waste form performance.[3] International organizations and large-scale chemical processing industries are also potentially rich sources of information. DOE-EM is already engaging with other organizations for some of its technology development needs: Examples include the development of fluidized bed steam reforming and cold crucible induction melter technologies, which are discussed in Chapter 4. With carefully targeted investments, the costs of establishing and maintaining such collaborations need not be high.

As discussed in Chapter 8, DOE-EM is operating its cleanup program under various and sometimes conflicting regulatory requirements and legal agreements with states and the U.S. Environmental Protection Agency. Modifications of existing requirements or agreements might be necessary before DOE-EM can implement the technologies identified in this report. However, it is outside of the committee's task to consider how the use of the technologies identified in this report might impact those requirements and agreements.

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[3] The Office of Science, for example, sponsors research needs workshops that are relevant to EM needs (see http://www.er.doe.gov/bes/reports/files/brn_workshops.pdf and http://www.er.doe.gov/bes/reports/list.html). The Office of Nuclear Energy sponsors a fuel cycle R&D program. See http://www.ne.doe.gov/fuelcycle/neFuelCycle.html.

2

Background and Study Task

The Department of Energy's Office of Environmental Management (DOE-EM) is responsible for cleaning up radioactive waste and environmental contamination resulting from five decades of nuclear weapons production and testing. The cleanup program is arguably the largest such effort in the world, encompassing some 2 million acres at more than 100 sites across the United States (Figure 2.1). The program was initiated about two decades ago and is scheduled to last for another four to five decades (Figure 2.2).

A major focus of this program involves the retrieval and processing of stored waste to reduce its volume and incorporation of this waste into suitable *waste forms* to facilitate safe handling and disposal. This report, which was requested by DOE-EM, examines requirements for waste form technology and performance in the DOE-EM cleanup program. It is intended to provide information to DOE-EM to support improvements in methods for processing waste and selecting and fabricating waste forms for disposal. The complete study task is shown in Box 2.1.

The DOE-EM cleanup program is successfully processing waste and producing waste forms at several sites. However, as discussed in Section 2.2, the cleanup program is planned to last for several decades and cost several hundreds of billions of dollars. DOE-EM recognizes that during the remaining decades of this program there will be opportunities to incorporate emerging developments in science and technology on waste forms, waste form production technologies, and waste form/disposal system modeling. Incorporating new science and technology could lead to increased program

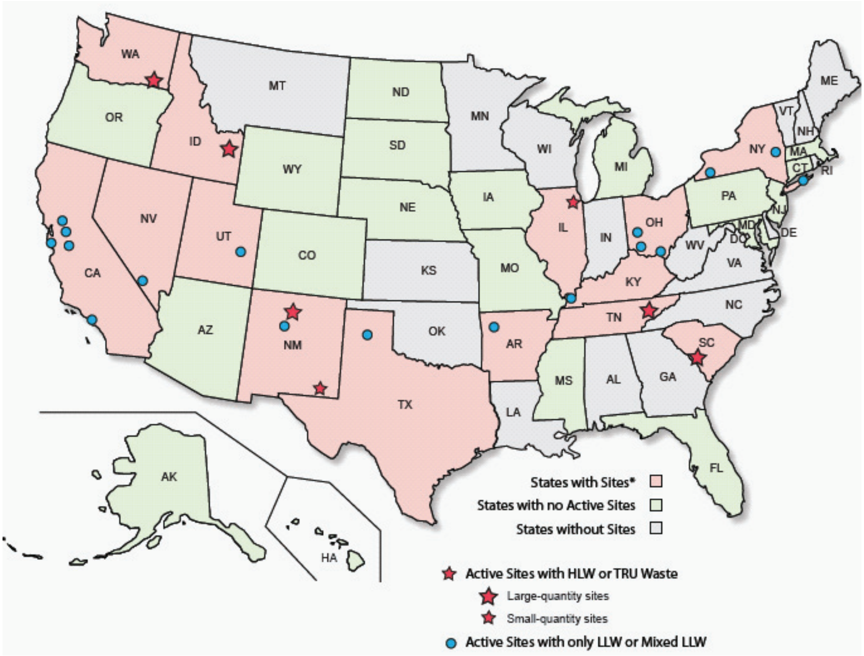

FIGURE 2.1 Locations of current sites in the DOE-EM cleanup program. Sites labeled as *active* have ongoing cleanup projects involving high-level waste/transuranic waste or low-level waste/mixed low-level waste.
SOURCE: DOE-EM: http://www.em.doe.gov/pages/siteslocations.aspx. Last accessed March 7, 2010.

efficiencies, reduced lifecycle costs and risks, and advanced scientific understanding of, and stakeholder confidence in, waste form behavior in different disposal environments (NRC, 2010).

2.1 BACKGROUND ON WASTE FORMS

The term *waste form* is defined by the International Atomic Energy Agency (2003) as waste in its physical and chemical form after treatment and/or conditioning (resulting in a solid product) prior to packaging. The term is defined by the American Society for Testing and Materials (ASTM) standards[1] and in federal regulations[2] as a radioactive waste material and

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[1] For example, ASTM C-1174, C-1454, and C-1571; see Chapter 5.

[2] Title 10, Part 60 of the Code of Federal Regulations, Disposal of High-Level Radioactive Wastes in Geologic Repositories; see Part 60.2.

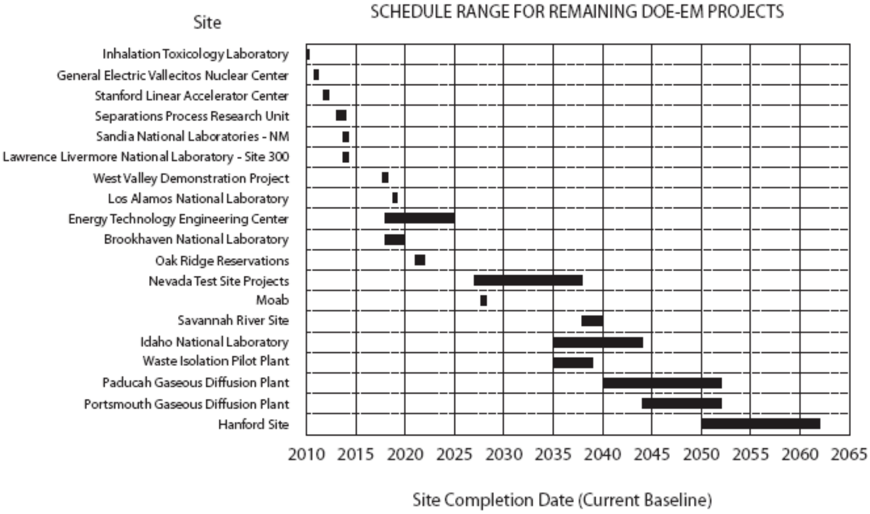

FIGURE 2.2 Projected dates for completion of DOE-EM site cleanup. This schedule does not reflect accelerated cleanup schedules resulting from work funded by the 2009 American Recovery and Reinvestment Act.
SOURCE: Data from the DOE FY 2011 Congressional Budget Request. Available at http://www.mbe.doe.gov/budget/11budget/Content/Volume%205.pdf. Last accessed on August 25, 2010.

any encapsulating or stabilizing matrix in which it is incorporated. A wide range of materials are potentially usable as waste forms; these include amorphous materials (e.g., glass), crystalline materials (e.g., ceramics, mineral analogues, metals, cements), or a combination of amorphous and crystalline materials (e.g., glass-ceramic materials). These materials are described in some detail in Chapter 3.

The solidification, embedding, or encapsulation of radioactive and chemically hazardous waste to create a waste form is referred to as *immobilization*. Radioactive and chemically hazardous constituents in the waste can be immobilized into a waste form material through two processes: Constituents can be (1) bound into the material at atomic scale (*chemical incorporation*) or (2) physically surrounded and isolated by the material (*encapsulation*). Some waste form materials can perform both functions. Additional discussion of immobilization mechanisms is provided in Chapter 3.

Several factors must be considered when selecting a waste form material for immobilizing a specific waste stream. The key considerations include the following:

BOX 2.1
Statement of Task

The National Academies will examine the requirements for waste form technology and performance in the context of the disposal system in which the waste form will be emplaced. Findings and recommendations will be developed to assist DOE in making decisions for improving current methods for processing radioactive wastes and for selecting and fabricating waste forms for disposal. The study will identify and describe:

- Essential characteristics of waste forms that will govern their performance within relevant disposal systems. This study will focus on disposal systems associated with high-cost waste streams such as high-level tank waste and calcine but include some consideration of low-level and transuranic waste disposal.
- Scientific, technical, regulatory, and legal factors that underpin requirements for waste form performance.
- The state-of-the-art tests and models of waste forms used to predict their performance for time periods appropriate to their disposal system.
- Potential modifications of waste form production methods that may lead to more efficient production of waste forms that meet their performance requirements.
- Potential new waste forms that may offer enhanced performance or lead to more efficient production.

The committee will not make recommendations on applications of particular production methods or waste forms to specific EM waste streams.

- *Waste loading*: The waste form must be able to accommodate a significant amount of waste (typically 25-45 weight percent) to minimize volume, thereby minimizing the space needed for disposal.
- *Ease of production*: Fabrication of the waste form should be accomplished under reasonable conditions, including low temperatures and, ideally, in an air atmosphere, using well-established methods to minimize worker dose and the capital cost of plant.
- *Durability:* The waste form should have a low rate of dissolution when in contact with water to minimize the release of radioactive and chemical constituents.
- *Radiation stability*: The waste form should have a high tolerance to radiation effects from the decay of radioactive constituents. Depend-

ing on the types of constituents being immobilized, the waste form could be subjected to a range of radiation effects, including ballistic effects from alpha decay and ionizing effects from decay of fission product elements.

- *Chemical flexibility:* The waste form should be able to accommodate a mixture of radioactive and chemical constituents with minimum formation of secondary phases that can compromise its durability.
- *Availability of natural analogues:* Because direct laboratory testing of the waste forms over the relevant time scales for disposal (typically 10^3-10^6 years for DOE-managed wastes) is not possible, the availability of natural mineral or glass analogues may provide important clues about the long-term performance of the material in the natural environment, thereby building confidence in the extrapolated behavior of the waste form after disposal.
- *Compatibility with the intended disposal environment:* The waste form should be compatible with the near-field environment[3] of the disposal facility. The near-field environment provides the physical and chemical conditions that are favorable for maintaining waste form integrity over extended periods, which helps to slow the release of constituents and their transport out of the facility.

2.2 BACKGROUND ON DOE-EM WASTE STREAMS

The production of nuclear materials for the U.S. defense program began during the Manhattan Project in World War II and continued through the end of the Cold War.[4] A large number of processes were used to produce nuclear materials. These included isotope enrichment and separation; fuel and target fabrication, dissolution, and chemical separation; and casting, machining, and plating. The wastes generated by these operations ranged from slightly contaminated trash to highly radioactive and chemically toxic liquids. These wastes were managed using practices analogous to those for other process industries of the era, including disposal of solid waste in landfills, disposal of liquid wastes in ponds and through underground injection, and temporary storage. Some highly radioactive liquid wastes have been in temporary storage at DOE sites for more than six decades.

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[3] The near-field environment is generally taken to include the engineered barriers in a disposal system (e.g., waste canisters) as well as the host geologic media in contact with or near these barriers whose properties have been affected by the presence of the repository. The far-field environment is generally taken to include areas beyond the near field, including the biosphere (e.g., OECD-NEA, 2003).

[4] The Cold War ended in 1991 with the breakup of the Soviet Union.

Information about these processes and waste streams are available from a variety of sources, including DOE reports (e.g., DOE, 1995, 1997, 1998), reports by other federal agencies (e.g., OTA, 1991a,b), reports from national laboratories (Gephart, 2003), and reports from the National Academies (e.g., NRC, 2001a,b,c, 2002a,b, 2003, 2006). DOE-EM maintains an online database, the Central Internet Database[5] (CID), which contains information on spent fuel, radioactive waste, facilities, and contaminated media being managed at current and former production facilities.

The principal waste streams that are being managed by DOE-EM are shown in Table 2.1.[6] As can be seen in this table, the volumes of waste being managed are varied and substantial, although it is important to note that not all waste has been well characterized or inventoried. As can also be seen in this table, some waste form and disposition decisions have not yet been made, particularly for orphan[7] waste streams.

DOE-EM's current strategies for treatment and disposition of these waste streams can be summarized as follows (see Box 2.2 for definitions of waste types):

- Spent nuclear fuel (SNF) is being consolidated at the Hanford Site (Washington), Idaho Site, and Savannah River Site (South Carolina). Most SNF will be dried and stored in canisters suitable for deep disposal in a Federal repository. Some SNF at the Idaho and Savannah River Sites is being stabilized by melting (Savannah River) or metallurgical processing (Idaho).
- High-level radioactive waste (HLW) at West Valley, New York, has been immobilized in borosilicate glass for eventual disposal in a Federal repository. However, residual liquid and sludge heels remain in the tanks.
- HLW in the form of sludge, precipitated salt, and liquid is currently stored in tanks at the Hanford and Savannah River Sites. At Savannah River, this waste is being retrieved and separated into two process streams: A high-activity stream that is being immobilized in a borosilicate glass waste form for deep disposal in a Federal repository, and a low-activity stream that is being immobilized in a cement waste form (Saltstone) for shallow disposal onsite.

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[5] The CID is available at http://cid.em.doe.gov/Pages/CIDHome.aspx. Last accessed on August 25, 2010.

[6] DOE-EM is responsible for cleanup of legacy wastes (including surplus facilities) that have been transferred into the cleanup program. There are a large number of facilities in the DOE complex that will continue to operate for decades and generate new wastes. Those facilities and wastes are not currently part of the cleanup program, but they could be transferred into that program in the future.

[7] A waste stream is referred to as *orphan* when it has no clear-cut disposition pathway.

TABLE 2.1 Principal Waste Streams, Waste Forms, and Disposition Pathways for the DOE-EM Cleanup Program

Waste Stream	**Approximate Quantities**	**Current Principal Waste Forms**[a]	**Likely Disposition Pathways**
Spent nuclear fuel	2,400 MTHM	As is[b]	Deep disposal (Federal repository)
High-level waste			
Tank waste	340,000 m^3	HAW: Glass LAW: Grout, glass, other	HAW: Deep disposal (Federal repository) LAW: Shallow disposal
Bin waste	4,400 m^3	Glass-ceramic	Deep disposal (Federal repository)
Transuranic waste	164,000 m^3	As is[c]	Deep disposal (WIPP)
Low-level waste (including mixed LLW)	1,400,000 m^3	LLW: As is[d] Mixed LLW: Grout, other[e]	Shallow disposal
Mill tailings (byproduct waste)	> 2 million m^3	As is	Shallow disposal
Depleted uranium	737,000 MT	Uranium oxide	Shallow disposal
Plutonium and uranium residues	108 MT	MOX fuel Glass	Deep disposal (Federal repository)
Excess facilities[f]	5,200	As is for decommissioning waste	Shallow disposal for LLW; WIPP for TRU waste
Orphan waste streams			
Cs and Sr capsules	5 m^3	TBD[g]	TBD
Other	various	TBD	TBD

NOTES: HAW = high-activity waste; LAW = low-activity waste; LLW = low-level radioactive waste; MT = metric tonnes; MTHM = metric tonnes of heavy metal; TBD = to be determined; TRU = transuranic; WIPP = Waste Isolation Pilot Plant.

[a] The entry "As is" indicates that the waste will be disposed of in its current form, although it may be conditioned (e.g., dried, sorted, volume reduced, and/or packaged) prior to disposal.

[b] Small quantities of SNF at Savannah River and Idaho are also being reprocessed.

[c] Liquid sodium-bearing waste at the Idaho Site will be steam reformed.

[d] Some LLW may require treatment and immobilization prior to disposal.

[e] See NRC (1999).

[f] Includes nuclear, radiological, and industrial facilities.

[g] The Draft Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington (DOE/EIS-0391, October 2009) identifies treatment alternatives that involve the retrieval of cesium and strontium from the capsules for treatment in the Waste Treatment Plant.

SOURCES: Quantity data: Mill tailings: DOE, 2001; Other: Department of Energy FY 2011 Congressional Budget Request; ROO, 2002.

BOX 2.2
Types of Waste Materials in the DOE Inventory

The following terms are used in this report to refer to the materials that are being managed by the DOE cleanup program:

Spent nuclear fuel (SNF) is defined by the Nuclear Waste Policy Act (2 U.S.C. §10101 et seq., 1982) "as fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing." In the United States, SNF is not a waste material unless declared to be one.

High-level radioactive waste (HLW) is defined by the Nuclear Waste Policy Act as the highly radioactive waste material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and other highly radioactive material that the Nuclear Regulatory Commission, consistent with existing law, determines by rule to require permanent isolation.

Low-level radioactive waste (LLW) is defined in the Nuclear Waste Policy Act as radioactive material that is not high-level radioactive waste, spent nuclear fuel, transuranic waste, or 11(e)(2) byproduct material (mill tailings) that the Nuclear Regulatory Commission, consistent with existing law, classifies as low-level radioactive waste.

Hazardous waste is defined by the EPA in Title 40 of the Code of Federal Regulations, Parts 260 and 261. This waste is toxic or otherwise hazardous because of its chemical properties. Waste can be designated as hazardous in any of three ways: (1) It contains one or more of more than 700 materials listed as hazardous by the EPA; (2) it exhibits one or more hazardous characteristics, which include ignitability, corrosivity, chemical reactivity, or toxicity; or (3) it arises from treating waste already designated as hazardous.

Mixed low-level waste (MLLW) meets the above definitions of both low-level waste and hazardous waste and is therefore subject to dual regulations.

Transuranic (TRU) *waste* is defined in Title 40, Part 191 (Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes) as waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, with half-lives greater than twenty years, per gram of waste, except for: (1) High-level radioactive wastes; (2) wastes that the Department [of Energy] has determined, with the concurrence of the [EPA] Administrator, do not need the degree of isolation required by this part; or (3) wastes that the [Nuclear Regulatory] Commission has approved for disposal on a case-by-case basis in accordance with Title 10, Part 61 of the Code of Federal Regulations.

Mixed transuranic (MTRU) *waste* meets the definitions of both transuranic and hazardous wastes.

Other wastes being managed by DOE include *special nuclear materials* (uranium and plutonium), *source materials* such as depleted uranium, and *byproduct materials* such as the tailings from mining and milling of uranium ores.

HLW at Hanford will be processed in a similar fashion. However, current plans call for about a third of the low-activity stream at Hanford to be immobilized in borosilicate glass for onsite disposal. Plans for immobilizing the other two-thirds of the low-activity stream are still being developed.

HLW in the form of granular calcine is stored in bins at the Idaho Site. Current plans call for this waste to be immobilized by hot isostatic pressing, with or without additives, to produce a glass-ceramic waste form (see NRC, 2010, and Chapter 4 of this report) for deep disposal in a Federal repository.

- Most transuranic (TRU) waste will be packed into barrels, boxes, and shielded casks (i.e., packaged) and disposed of at the Waste Isolation Pilot Plant (WIPP) in New Mexico. Liquid TRU waste at the Idaho Site will be immobilized by steam reforming (see NRC, 2010, and Chapter 4) prior to disposal at WIPP.
- Mill tailings waste is being disposed of in near-surface disposal cells with engineered covers.
- Most LLW will be packaged and disposed of in DOE and commercial shallow disposal facilities.[8] However, there are some LLW streams (e.g., spent resins) that may require processing to make them suitable for disposal.
- Depleted uranium (in the form of uranium hexafluoride) is being stored at the Portsmouth (Ohio) and Paducah (Kentucky) sites. It will be converted to uranium oxide and packaged for shallow disposal.
- Some plutonium that is excess to U.S. defense needs will be used to produce mixed oxide fuel for commercial reactors. Other plutonium and uranium residues will be packaged and disposed of at WIPP or in a Federal repository.
- Facilities will be demolished, disposed of in place, or reused for other purposes. Decommissioning of the facilities will generate TRU waste, LLW, and nonhazardous debris.
- There are a number of orphan waste streams that lack clear disposition pathways, either because they are not HLW, TRU waste, or LLW, or because they do not meet waste acceptance criteria (see Chapter 8) for disposal. These orphan waste streams include, for example, actinide targets, beryllium neutron reflectors, and highly

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[8] The disposal pathway for Greater-than-Class C LLW is still under development by DOE. See http://www.gtcceis.anl.gov/. Last accessed on August 25, 2010.

contaminated process equipment. Additionally, wastes generated during cleanup operations[9] may also become orphan.

The disposal pathways for SNF/HLW, TRU waste, and LLW are established in U.S. laws and regulations. SNF/HLW and TRU waste require deep disposal hundreds of meters below the Earth's surface. Defense-related TRU wastes are currently being disposed of at WIPP. SNF/HLW will be disposed of in a Federal repository. Yucca Mountain, Nevada, has been designated by the Federal government as the site for this repository, but efforts are underway within the Executive Branch to withdraw this site from consideration. LLW is being disposed of in shallow facilities within 10 meters or so of the Earth's surface at a number of sites in the United States.

According to the Fiscal Year 2011 DOE Budget,[10] total life cycle costs for the DOE-EM cleanup program are currently estimated to be between $275 billion and $329 billion. HLW cleanup is the largest lifecycle cost element of the cleanup program, with lifecycle costs estimated to be between $87 billion and $117 billion. The Hanford Site, Idaho Site, and Savannah River Site are responsible for the majority of past and projected lifecycle cleanup costs, totaling almost $200 billion (Figure 2.3). Cleanup of these three sites and the gaseous diffusion plants in Tennessee and Kentucky will also take the longest to complete: projected cleanup schedules range from about 2030 to beyond 2060 (see Figure 2.2).

2.3 STUDY PLAN

The National Academies appointed the Committee on Waste Forms Technology and Performance to carry out this study. It consists of 11 members with expertise that spans the scientific and engineering disciplines relevant to the study task, including chemical and process engineering; geosciences; materials science; radiochemistry; risk assessment; waste disposal regulations; waste form performance; and waste management practices and technologies. Biographical sketches of the committee members are provided in Appendix A.

The information used in this study was collected from several sources. The committee availed itself of the voluminous existing scientific and engineering literature on waste forms and processing technologies. The committee has made no attempt to summarize this literature in this report; instead, it has cited key papers and review articles where needed to support its discussions.

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[9] These include gaseous and liquid effluents and solid wastes, for example, process condensates, scrubber wastes, spent resins, and failed equipment.

[10] Available at http://www.mbe.doe.gov/budget/11budget/Content/Volume%205.pdf. Last accessed August 25, 2010.

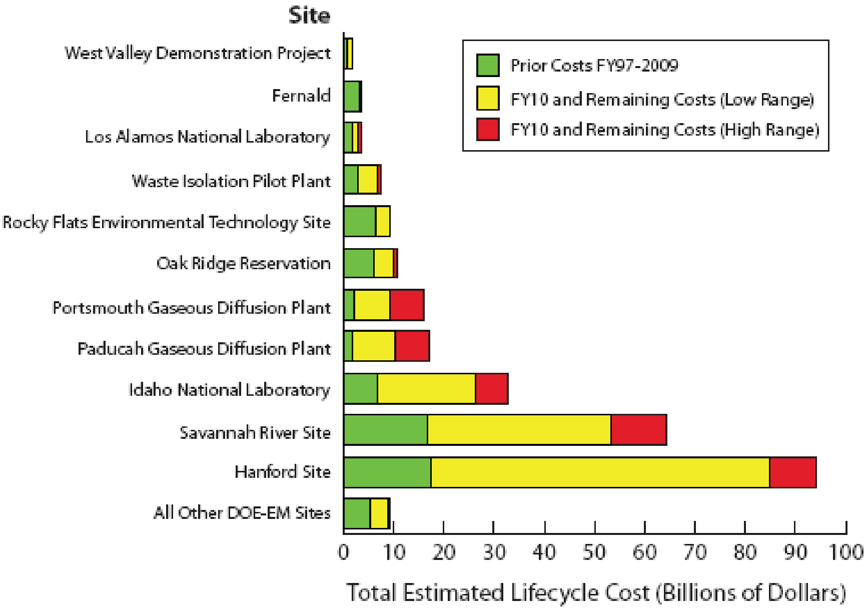

FIGURE 2.3 Lifecycle costs for DOE-EM site cleanup.
SOURCE: Data from the DOE FY 2011 Congressional Budget Request. Available at http://www.mbe.doe.gov/budget/11budget/Content/Volume%205.pdf. Last accessed on August 25, 2010.

The committee also obtained information through a series of briefings by representatives of DOE and other organizations, site visits, and a scientific workshop. The committee received briefings on DOE's current programs and future plans for waste processing, storage, and disposal from DOE-EM, national laboratory, and contractor staff, including information on comparable international programs. The committee visited the Hanford Site, Idaho Site, Savannah River Site, and their associated national laboratories (Pacific Northwest National Laboratory, Idaho National Laboratory, and Savannah River National Laboratory, respectively) to observe DOE's waste processing and waste form production programs and to hold technical discussions with site and laboratory staff. The committee also organized a workshop to discuss scientific advances in waste form development and processing. This workshop, which was held in Washington, D.C., on November 4, 2009, featured presentations from researchers in the United States, Russia, Europe, and Australia. The workshop agenda is provided in Appendix B.

At the request of DOE-EM, the committee issued an interim report to provide timely information for Fiscal Year 2011 technology planning (NRC, 2010[11]). That report, which was released to the public on June 15, 2010, identified opportunities associated with the last three bullets of the statement of task (see Box 2.1). The interim report is provided in its entirety in Appendix C of this report.

This final report addresses the statement of task in its entirety. However, in addressing the task, the committee decided to focus on waste forms and processing technologies for HLW, because HLW cleanup has the longest schedule, highest cost, highest risk, and is arguably DOE-EM's most difficult technical challenge (see, for example, DOE, 1998, 2010; NRC, 2001a, 2006). HLW is also a major focus of the DOE-EM Science and Technology Roadmap (DOE, 2008; see also NRC, 2009).

Most other waste types will be much less challenging and expensive to manage and dispose of than HLW. As noted in Table 2.1, most TRU waste and LLW are being disposed of "as is"—that is, without processing it into waste forms—although some conditioning (i.e., drying, sorting, volume reduction, and packing) is being undertaken. Additionally, the process for characterizing TRU waste prior to disposal is time consuming and expensive, but these characterization issues have been addressed in previous National Research Council reports (NRC, 2002b, 2004).

DOE is currently storing its SNF in pools (wet storage) and casks (dry storage). Additionally, some corroded aluminum-clad SNF at Savannah River has been stabilized by processing it into metal. DOE plans to eventually direct dispose its SNF in a geologic repository assuming that it meets repository waste acceptance criteria (see Chapter 8). However, with the apparent cancellation of the Yucca Mountain project, extended storage of SNF might be required at DOE sites until another repository is identified, licensed, and opened. In this case, SNF in wet storage might need to be stabilized to reduce corrosion (see NRC, 2003).

At present, tank waste retrieval and closure are limited by schedules for treating and immobilizing HLW in the Defense Waste Processing Facility, which is currently operating at the Savannah River Site; the Waste Treatment Plant, which is under construction at the Hanford Site; and a facility to be designed and constructed for immobilizing calcine HLW at the Idaho Site. Accelerating schedules for treating and immobilizing HLW by introducing new and/or improved waste forms and processing technologies could also accelerate tank waste retrieval and closure schedules.

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[11] Available at http://www.nap.edu/catalog.php?record_id=12937. Last accessed on August 25, 2010. See Appendix C

2.4 REPORT ORGANIZATION

This report is organized into eight chapters to address the statement of task for the study. The chapter topics and their relation to the study charges in the statement of task (i.e., the bulleted items in Box 2.1) are as follows:

- Chapter 2 (this chapter) provides background on the study.
- Chapter 3 describes the physical and chemical properties of waste form materials that are potentially relevant to the DOE-EM cleanup program (addresses Charge 1 in Box 2.1).
- Chapter 4 describes key technologies for producing waste forms (Charge 4).
- Chapter 5 describes how testing is used to elucidate waste form properties and support modeling of long-term waste form performance in disposal environments (Charge 3).
- Chapter 6 provides a brief description of disposal environments, systems, and processes that can affect waste form performance (Charge 1).
- Chapter 7 describes the use of models for evaluating waste form performance in disposal environments (Charge 3).
- Chapter 8 describes the legal and regulatory factors that underpin requirements for waste form performance (Charge 2).
- Chapter 9 provides examples of possible opportunities for new and improved waste form materials, processing technologies, and computational modeling (Charges 4 and 5).

A glossary of terms and an acronym list are provided in Appendixes D and E, respectively.

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3

Waste Forms

The final charge of the statement of task for this study (see Box 2.1 in Chapter 2) calls for the identification and description of “potential new waste forms that may offer enhanced performance or lead to more efficient production.” This chapter, which is written primarily for technical audiences, addresses this charge by providing a brief review of waste form materials and an assessment of their potential applicability to Department of Energy, Office of Environmental Management (DOE-EM) waste streams. Possible applications are also highlighted in Chapter 1.

A voluminous technical literature on waste form materials has developed over the past six decades. A comprehensive review of this literature is well beyond the scope of this study. However, the committee has included key historical and review article references in this chapter for interested readers.

3.1 WASTE FORM DEVELOPMENT

The concept of immobilizing radioactive waste in either vitreous or crystalline materials is more than 50 years old. In 1953, Hatch (1953) of Brookhaven National Laboratory introduced the concept of immobilizing radioactive elements in an assemblage of mineral phases. The first borosilicate glass formulations were developed in the United States between 1956 and 1957 by Goldman and others at the Massachusetts Institute of Technology (Eliassen and Goldman, 1959; Goldman et al., 1958; Mawson, 1965). These researchers examined calcium-aluminosilicate porcelain glazes to which boron oxide (B_2O_3) had been added to achieve a pourable glass and minimize radionuclide volatilization. The most promising vitreous systems for future development were determined to be borosilicate based, e.g., CaO-Al_2O_3-B_2O_3-SiO_2 and Na_2O-CaO-Al_2O_3-B_2O_3-SiO_2.

In 1970, the singular requirement for a waste form from the Office of Nuclear Waste Isolation[1] (ONWI) was that it be a stable solid (DOE, 1981; Walton et al., 1983). By the mid-1970s, innovative proposals for producing stable solid waste forms were being offered—for example, supercalcine ceramics by Rustum Roy and colleagues at Pennsylvania State University (McCarthy, 1977; Roy, 1975, 1977, 1979); alumina-based tailored ceramics by Rockwell International Science Center (Jantzen et al., 1982b; Morgan et al., 1981); and titania-based SYNthetic ROCk (SYNROC) by Ted Ringwood and colleagues at the Australian National University and the Australian Nuclear Science and Technology Organisation (Reeve et al., 1984; Ringwood, 1978, 1985; Ringwood et al., 1978). The first systematic compilations of potential crystalline waste form phases were also made at this time (Haaker and Ewing, 1981).

There were extensive research and development (R&D) programs on nuclear waste forms during the late 1970s and early 1980s, resulting in the examination of a wide variety of single-phase and polyphase ceramics. By this time "low leachability" had become the main criterion for waste form comparisons (DOE, 1981; Walton et al., 1983), and such comparisons between crystalline ceramics and glass generated considerable controversy (Kerr, 1979a,b).

Beginning in 1978, there was intense study of alternative waste forms that culminated in a review (Garmon, 1981) that recommended borosilicate glass for immobilizing high-level radioactive waste (HLW) at the Savannah River Site (SRS) in South Carolina and West Valley in New York and also identified SYNROC/tailored ceramics as promising alternatives (Hench et al., 1981). Glass was considered to be a more proven technology, and there were questions about the maturity of production technologies for ceramic waste forms. Nevertheless, Hench et al. (1981) made a strong recommendation for continued research and development for ceramic waste forms, including SYNROC and titanate- and alumina-based ceramics. These alternative waste forms were later determined to be difficult to process, more costly to implement, and not as flexible for accommodating variations in waste composition as borosilicate glass (De et al., 1976; Dunson et al., 1982; Lutze et al., 1979; McCarthy, 1973; McCarthy and Davidson, 1975; Morgan et al., 1981; Ringwood et al., 1981; Schoebel, 1975), even though

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[1] The Office of Nuclear Waste Isolation was located at the Battelle Memorial Institute. It conducted research and published technical reports on technical aspects of nuclear waste isolation.

many were found to have superior product quality (Hench et al., 1981; Walton et al., 1983).

High-temperature processing of these alternative waste forms frequently resulted in the formation of an intergranular glass phase, especially when alkali-containing wastes were processed. This intergranular glass limited product stability and durability because radionuclides such as cesium-137 and strontium-90, which were frequently incorporated into the intergranular glass phases (Buykx et al., 1988; Clarke, 1981; Cooper et al., 1986; Zhang and Carter, 2010), were determined to leach at the same rates as those from glass waste forms (Jantzen et al., 1982a). Because little was understood at the time about the degradation mechanism of a single-phase glass versus glass-ceramic materials (i.e., materials that contain both glass and crystalline phases), borosilicate glasses were selected for continued development over the alternative waste forms (Walton et al., 1983).

Research activity on alternative waste forms was severely curtailed as a result of the 1981 decision in the United States to immobilize defense HLW in borosilicate glass and the subsequent construction of the Defense Waste Processing Facility (DWPF) at SRS and the West Valley Demonstration Project (WVDP) at West Valley. The R&D effort on nuclear waste forms during this period has been summarized by Lutze and Ewing (1988).

More recently, there has been a resurgence of interest in crystalline waste forms because of the need to develop durable materials for the stabilization and disposal of actinides such as plutonium from defense and civilian programs (Burakov et al., 2010; Ewing, 1999; Ewing et al., 1995b; Oversby et al., 1997). There has been additional R&D work on minerals and their analogues (e.g., apatite, monazite, zirconolite, zircon, and pyrochlore) (Ewing et al., 1995a) and SYNROC formulations (Ryerson and Ebbinghaus, 2000) as well as another down selection between glass and ceramic waste forms (Meyers et al., 1998).

Crystalline waste forms made from clay have been studied almost continuously since 1953 (Hatch, 1953; Lutze et al., 1979). Roy (1981) proposed low-temperature, hydrothermally processed, low-solubility phase assemblages consisting of mineral analogues of mica, apatite, pollucite, sodalite-cancrinite, and nepheline, many of which could be made from reactions between clays (kaolin, bentonite, and illite) and waste. Mineral analogue waste forms made from clays have been recently re-examined for the immobilization of high-sodium, salt supernate HLW at the Hanford Site in Washington; high-sodium recycle streams from tank cleaning at the Idaho National Laboratory (INL), and low-activity waste melter off-gas condensates at Hanford. These mineral analogue waste forms are made using a moderate-temperature (700°C-750°C) thermal pyrolysis treatment (Mason et al., 1999, 2003) (i.e., steam reforming; see Chapter 4) by adding clay to the waste to form feldspathoid mineral analogues (sodalite and nepheline) or dehyroxylated mica (Jantzen et al., 2008), depending on clay composition.

Stabilization and solidification with cement-based binders has been used to immobilize radioactive wastes since the beginning of the nuclear age. The process has been used to encapsulate solid waste, solidify liquid waste (including tritiated water), stabilize contaminated soils, stabilize tank-heel residues after tanks are emptied, and as low-permeability barriers. Cements have also been used as binders and to encapsulate granular or cracked waste forms. A recent comprehensive review of cement systems for radioactive waste disposal can be found in Pabalan et al. (2009). Long-term cement durability comparisons have been made using ancient cements, geopolymers, and mortars (Jiang and Roy, 1994; Kovach and Murphy, 1995; Krupka and Serene, 1998; Miller et al., 1994; Roy and Langton, 1983, 1984, 1989; Steadman, 1986), some of which may also serve as natural analogues for geopolymer waste forms (Barsoum et al., 2006, but see also Jana, 2007).

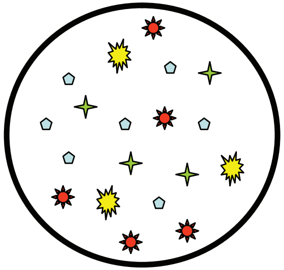
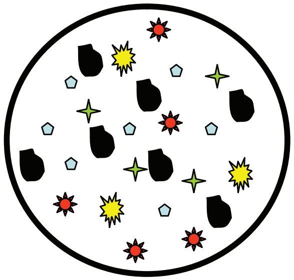
Recent reviews of developments in waste form research are provided in the following papers: Caurant et al. (2009); Donald et al. (1997); Ewing (1999, 2001); Ewing et al. (2004); Lee et al. (2006); Lumpkin (2001, 2006); Lutze and Ewing (1988); Ojovan and Lee (2005, 2007); Stefanovsky et al. (2004); Weber et al. (2009); and Yudintsev et al. (2007). The most recent interest has been associated with the desire to create new waste forms as part of advanced nuclear fuel cycles involving recycling of irradiated fuel (Peters and Ewing, 2007). Recent reviews of radiation effects in waste forms can be found in a series of papers by Ewing and others (1995b); Ewing and Weber (2010); and Weber and others (1997, 1998). Reviews of natural analogues that provide long-term data on the durability of glass and crystalline ceramics have been provided in a number of papers, including Allen (1982); Ewing (1979, 1999); Haaker and Ewing (1981); Jantzen and Plodinec (1984); Malow et al. (1984); Morgenstein and Shettel (1993); and Verney-Carron et al. (2010).

3.2 ROLE OF WASTE FORM IN WASTE IMMOBILIZATION

As noted in Chapter 2, the primary role of a waste form is to immobilize radioactive and/or hazardous constituents (hereafter simply referred to as *constituents*) in stable, solid matrices for storage and eventual disposal. Immobilization can occur through *chemical incorporation*, *encapsulation*, or a combination of both processes. Table 3.1 provides a pictorial representation of the different combinations of chemical incorporation and encapsulation for the waste form materials described in Section 3.3.

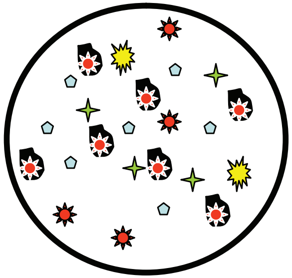
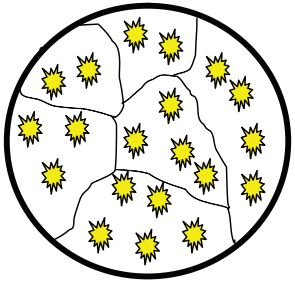
Encapsulation is achieved by physically surrounding and isolating constituents in a matrix material, which traps waste ions on grain boundaries and in some cases sequesters constituents in hydrated products. Cements,

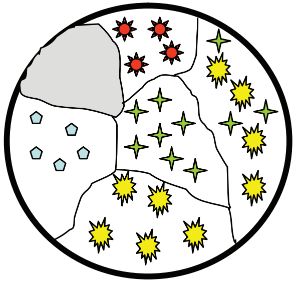
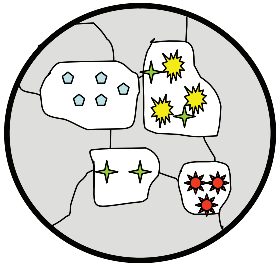
TABLE 3.1 Key Properties of the Waste Form Materials Described in this Chapter

Waste Form Class (see text)	Retention Mechanism	Graphical Representation	Waste Form Properties	Examples
1. Single-Phase Glasses Constituents are atomically bonded in the glass structure, usually to oxygen that is also bonded to other matrix elements (e.g., Si, Al, B, P) by short-range order (SRO) and medium-range order (MRO).	Chemical incorporation		a. Moderate waste loading b. Good overall durability c. Easy to model constituent release from a single phase	Borosilicate glasses, aluminosilicate glasses, phosphate glasses
2a. Glass-Ceramic Material Constituents are present in the glass matrix, and benign crystals such as spinels (Cr, Ni, and Fe species) are allowed to crystallize (●). These crystals do not contain radionuclides but may contain hazardous constituents (e.g., Cr, Ni).	Chemical incorporation		a. Higher waste loadings for high Cr, Ni, and Fe wastes b. Good overall durability c. Easy to model constituent release from single-phase glass because there is minimal impact from grain boundary dissolution (has to be determined by experimentation)	Higher waste-loaded borosilicate, alumino-silicate, or phosphate glasses

continued

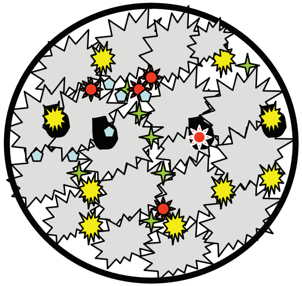
TABLE 3.1 Continued

Waste Form Class (see text)	Retention Mechanism	Graphical Representation	Waste Form Properties	Examples
2b. Glass-Ceramic Material Constituents are present in the glass matrix and in the crystalline phases. Example shows Cs in the glass and in a secondary phase (●). Secondary phase may be more soluble than glass (e.g., $(Na,Cs)_2SO_4$) or more durable than glass (e.g., pollucite $(Cs,Na)_2Al_2Si_4O_{12}$).	Chemical incorporation and encapsulation		a. Higher waste loadings if soluble constituent phases are not formed b. Overall durability may be greater or less than homogeneous glass c. More complex to model constituent release from multiple phases (glass and crystal) and grain boundaries (has to be determined by experimentation)	Glass-bonded sodalite
3a. Crystalline Ceramics: Single Phase **4a. Metals: Single Phase** Consists of only one main crystalline phase which contains the same radionuclide(s). May be granular or monolithic.	Chemical incorporation		a. High waste loading for single constituents b. Good overall durability c. Easy to model constituent release from a single phase	Pyrochlores for single actinide stabilization, zeolites for single radionuclide stabilization

3b. Crystalline Ceramics: Multi-Phase **4b. Metals: Multi-Phase** Individual phases contain one or multiple constituents (e.g., solid solution indicated between UO_2 and ThO_2). Some phases do not incorporate any constituents (gray shading). May be granular or monolithic.	Chemical incorporation		a. High waste loading b. Superior overall durability c. Difficult to model constituent release from multiple phases d. Need to tailor for and know/determine radionuclide partitioning amongst phases e. May require precalcining for waste form processing to work efficiently	SYNROC, tailored ceramics, Pu ceramics, supercalcines, minerals for actinide stabilization
3a, 3b. Granular Crystalline Ceramic **4a, 4b. Metal Composites** Granular waste forms must be monolithed for disposal if not containerized. The monolithing agent does not incorporate constituents (gray shading). Also known as composite waste forms.	Chemical incorporation and encapsulation		a. High waste loadings only if binder (monolithing agent) is minimized b. Superior overall durability-double containment c. Difficult to model constituent release from multiple phases d. Need to tailor for and know/determine radionuclide partitioning amongst phases e. May require precalcining for waste for processing to work efficiently	Fluidized bed seam reforming for Hanford low-activity waste or Waste Treatment Plant secondary wastes in geopolymer matrices

continued

TABLE 3.1 Continued

Waste Form Class (see text)	Retention Mechanism	Graphical Representation	Waste Form Properties	Examples
5, 6, 7, 8. Cements, Geopolymers, Hydroceramics, Ceramicretes Hydrated phases weakly incorporate constituents or retain them by sorption. Encapsulation is by solidification or precipitation of constituents on grain boundaries where non-constituent phases hydrate or crystallize. Example shows Tc sequestered by C-S-H hydrates and sequestered by secondary fly-ash granules.	Encapsulation		a. Low waste loading b. Lower overall durability c. Difficult to model constituent release from multiple phases and hydrated secondary phases d. Easy to process—usually mix and set	Savannah River Site Saltstone

Key:

✹ Cs ✸ U ⬠ Tc ✦ Pu

geopolymers, ceramicrete, and hydroceramics (see Section 3.3) can be used as waste forms or as binders for other waste form materials. Encapsulation is typically used to immobilize low-level or intermediate-level wastes.

Chemical incorporation involves the atomic-scale bonding of radioactive constituents into *radiophases* of the waste form material, which are durable structures with any combination of short-range order (SRO),[2] medium-range order (MRO),[3] or long- range order (LRO).[4] Glasses incorporate constituents into their atomic structures by SRO and MRO. Recent experimentation has shown the existence of large, cation-rich clusters in glass. These more highly ordered regions of MRO often have atomic arrangements that approach those of crystals (Box 3.1). Crystalline ceramics incorporate constituents by a combination of SRO, MRO, and LRO. LRO defines the periodic structural units characteristic of crystalline ceramics.

There are two approaches for immobilizing radioactive waste in crystalline materials (Roy, 1975, 1977):

1. Radionuclides can be incorporated into the atomic structure of the phase. Individual radionuclides occupy specific sites in the structure, generally according to atomic size and charge constraints. For complex waste streams, crystalline structures with multiple cation sites are required to accommodate different radionuclides.
2. The radionuclide-bearing radiophases can be encapsulated in another non-radionuclide bearing material to form a *composite waste form*.[5] Encapsulating materials, such as TiO_2 or ZrO_2, can have high durability.

3.3 WASTE FORM MATERIALS

A wide range of materials are potentially suitable for immobilizing radioactive waste. For simplicity of discussion, these *waste form materials* have been grouped into eight classes based on their phase properties:

1. Single-phase (homogeneous) glasses
2. Glass-ceramic materials

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[2] SRO: radius of influence ~1.6Å-3Å around a central atom, e.g., such as tetrahedral and octahedral structural units.

[3] MRO: radius of influence ~3Å-6Å encompasses second- and third-neighbor environments around a central atom. The more highly ordered regions, referred to as clusters or quasicrystals, often have atomic arrangements that approach those of crystals.

[4] LRO extends beyond third-neighbour environments and gives crystalline ceramic/mineral structures their crystallographic periodicity.

[5] For example, waste constituents can be chemically incorporated into a crystalline ceramic phase and then encapsulated in another material that provides an additional barrier to release.

BOX 3.1
How Structural Characteristics of Borosilicate Waste Glass Control Physical and Chemical Characteristics

The polymerization of the SRO and MRO in borosilicate glasses provides more flexibility for atomically bonding waste constituents than in crystalline materials. The glass-forming SRO structural groups are usually tetrahedral Si, B, Al, Fe, P surrounded by four oxygen atoms or trigonal B surrounded by three oxygen atoms. The tetrahedra link to each other via bridging oxygen bonds (BO). The remaining non-bridging oxygen atoms (NBO) carry a negative charge and, in turn, ionically bond to positively charged cations such Cs^+, Sr^{+2}, Ca^{+2}, and other positively charged constituents. These linkages create MRO structural groups, e.g., $(Cs,K,Na,Li)AlO_2$, $(Cs,K,Na,Li)FeO_2$, $(Cs,K,Na,Li)BO_2$, $(Cs,K,Na,Li)SiO_4$ (Ellison and Navrotsky, 1990), or $(Cs,K,Na)AlSiO_4$ (Li et al., 2000), which form sheet-like units, chain-like units, and monomers (White, 1988) that further bond waste constituents ionically.

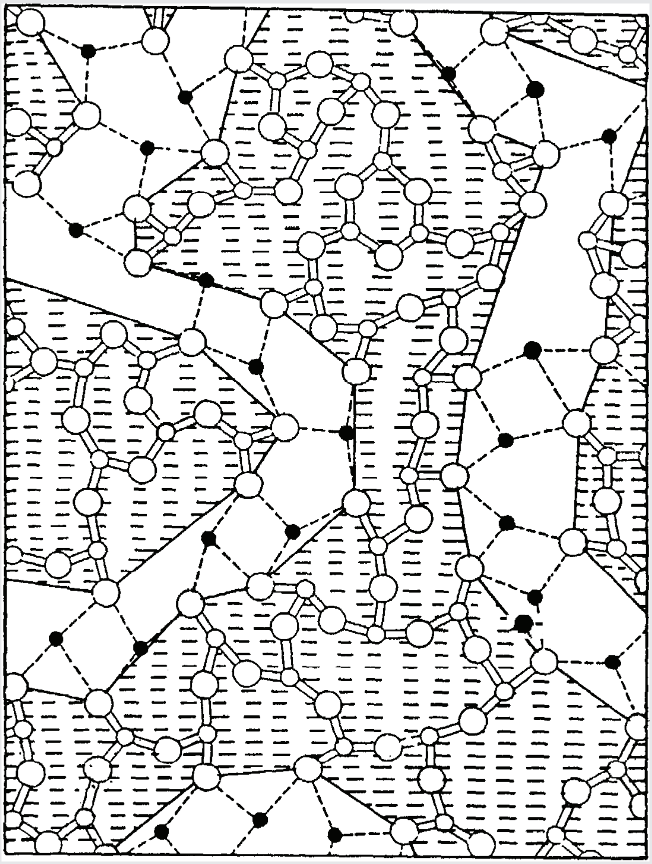
The *modified random network model* (MRN Model) (Porai-Koshits, 1958; Warren, 1933; Zachariasen, 1932, 1933) for glass is able to account for the existence of large cation-rich clusters in glass (e.g., clusters of Ca in $CaSiO_3$ glasses and Na in Na_2MoO_4). These more highly ordered regions of MRO, which are referred to as *clusters* (or *quasicrystals* in the older literature) can have atomic arrangements that approach those of crystals (Burnham, 1981). These clusters govern constituent solubility (Calas et al., 2003; Cauranta et al., in press; Hyatt et al., 2004; Nyholm and Werme, 1981) (see Box Table) and crystal formation during cooling. The process model in use at the DWPF uses a quasicrystal model to prevent unwanted crystallization in the Joule heated melter.

In the MRN model, tetrahedra define the network regions and the NBO-cation regions represent percolation channels (see Box Figures and Figure 9.1 in Chapter 9) that can act as ion-exchange paths for elements that are ionically bonded to the NBO. Such percolation channels are also found in rare-earth (lanthanide) alumino-borosilicate (LaBS) glasses (Caurant et al., 2009). The molecular structure of glass controls constituent release by establishing ion exchange sites, hydrolysis sites, and the access of water to those sites through the percolation channels. The mechanisms of constituent release are similar to those for natural analogues glasses (basalts) and minerals.

BOX TABLE Solubility of Elements in Silicate Glass

Element	Solubility (mass %)
Al, B, Ca, Cs, K, Na, Pb, Rb, Si, U	>25
Ba, Fe, La, Li, Mg, Nd, Sr, Zn	15-25
Be, Bi, Cu, F, Ga, Ge, Mn, P, Pr, Pu, Th, Ti, V, Zr	5-15
Am, As, C, Cd, Ce, Cl, Cm, Co, Cr, Cy, Eu, Hf, Mo, Ni, Np, Pm, Re, S, Sb, Se, Sm, Sn, Tc, Te, Tl, W, Y	1-5
Ag, Au, Br, Hg, I, N, Pd, Pt, Rh, Ru	<1

SOURCE: Ojovan and Lee (2007).

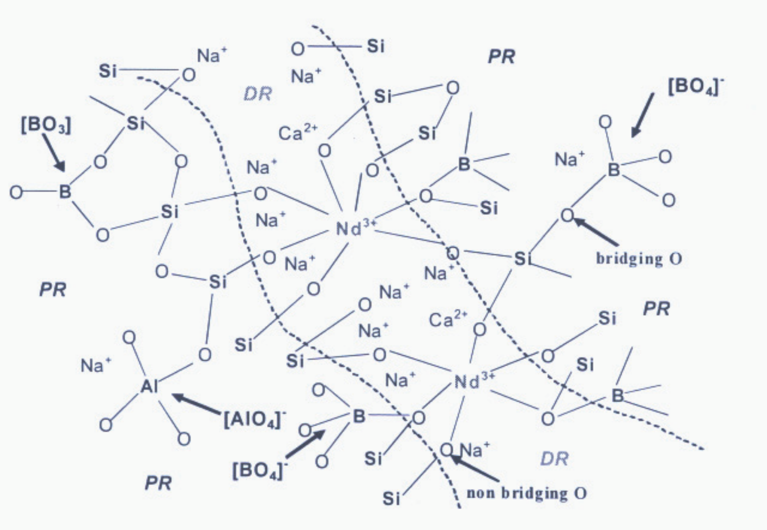


● Modifying Cations (M) ○ Network Formers (G) ◯ Oxygen atoms

BOX FIGURE 1 A modified random network (MRN) for a glass of nominal composition $M_2O_3(G_2O_3)_2$, where M represents the modifying cations and G represents the tetrahedral cations. Covalent bonds are shown by the solid lines and ionic bonds by the dotted lines. The dashed regions are defined by the boundary, which runs along the G–O (i.e., non-bridging) bonds. The undashed regions represent the percolation channels defined by the M–O bonds that run through the glass network. SOURCE: Greaves (1989).

continued

BOX 3.1 Continued



BOX FIGURE 2 Proposed polymerization of SRO and MRO in the atomic structure of a French HLW rare earth bearing aluminoborosilicate glass. Na^+, Ca^{2+}, and Nd^{3+} exist in the proposed percolation channels. SOURCE: Caurant et al., (2009).

3. Crystalline ceramics
4. Metals
5. Cements
6. Geopolymers
7. Hydroceramics
8. Ceramicretes

Brief descriptions of these materials are provided in the following sections. More detailed descriptions of these materials are provided in the accompanying tables.

3.3.1 Single-Phase (Homogeneous) Glasses

Glass is an amorphous solid material produced by cooling a material from a molten to a solid state without crystallization. Glass waste forms can have a wide range of compositions, but they are generally classified using the dominant tetrahedral structural groups forming its structure, similar to the nomenclature for aluminosilicates, borates, and phosphates:

- *Borosilicate glasses* contain $(SiO_4)^{-4}$, $(BO_4)^{-5}$, $(BO_3)^{-3}$, and some $(AlO_4)^{-5}$ structural units.
- *Aluminosilicate glasses* contain $(SiO_4)^{-4}$ and $(AlO_4)^{-5}$ units.
- *Aluminoborate glasses* contain only $(BO_4)^{-5}$, $(BO_3)^{-3}$, and some $(AlO_4)^{-5}$ units.
- *Aluminophosphate glasses* contain $(PO_4)^{-3}$ and $(AlO_4)^{-5}$ units.
- *Iron phosphate glasses* contain $(PO_4)^{-3}$ and $(FeO_4)^{-5}$ units.

The major properties of glass waste form materials are summarized in Table 3.2.

Glass is being used worldwide to immobilize HLW from reprocessing of spent nuclear fuel and targets. The immobilization process, *vitrification*, is a continuous process capable of handling large-volume waste streams. This process is a well-demonstrated technology with more than 40 years of industrial experience (see Chapter 4).

Glass has several advantages for HLW immobilization: It can generally accommodate a wide range of waste stream compositions; has adequate-to-good durability in many disposal environments (see Chapters 5 and 8); and has good thermal and mechanical stability properties. In particular, borosilicate glasses melt at temperatures between 1,050°C-1,200°C, which limits the volatility of radionuclides such as technetium-99, cesium-137, and iodine-129. The melts are generally less corrosive than commercial glass melts, such as Pyrex, because of their lower temperatures.

The worldwide production of HLW glass is summarized in Table 3.3. To date, more than 5,000 metric tons of HLW borosilicate glass have been produced at SRS and 500 metric tons have been produced at West Valley, New York. More than 6,700 metric tons of HLW borosilicate glass have been produced in France. The compositions of these glasses, including the incorporated wastes, fall into a common region in the borosilicate glass forming system (Jantzen, 2011; Ramsey, 1989; Wicks et al., 1985). They contain ~60 weight percent or more of glass forming oxides (SiO_2, B_2O_3, ZrO_2, Al_2O_3, P_2O_5, and fission products), >15 weight percent glass modifier oxides (Na_2O, K_2O, Li_2O, CaO, MgO, SrO, and ZnO), and 0-25 weight percent glass intermediate oxides (Cr_2O_3, Fe_2O_3, CuO, NiO, MnO, PbO, TiO_2, and actinides).

3.3.2 Glass-Ceramic Materials

Glass-ceramic materials (GCMs) are materials that contain both crystalline and glass phases (see Table 3.1). Depending on the intended appli-

TABLE 3.2 Single-Phase (Homogeneous) Glass Waste Forms (Type 1 in Table 3.1)

Glass Type	Major Structural Components	Comments	Selected References
Alkali borosilicate	$(SiO_4)^{-4}$, $(BO_4)^{-5}$, $(BO_3)^{-3}$, and some $(AlO_4)^{-5}$ structural (tetrahedral or trigonal units) to which alkali, alkaline earth, and waste species bond	Flexible easy processing; low melt temperatures 1,150°C -1,200°C to minimize volatility; cold cap production (if feasible) minimizes volatility; most waste cations highly soluble in glass; overall waste solubility 25-40 weight percent.	Caurant et al., 2009; Donald et al., 1997; Jantzen, 2011; Lee et al., 2006; Lutze and Ewing, 1988; Ojovan and Lee, 2005, 2007; Stefanovsky et al., 2004
Lanthanide borosilicate (LaBS)	$(SiO_4)^{-4}$, $(BO_4)^{-5}$, $(BO_3)^{-3}$, and some $(AlO_4)^{-5}$ structural (tetrahedral or trigonal units) to which lanthanides, alkaline earth, and other waste species bond	Higher solubility for actinides than alkali borosilicate glass; many of the lanthanides used have large thermal neutron cross-sections and serve as neutron absorbers; 1,300°C-1,500°C melt temperatures cause increased volatilization of some radionuclides; corrosion behavior of LaBS glass is similar to HLW glasses in current use by DOE; existing repository models were deemed to be directly applicable to LaBS glass; waste solubility 16-59 weight percent lanthanides.	Bardez et al., 2006; Harrison and Scales, 2008a,b; Jantzen, 2011; Marra et al., 2006; Ramsey et al., 1995
Aluminosilicate glasses and/or alkali aluminosilicate glasses	$(SiO_4)^{-4}$ and $(AlO_4)^{-5}$	Higher melting temperature (~1,600°C) causes volatilization of radionuclides; waste loading dependent on rapid cooling, e.g., 20 weight percent UO_2 if cooled rapidly but <10 weight percent if cooled slowly; improved durability over borosilicate glass.	Donald et al., 1997; Lutze and Ewing, 1988
Aluminoborate glasses	$(BO_4)^{-5}$, $(BO_3)^{-3}$, and some $(AlO_4)^{-5}$	Not used for waste vitrification.	

High-silicate glasses (sintered glasses)	$(SiO_4)^{-4}$	High SiO_2 glasses must be made by hot pressing and sintering at 650°C -800°C to retain volatile fission elements such as Cs, Ru, Mo, and Tc; waste solubility 5-35 weight percent reported.	Donald et al., 1997; Lutze and Ewing, 1988
Alkali alumino-phosphate	$(PO_4)^{-3}$and $(AlO_4)^{-5}$	Phosphate can be added remotely as H_3PO_4; phosphate precipitates formed in feed solution are hydrous and non-caking; phosphate systems form melts at lower temperatures than silicate or borosilicate systems; most cations are readily incorporated into homogeneous phosphate melts; phosphate systems can be devised to accommodate more than 10 weight percent sulfate; melts are corrosive to materials of construction; glass product has a tendency to devitrify; durability can be comparable to borosilicate glass if alumina content is sufficient; composition ~24-27 weight percent Na_2O, 20-24 weight percent Al_2O_3+Me_mO_n, 50-52 weight percent P_2O_5.	Caurant et al., 2009; Donald et al., 1997; Ewing and Wang, 2002; Gombert, 2007; Hatch et al., 1962; Lee et al., 2006; Ojovan and Lee, 2005, 2007; Schneider, 1969; Stefanovsky, 2009; Stefanovsky et al., 2004
Lead iron phosphate	$(PO_4)^{-3}$and $(FeO_4)^{-5}$	Composition ~PbO, 40 to 66 weight percent; P_2O_5, 30 to 55 weight percent; and Fe_2O_3, 0 to 10 weight percent depending on the amount of iron in the waste; low melting (850°C -1,050°C); abandoned because of RCRA issues with Pb component, low waste loading (~20 weight percent); poor solubility of certain species compared to borosilicate glass; tendency to devitrify.	Chick et al., 1986; Donald et al., 1997; Jantzen, 1986a,b; Kahl, 1986; LLNL, 1996; Lutze and Ewing, 1988; Marasinghe et al., 2000; Sales and Boatner, 1984

continued

TABLE 3.2 Continued

Glass Type	Major Structural Components	Comments	Selected References
Iron phosphate	$(PO_4)^{-3}$and $(FeO_4)^{-5}$	Good chemical durability; high solubility for many heavy metals (e.g., uranium, chromium, zirconium, cesium, molybdenum), noble metals, and rare earths; low melting temperatures (950°C- 1,100°C); rapid melt rates (viscosity typically below one poise); low corrosion of oxide refractories and Inconel alloys commonly used in glass melting furnaces; waste loadings 25-50 weight percent; tendency to devitrify.	Badyal et al., 1999; Chen and Day, 1999; Day et al., 1997, 1998, 2004; Karabulut et al., 1999; Kim et al., 2003; Marasinghe et al., 1997, 1998, 1999, 2000, 2001; Mesko and Day, 1999; Mesko et al., 1998, 2000; Mogus-Milankovic et al., 1998; Ray et al., 1999; Yu and Day, 1995
Chalcogenide	TeO_2-XCl-B_2O_3 TeO_2-XCl-Li_2O TeO_2-XCl-Na_2O XCl = "mixed chlorides" simulant at ~19 weight percent	S, Se, and Te glasses for radionuclides that are otherwise difficult to immobilize (e.g., I-129) in conventional glass or borosilicate glass systems; gels such as $Pt_2Ge_4S_{9.6}$ are used to immobilize actinides, noble gases, carbon dioxide, and mixed chlorides.	Crum et al., 2009; Ryan et al., 2009

TABLE 3.3 Global Production of HLW Glass at Industrial Scales

Plant Name	Location	Vitrification Process	Waste Glass Quantities (metric tons)	Waste Loading Range (weight percent)	Canister Size (Meters) [Number of Canisters Produced]	Activity (TBq)[a]
Defense Waste Processing Facility (DWPF)	Aiken, South Carolina, USA	Joule-heated melter	5,000[b]	28-40[c]	0.6 × 3 [2,845]	7.7 × 10^5
West Valley Demonstration Project (WVDP)	West Valley, New York, USA	Joule-heated melter	~500[d]	~20.4-23.5[e]	0.6 × 3 [275]	8.9 × 10^5
Waste Vitrification Plant (WVP), BNFL	Sellafield, UK	Induction, hot crucible	~1,800[f]	~25[g]	0.43 × 1.34 [4,319[h]]	1.9 × 10^7
Areva NC (R7/T7)[i]	La Hague, France	Induction, hot crucible	5,573[j]	12-18[k]	0.43 × 1 [14,045]	2.38 × 10^8
AVM or Atelier de Vitrification de Marcoule[i]	Marcoule, France	Induction, hot crucible	1,138[m]	12-18[k]	0.43 × 1 [3,159]	1.69 × 10^6
Pamela	Mol, Belgium	Joule-heated melter	500[l]	15-25[k]	0.30 × 1.2 0.43 × 1.34 [2,200]	4.5 × 10^5
Tokai Vitrification Facility[o] (TVF)	Tokaimura, Ibaraki Perfecture, Japan	Joule-heated melter	>100	20-30[k]	0.43 × 1 [247[n]]	1.5 × 10^4

continued

TABLE 3.3 Continued

Plant Name	Location	Vitrification Process	Waste Glass Quantities (metric tons)	Waste Loading Range (weight percent)	Canister Size (Meters) [Number of Canisters Produced]	Activity (TBq)[a]
Mayak Vitrification Facility[p] (EP-500)	Ural Region, Russia	Joule-heated melter	~8,000	33[k]	0.57 × 1 [17,600]	3.33×10^7

[a] 1 Tera-Becquerel (TBq) = 10^{12} decays per second.

[b] 1996-2009.

[c] Jantzen et al. (2005).

[d] 1996-2002; mission complete.

[e] Perez et al. (2001).

[f] 1991-2007 at 150 L glass per canister and an assumed glass density of 2.75 g/cm^3.

[g] Riley et al. (2009).

[h] Predicted mission completion is 6582 canisters.

[i] Caterine Veyer of AREVA, personnel communication (2010).

[j] P.P. Poluektor, personal communication (2010).

[k] Acidic waste loadings are comprised of fission products and minor actinides; corrosion products and alkali are not included as for neutralized wastes.

[l] 1978-2008

[m] 1985-1991

[n] 1995-2006

[o] Seiichiro Mitsui of Japan Atomic Energy Association (JAEA), personnel communication (2010).

[p] 1989-2008

cation, the major component may be a crystalline phase with a vitreous phase acting as a bonding agent. Alternatively, the vitreous phase may be the major component with particles of a crystalline phase dispersed in the vitreous matrix. GCMs can be formed by a number of processes, including melt crystallization (controlled or uncontrolled), multiple heat treatments, or by encapsulation of ceramic material in glass (Lee et al., 2006).

In practice, crystalline materials frequently contain glass remnants along grain boundaries, and unreacted radiophases may persist rather than be completely incorporated into the crystal structures. A virtual continuum exists between 100 percent glass and 100 percent crystalline materials with GCMs falling in between as shown in Figure 3.1.

GCMs offer a useful compromise between glasses and ceramics. They are easier and less expensive to prepare than conventional ceramics but offer higher durability than glasses, provided that the soluble species that can sequester radionuclides (e.g., Na_2SO_4, which can sequester cesium and strontium) (Plodinec and Wiley, 1979) are prevented from crystallizing (Figure 3.1 and Table 3.1).

GCMs offer several potential advantages over glass for use as waste form materials, including increased waste loadings, increased waste form density, and thus smaller disposal volumes. These waste forms can also be used to immobilize glass-immiscible components such as sulphates, chlorides, molybdates, and refractory materials that have very high melting temperatures. They can also be used to immobilize long-lived radionuclides (e.g., actinides) by incorporating them into the more durable crystalline phases; short-lived radionuclides (e.g., many fission products) can be accommodated in the less durable vitreous phase (Lee et al., 2006). Relatively low leach rates (see Chapter 5) have been observed for some glass ceramics, which may make them potential candidates for immobilization of HLW. For example, allowing the formation of crystalline phases that have little to no impact on durability (see Figure 3.1) would be an achievable incremental strategy for increasing HLW loading in glass (and throughput of waste) at SRS and Hanford.

A number of different GCMs have been proposed for the immobilization of HLW; summaries can be found in Donald et al. (1997), Lee et al. (2006), and Stefanovsky et al. (2004). A brief synopsis of GCMs is given in Table 3.4.

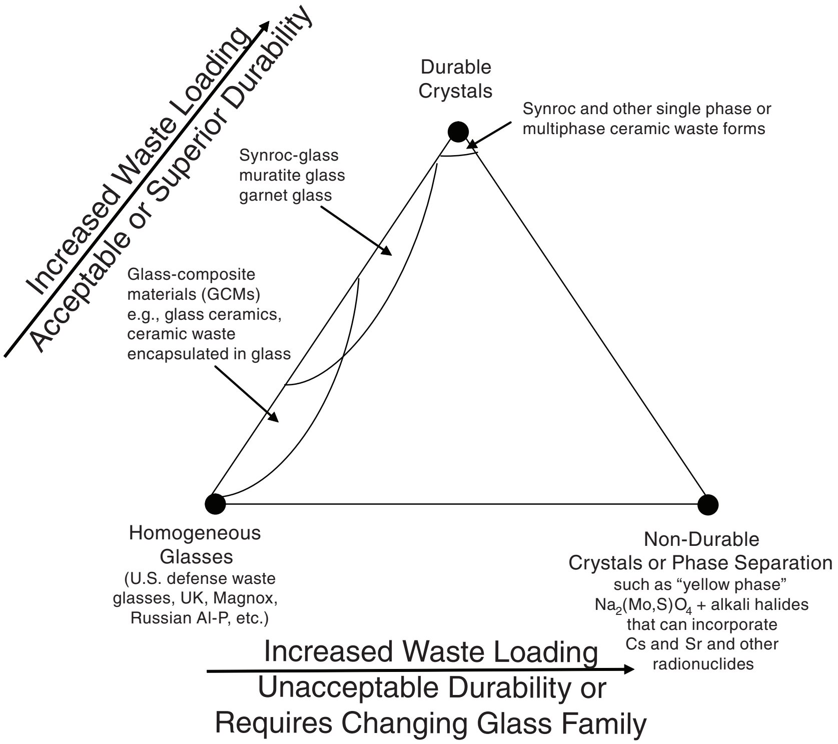


FIGURE 3.1 Schematic diagram illustrating the durability and waste loading of waste form materials relative to single-phase (homogeneous) glass. Single-phase glass formulations are shown in the lower left corner of the triangle. If crystals (e.g., spinels) are allowed to form in the glass, then glass-ceramic materials (GCMs) can be produced (left leg of triangle) that have superior waste loading and durability relative to single-phase glass. Fully crystalline materials (upper corner of triangle) are considered to be exceptionally durable waste forms with high waste loadings relative to single-phase glass. However, the incorporation of certain species (e.g., Mo, S, and P) into glass creates non-durable secondary phases (lower right corner or triangle) that may have unacceptable durabilities.
SOURCE: After Ojovan and Lee (2007).

3.3.3 Crystalline Ceramics

Crystalline ceramics are inorganic, non-metallic solids that contain one

TABLE 3.4 Glass Ceramic Materials (Types 2a and 2b in Table 3.1)

Material	Glass Phase	Crystalline Phase(s)	Comments	Selected References
Borosilicate based				
Alkali borosilicates	Borosilicate	$NiFe_2O_4$ spinels $ZrSiO_4$ Al_2O_3	Glasses are allowed to partially crystallize in the melt pool or spontaneously crystallize during cooling; spinels do not sequester radionuclides and have little or no impact on glass durability; zircon and alumina are likewise benign; crystallization alters the glass viscosity, making it non-newtonian; soluble phases like Na_2SO_4 should be avoided because they sequester Cs and Sr.	Bickford and Jantzen, 1984; Cicero et al., 1993; Hrma et al., 1994; Jantzen et al., 1984; Plodinec and Wiley, 1979
Glass-bonded sodalites	Borosilicate	I in NaI I in sodalite: $Na_8Al_6Si_6O_{24}(I)_2$, Cl in sodalite: $Na_8Al_6Si_6O_{24}(Cl)_2$	Glass-bonded sodalites are formed by hot isostaic pressing or cold pressing/sintering of high alkali containing electrorefiner wastes at 1,000°C-1,200°C; release of radionuclides is controlled by the dissolution rate of the binder glass.	Ebert, 2005; Morss et al., 2000; Moschetti et al., 2000; Sinkler et al., 2000
Synroc alumino-borosilicates	Alumino-borosilicate	Zirconolite: $CaZrTi_2O_7$	Made by hot isostatic pressing; zirconolite is the major crystalline phase; for low-purity actinide wastes, Pu partitions into the zirconolite over the glass phase by a factor of 100:1 and Gd neutron absorbers partition into zirconolite; accommodates both actinides and any associated impurities: proliferation resistant because of the low purity and concentration of Pu in the waste form.	B. Begg and K. Smith, ANSTO, written communication

continued

TABLE 3.4 Continued

Material	Glass Phase	Crystalline Phase(s)	Comments	Selected References
Barium aluminosilicates Celsian analogues	Borosilicate (sodium aluminosilicate with 2-7 weight percent B_2O_3 and 3-4 weight percent TiO_2)	Celsian: $BaAl_2Si_2O_8$ Pyrochlore: $RE_2Ti_2O_7$; RE = rare earth Scheelite: $BaMoO_4$ Pollucite: $CsAlSi_2O_6$ Molybdenum-nosean: $Na_8Al_6MoO_4(SiO_4)_6$ Perovskite: $CaTiO_3$ Diopside: $CaMgSi_2O_6$ Eucryptite: $LiAlSi_2O_6$ Spodumene: $LiAlSi_2O_6$ Nepheline: $NaAlSiO_4$	Melt temperatures from 1,100°C-1,400°C; controlled crystallization temperatures between 530°C -720°C; pyrochlore phase is a host for actinides and Sr; pollucite is a host for Cs and Rb; noble metal fission products form small metallic droplets; leaching characteristics have been noted to be comparable to the borosilicate glasses; research on this material has been limited.	Donald et al., 1997; Lutze and Ewing, 1988; Lutze et al., 1979
Diopside borosilicates	Borosilicate	Diopside: $CaMgSi_2O_6$ Powellite: $CaMoO_4$ Perovskite: $CaTiO_3$	Waste loadings of ~30 weight percent could be achieved using these materials for European and Japanese commercial wastes, which normally accommodate ~16 weight percent; glasses were melted at 1,300°C and controlled crystallization was carried out at temperatures in the range 800°C-1,100°C; Cs was in the diopside phase; La, Ce, Nd, and Pr were in the perovskite phase; Sr and Sm were in the glass phase; noble metals were metallic.	Donald et al., 1997; Lutze and Ewing, 1988; Lutze et al., 1979; Ninomiya et al., 1981

Titania based				
SYNROC and sphene	Sodium aluminosilicate with TiO_2 and CaO	Sphene: $CaTiSiO_5$ Pyrochlore: $Ca(RE,U)Ti_2O_7$ Zirconolite: $CaZrTi_2O_7$ Perovskite: $(Ca,Re,U,Sr)TiO_3$ Anorthite: $CaAl_2Si_2O_8$	GCMs containing TiO_2 are known as sphene glass ceramics; other formulations that produce the same phases as the SYNROC crystalline ceramic forms, mainly zirconolite, can also be produced. Forms between 1,300°C-1,500°C. Actinides and REEs, and some Sr are incorporated into zirconolite phase; Cs and the remaining Sr are incorporated into the vitreous phase. As a rule, leach rates for the actinides and REEs from zirconolite glass-ceramics are between 10^{-4} and $10^{-2} g/m^2 day$.	Advocat et al., 1998; Donald et al., 1997; Hayward, 1988; Lashtchenova and Stefanovsky, 1998a,b; Loiseau et al., 2001; Lutze and Ewing, 1988; Martin et al., 2002; McGlinn et al., 2001; O'Holleran et al., 1997; Stefanovsky et al., 2004; Vance et al., 1996a,b; Zyryanov and Vance, 1997
Alkali titanium silicate	Sodium titanium silicates	Corundum: Al_2O_3 Cristobalite: SiO_2 Albite: $NaAlSi_3O_8$ Zirconolite: $CaZrTi_2O_7$ Perovskite: $(Ca,Re,U,Sr)TiO_3$ Zircon: $ZrSiO_4$	Formed by HIPing calcine (70 weight percent) with Si, Ti, Al metal, and alkali oxides; for high Zr containing ICPP wastes.	Donald et al., 1997; Lutze and Ewing, 1988; Vinjamuri, 1995

continued

TABLE 3.4 Continued

Material	Glass Phase	Crystalline Phase(s)	Comments	Selected References
Barium titanium silicate	Barium silicates with TiO_2	Fresnoite: $Ba_2TiSi_2O_8$ Ba priderite: $BaFe_2Ti_6O_{16}$ Pyrochlore: $RE_2Ti_2O_7$ Scheelite: $BaMoO_4$	Forms at 1,200°C. Fresnoite phase hosts Ba and Sr; priderite phase hosts Ba; pyrochlore phase hosts RE, actinides, and Sr. Cs remains in the glassy phase. Glass is 50 percent and crystalline phases are 50 percent. A reheat step is required and Ba is a RCRA metal.	Donald et al., 1997; Hayward, 1988; Lutze and Ewing, 1988; Stefanovsky et al., 2004
Silicate based				
Basalt	Complex natural oxide based on Si, Ca, Mg, Fe, Al, and Ti	For Purex wastes: Augite: $(Ca, Mg, Fe)_2Si_2O_6$ Powellite: $(Ca, Sr)MoO_4$ Spinel: $(NiFe_2O_4)$	Different waste loadings from different waste sources are possible; glasses melt in the range 1,300°C-1,400°C. Crystallization is carried out at temperature ranges 670°C-700°C and 900°C-950°C. The chemical durabilities of these glass-ceramic materials are superior to borosilicate glass.	Donald et al., 1997; Hayward, 1988; Lutze and Ewing, 1988; Saidl and Ralkova, 1966; Stefanovsky et al., 2004; Tolstova et al., 2002
Iron enriched basalt (IEB)	Aluminosilicate glass	Iron spinel Feldspars: $NaAlSi_3O_8$ to $CaAl_2Si_2O_8$ Augite: $(Ca, Mg, Fe)_2Si_2O_6$ Fluroapatite: $Ca_5(PO_4)_3F$ Zircon: $ZrSiO_4$ Fluorite: CaF_2 Cristobalite: SiO2 Hematite: Fe_2O_3 Mullite: $Al_6Si_2O_{13}$	Applications to commercial and defense wastes, including decontamination of Three Mile Island containment water together with core debris; Melts at 1,400°C-1,500°C and controlled cooling after casting the glass into containers.	Donald et al., 1997; Hayward, 1988; Lutze and Ewing, 1988; Stefanovsky et al., 2004

IEB with TiO_2 and ZrO_2	Aluminosilicate glass	Same as above plus: Zirconolite Pseudobrookite: Fe_2TiO_5 Chevkinite: $Ce_4Fe_2Ti_3Si_4O_{22}$	Cast glasses crystallized by holding at 1,200°C for 16 h; Ti phases retain actinides.	Donald et al., 1997; Hayward, 1988; Lutze and Ewing, 1988; Stefanovsky et al., 2004
Magnesium aluminosilicate (MAS)	Magnesium aluminosilicate	Enstatite: $MgSiO_3$ Indialite/Corderite: $Mg_2Al_4Si_5O_{18}$	Used as an encapsulant for Zr alloy cladding wastes; made by press and sinter and accommodated 20 weight percent ZrO_2.	Donald et al., 1997
Phosphate-based				
Apatite/monazite glass ceramics	Calcium phosphate	Apatite: $Ca_5(PO_4)_3(F,Cl)$ Monazite: $(Ce,U)PO_4$	Apatite hosts Ca, P, F, Cl, S, Sr, Cs, As, Pb, Ba, Hg, Cd, Cr, U, and Ce; Melts at 1,400°C, crystallizes at 1,150°C and allowed to furnace cool; investigated primarily for phosphate-rich or fluoride-rich waste streams including ICPP CaF_2 wastes.	Knecht and Berreth, 1981; Wronkiewicz et al., 1996; Zhao et al., 2001
Low temperature sintering glasses	Bi-oxide based glasses	Mordenite zeolite	Low-temperature sintering allows for glass encapsulation of volatile gas-containing matrices (e.g., AgI-MOR)	Garino and Nenoff, 2011; Garino, et al., 2010; Sava et al, 2011

TABLE 3.5 Single-Phase Crystalline Ceramic Materials (Type 3a in Table 3.1)

Crystalline Ceramic Phase	Nominal Composition(s)	Selected References
Simple Oxides		
XO_2 Oxides	ZrO_2, UO_2, ThO_2, HfO_2, and PuO_2 have the simple fluorite CaF_2 cubic structure.	Burghatz et al., 1998; Gong et al., 2000; Poinssot et al., 2005; Sickafus et al., 1999
Complex Oxides		
Pyrochlore	A derivative of the fluorite structure type, $A_2B_2O_7$, where A-site contains large cations (Na, Ca, U, Th, Y, and lanthanides) and the B-site contains smaller, higher-valence cations (Nb, Ta, Ti, Zr, and Fe^{3+}).	Chakoumakos, 1984; Chakoumakos and Ewing, 1985; Ewing et al., 2004; Laverov et al., 2010
Murataite	Also a derivative of the isometric fluorite structure $A_6B_{12}C_5TX_{40-x}$ with multiple units of the fluorite unit cell; hosts U, Pu, and rare earth elements.	Lian et al., 2002; Morgan and Ryerson, 1982; Sobolev et al., 1997a,b; Stefanovsky et al., 2004, 2007a,b,c; Urusov et al., 2005; Yudintsev et al., 2007
Zirconolite	Monoclinic $CaZrTi_2O_7$ has a fluorite-derived structure closely related to pyrochlore, where plutonium may be accommodated on the Zr-site, as in the case of $Ca(Zr,Pu)Ti_2O_7$.	Boult et al., 1987; Clinard et al., 1982, 1984; Vance et al., 1994a,b; Zhang et al., 2009
Perovskite	$CaTiO_3$ has a wide range of compositions as stable solid-solutions; orthorhombic; consists of a 3-dimensional network of corner-sharing TiO_6 octahedra, with Ca occupying the large void spaces between the octahedra (the corner-sharing octahedra are located on the eight corners of a slightly distorted cube); plutonium, other actinides, and rare-earth elements can occupy the Ca site in the structure, as in $(Ca,Pu)TiO_3$.	Boult et al., 1987; Vance et al., 2004
Ba-Hollandite	$Ba_{1.2}(Al,Ti)_8O_{16}$	Carter et al., 2002, 2004

TABLE 3.5 Continued

Crystalline Ceramic Phase	Nominal Composition(s)	Selected References
Ferrite garnet	${}^{[8]}A_3{}^{[6]}B_2[TiO_4]_3$, e.g., $\cdot[^{8}]^{(}$Ca,Gd, actinides$)^{[6]}Fe_2{}^{[4]}Fe_3O_{12}$	Laverov et al., 2010
Crichtonite	$(Sr,La,Ce,Y)(Ti,Fe^{3+},Mn)_{21}O_{38}$	Gong et al., 1995
Freudenbergite	$Na_2(Ti,Fe)_8O_{16}$	Vance et al., 1994c
Simple Silicates		
Zircon/Thorite	$ZrSiO_4$/$ThSiO_4$; zircon is an extremely durable mineral that is commonly used for U/Pb age-dating, because high uranium concentrations (up to 20,000 ppm) may be present.	Ewing et al., 1995a; Meldrum et al., 2000
Titanite (sphene)	$CaTiSiO_5$	Hayward, 1988; Park et al., 2009
Garnet	$A_3B_2(XO_4)_3$; distorted cubic structure; BO_6 octahedra and XO_4 tetrahedra establish a framework structure alternately sharing corners; A and B sites can host actinides and rare earth elements, and X =Si^{4+}, Fe^{3+}, Al^{3+}, Ga^{3+}, Ge^{4+}, and V^{5+}, making silicate, ferrite, aluminate, gallate, germinate, and vanadate garnets.	Utsonomiya et al., 2002; Yudintsev, 2001, 2003; Yudintsev et al., 2002
Britholite (silicate apatite) Also known as oxy-apatites in the literature.	$(REE, Ca)_5(SiO_4,PO_4)_3(OH,F)$; i.e., $Ca_2Nd_8(SiO_4)_6O_2$, $Ca_2La_8(SiO_4)_6O_2$, where REE = rare earth elements; based on ionic radii of Nd^{3+}, La^{3+}, and Pu^{3+}, an extensive range of solubility for Pu^{3+} substitution for the Nd or La, particularly on the *6h* site, is expected. Because there is an extensive range in the Ca/REE ratio in these silicate apatites, a fair amount of Pu^{4+} substitution may be possible; La^{3+} through Lu^{3+} can substitute for Ca^{2+} and form oxyapatites, $RE_{4.67}\square_{0.33}[SiO_4]_3O$ (where $\square$ = vacancy site) and can also accommodate Sr and Cs.	Fahey et al., 1985; Felsche, 1972; Jantzen and Glasser, 1979; McCarthy and Davidson, 1975; Utsunomiya et al., 2003; Weber, 1983, 1993

continued

TABLE 3.5 Continued

Crystalline Ceramic Phase	Nominal Composition(s)	Selected References
Framework Silicates		
Zeolites[a]	$X_{x/n}(AlO_2)_x\ (SiO_2)_y$ where X is the charge balancing counter-ion, n is the charge of the counter-ion, x is the number of charge-deficient alumina sites, and y is the number of charge-neutral silica sites; characterized by internal voids, channels, pores, and/or cavities of well-defined size in the nanometer range, ≈4Å-13Å; channels and/or cavities may be occupied by charge-compensating ions and water molecules; zeolites such as Ag-Mordenite selectively sorbs I_2 (I-129); certain zeolites can be converted to condensed oxide ceramics by heating. This process is particularly attractive for waste form fabrication because capture and storage is preformed with minimal steps.	Breck, 1974; Chapman et al., 2010; Cronstedt, 1756; Higgins et al., 2002; Smith, 1963, 1976; Yudintsev et al., 2002
Pollucite	$(Ca, Na)_2Al_2Si_4O_{12}\bullet 2H_2O$; host for fission products such as Cs-137.	Gallagher and McCarthy, 1981; Kaminski et al., 2009; Komameni and White, 1981; Mimura et al., 1990; Strachan and Schulz, 1979; Yanagisawa et al., 1987
Pollucite (Cs/Ti version)	$CsTiSi_2O_{6.5}$	Anthony et al., 1993; Balmer and Bunker, 1995; Garino et al., 2009; McCready et al., 1997; Su et al., 1996, 1999; Xu et al., 2000, 2001
Nepheline	$NaAlSiO_4$ silica "stuffed derivative" ring type structure; some polymorphs have large nine-fold cation cage sites while others have 12-fold cage-like voids that can hold large cations (Cs, K, Ca); natural nepheline structure accommodates Fe, Ti and Mg.	American Mineralogist Crystal Structure Database, 2010; Berry and Mason, 1959; Deer et al., 1963; Jantzen, 2008; Kim et al., 2007; Klingenberg and Felsche, 1986; Sinkler et al., 2000
Leucite	$KAlSi_2O_6$; K analogue of nepheline	

TABLE 3.5 Continued

Crystalline Ceramic Phase	Nominal Composition(s)	Selected References
Sodalite group (Note: The name of the mineral changes with anions sequestered in cage structure).	Sodalite $Na_8Cl_2Al_6Si_6O_{24}$, also written as $(Na,K)_6[Al_6Si_6O_{24}]\bullet(2NaCl)$ to demonstrate that 2Cl and associated Na atoms are in a cage structure defined by the aluminosilicate tetrahedra of six adjoining $NaAlSiO_4$; a naturally occurring feldspathoid mineral; incorporates the alkali, alkaline earths, rare earth elements, halide fission products, and trace quantities of U and Pu; sodalite is being investigated as a durable host for the waste generated from electrorefining operations deployed for the reprocessing of metal fuel; minor phases in HLW supercalcine waste forms[b] where they retained Cs, Sr, and Mo, e.g., $Na_6[Al_6Si_6O_{24}](NaMoO_4)_2$; sodalite structures are known to retain B, Ge, I, Br, and rare earth elements in cage-like structures.	Brookins, 1984; Buhl et al., 1989; Deer et al., 1963; Fleet, 1989; Jantzen, 2008; Kim et al., 2007; Mattigod et al., 2006; McFarlane et al., 1997; Olson et al., 2004; Nakazawa et al., 2001; Sinkler et al., 2000
	Nosean: $(Na,K)_6[Al_6Si_6O_{24}](Na_2SO_4)$, silica "stuffed derivative" sodalite cage-type structure host mineral for sulfate or sulfide species.	
	Hauyne: $Na_6[Al_6Si_6O_{24}]((Ca,Na)SO_4)_{1\text{-}2}$ sodalite family; can accommodate either Na_2SO_4 or $CaSO_4$.	
	Helvite: $Mn_4[Be_3Si_3O_{12}]S$; Be can be substituted in place of Al and S_2 in the cage structure along with Fe, Mn, and Zn.	
	Danalite $(Fe_4[Be_3Si_3O_{12}]S)$.	
	Genthelvite $(Zn_4[Be_3Si_3O_{12}]S)$.	
	Lazurite $(Ca,Na)_6[Al_6Si_6O_{24}]((Ca,Na)S, SO_4,Cl)_x$; can accommodate either SO_4 or S_2, Ca or Na and Cl.	

continued

TABLE 3.5 Continued

Crystalline Ceramic Phase	Nominal Composition(s)	Selected References
Cancrinite	$(Na,Ca,K)_6[Al_6Si_6O_{24}]((Na,Ca,K)_2CO_3)_{1.6}\bullet 2.1H_2O$: Only found in hydroceramic waste forms.	International Zeolite Association (IZA) website
Crystalline silicotitanate (CST)	$Na_2(H_2O)_2Ti_4O_5(OH)(SiO_4)_2Na(H_2O)_{1.7}$; similar in structure to natural sitinakite: $Na_2(H_2O)_2Ti_4O_5(OH)(SiO_4)_2K(H_2O)_{1.7}$ and natural titanosilicate pharmocosiderite minerals; selectivity for monovalent cations (e.g., Cs); enhanced selectivity for Cs over entire pH range when doped with specific transition metals (e.g., Nb).	Andrews and Harbour, 1997; Anthony et al., 1993; Miller and Brown, 1997; Nyman et al., 2001; Sokolova et al., 1989; Yakovenchuk et al., 2008; Yu et al., 2002; Xu et al., 2000
Phosphates		
Monazite	$CePO_4$ or $LaPO_4$; very corrosion resistant and can incorporate a large range of radionuclides including actinides and toxic metals into its structure; has been proposed as a potential host phase for excess weapons plutonium and as a host phase for radionuclides and toxic metals in glass-ceramic waste forms for low-level and hazardous wastes.	Boatner and Sales, 1988; Ewing and Wang, 2002; Ewing et al., 1996; Glorieux et al., 2009; Montel et al., 2006; Wronkiewicz et al., 1996; Zhang and Vance, 2008
Apatite	$Ca_{4-x}RE_{6+x}(SiO_4)_{6-y}(PO_4)_y(O,F)_2$; actinide-host phases in HLW glass, glass-ceramic waste forms, ceramic waste forms, and cement; actinides can readily substitute for the rare earth elements in the crystal structure, as in $Ca_2(Nd,Cm,Pu)_8(SiO_4)_6O_2$, and fission products are also readily incorporated; however, the solubility for tetravalent Pu may be limited without other charge-compensating substitutions; has been proposed as a potential host phase for Pu and high-level actinide wastes.	Audubert et al., 1997; Boyer et al., 1997; Bros et al., 1996; Carpena and Lacout, 2005; Carpena et al., 2001; De et al., 1976; Ewing and Wang, 2002; Ewing et al., 1996; Jantzen and Glasser, 1979; Kim et al., 2005; McCarthy, 1977; McCarthy and Davidson, 1975; Park et al., 2002; Weber, 1982, 1993; Weber et al., 1997a,b; Wronkiewicz et al., 1996

TABLE 3.5 Continued

Crystalline Ceramic Phase	Nominal Composition(s)	Selected References
Xenotime	YPO_4	Ewing and Wang, 2002
Sodium zirconium phosphate (NZP)	$NaZr_2(PO_4)_3$; structure can incorporate a complex variety of cations, including plutonium; three-dimensional network of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra in which plutonium can substitute for Zr, as in $Na(Zr,Pu)_2(PO_4)_3$; complete substitution of Pu^{4+} for Zr has been demonstrated in NZP.	Ewing and Wang, 2002; Orlova et al., 1994; Scheetz and Roy, 1988; Scheetz et al., 1994
Thorium phosphate diphosphate	$Th_4(PO_4)_4P_2O_7$; a unique compound for immobilization of Pu and U; partial substitution of Pu for Th has been demonstrated (up to 0.4 mole fraction), complete substitution is not possible.	Dacheux et al., 1998a,b; Ewing and Wang, 2002; Pichot et al., 2000

[a] In recent usage, *zeolite* represents the framework topology of the 3D porous crystalline inorganic frameworks (with or without water); it can be applied to the framework of related minerals, their synthetic analogues, and/or non-aluminosilicate porous crystalline 3D frameworks. Structural information from the International Zeolite Association (IZA) website, http://www.iza-structure.org/databases/; see Analcime analogues (ANA).

[b] Supercalcines were the high-temperature silicate-based "natural mineral" assemblages proposed for HLW waste stabilization in the United States (1973-1985).

or more crystalline phases.[6] Single-phase crystalline ceramics (Table 3.5) can be used to immobilize separated radionuclides (e.g., plutonium-239) or more chemically complex waste streams (e.g., HLW). In the latter case, the atomic structure of the ceramic phase must have multiple cation and anion sites that can accommodate the variety of radionuclides present in the waste stream. These materials are potentially attractive for immobilizing long-lived alpha emitting actinides such as plutonium, neptunium, and americium (Burakov et al., 2010). However, some of these materials are susceptible to radiation damage effects associated with alpha decay from actinides; these effects have recently been summarized in Ewing and Weber (2010).

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[6] However, as noted previously, even materials that are predominantly a single phase will frequently have trace amounts of other phases segregated along grain boundaries or as inclusions of unreacted material.

TABLE 3.6 Multiphase Crystalline Ceramic Materials (Type 3b in Table 3.1)

Multiphase Ceramic Waste Form	Description	Selected References
SYNROC		
Titania Based	Dense, multiphase titanate-based waste form designed for the immobilization of HLW; interest in this multiphase crystalline ceramic stems from the robust nature of individual phases and because this phase assemblage is very tolerant to changes in the waste-to-precursor-titanate oxide ratio; in most cases the ratios of the phases vary as the waste loading changes but new phases are not introduced. The original SYNROC phase assemblage included: zirconolite ($CaZrTi_2O_7$), which incorporates rare earths and actinides; perovskite ($CaTiO_3$), which incorporates rare earths, actinides, and Sr; and hollandite ($BaAl_2Ti_6O_{16}$), which incorporates Cs, Rb and Ba, and rutile (TiO_2). Though the original SYNROC-C was designed for the immobilization of HLW, new variants for actinides and Pu and U have been developed.	Ewing and Weber, 2010; Maddrell, 2001; Reeve et al., 1984; Ringwood, 1978,1985; Ringwood et al., 1978, 1979, 1988; Vance, 1994; Vance et al., 1996b
Supercalcine Ceramics		
Silicate based	Supercalcines are silicate-, phosphate-, and oxide-based ceramics and can include some minor titanate phases. They are specifically tailored for HLW from different reprocessing schemes. They have very high loadings of fission products, typically 70 weight percent (simulated by stable isotopes in the experimental work), and the chemistry of the different phases is driven by the fission products as majority components. Typical phases are pollucite ($CsAlSi_2O_6$); powellite ($CaMoO_4$); and rare earth apatites and phosphates (e.g., monazite, $REPO_4$, where RE = trivalent rare earths) with monazite; fluorite ($(U,Zr,Pu)O_2$), scheelite ($SrMoO_4$); corundum, spinel, rutile, and sodalite phases found as well.	Felsche, 1972; Jantzen and Glasser, 1979; McCarthy, 1977; McCarthy et al., 1979a,b; Roy, 1977, 1979

TABLE 3.6 Continued

Multiphase Ceramic Waste Form	Description	Selected References
Tailored Ceramics		
Alumina based	Tailored ceramics are primarily aluminate-based with compatible phases of alumina, spinel (nominally $MgAI_2O_4$), magnetoplumbite (nominally $X(Al, Fe)_{12}O_{19}$ where X = Sr, Ba, or charge substituted paris such as $[Cs_{0.5} + La_{0.5}]$), and a fluorite-related uraninite ($(U,Th)O_2$). For wastes containing a high concentration of sodium, an additional crystalline phase, nepheline ($NaAISiO_4$) is produced to accommodate the monovalent ion. The magnetoplum-bite phase acts as a host for the radionuclides Sr and Cs, and the phase assemblage is analogous to a naturally occurring placer deposit of alumina-spinel-hibonite (magnetoplumbite)-thoria, found in Fort Dauphin, Malagasy.	Clarke et al., 1982; Harker, 1988; Harker et al., 1981a,b, 1983; Jantzen et al., 1982a,b; Morgan et al., 1981

Multiphase crystalline ceramics (Table 3.6) consist of an assemblage of crystalline phases. Individual phases are selected for the incorporation of specific radionuclides, with the proportions of phases varying depending on the composition of the waste stream. An individual phase can host one or more radionuclides, including solid solutions of radionuclides. However, not all phases will host radionuclides.

The three best known examples of multiphase waste forms are SYNROC, which is based on titanium ceramic phase assemblages; supercalcine ceramics, which are silicate-based ceramic phase assemblages; and tailored ceramics, which are alumina-based ceramic phase assemblages.

3.3.4 Metals

Several different types of metallic materials have been studied as potential waste forms. Like crystalline ceramics, metal waste forms can consist of single or multiple phase assemblages, and the waste form itself can be granular or monolithic. Metal waste forms can be fabricated sintering or casting. Each of these techniques has drawbacks; in particular, it can be difficult to find metal compositions and processes that effectively wet and encapsulate dispersed phases or fines.

Metal waste forms composed predominantly of lead and lead-based alloys are being used in Russia (and have been used in Belarus and Ukraine) to immobilize radioactive sources (Arustamov et al., 1999; Ojovan et al., 2004). Metal waste forms are being used by DOE-EM to immobilize metallic fuel waste, including fuel hulls, at INL. The waste is solidified by melting at 1,560°C into a uniform, homogeneous waste form. Typically, zirconium is added to the waste, which lowers its melting point and generates enough Fe_2Zr intermetallic phase to accommodate the transuranic elements (Ebert, 2005). As a result, waste loading is typically above 90 percent (Marsden and Westphal, 2006).

Metallic composite waste forms produced by hot isostatic pressing (see Chapter 4) are under study by the Australian Nuclear Science and Technology Organisation (ANSTO) for applications in the United Kingdom (Begg and Smith, written communication). Metal encapsulation will be used to immobilize debris waste streams (e.g., cermets, silicon carbide, graphite, broken fuel pins, fuel hulls) that are not economically feasible to process by other means. The encapsulant material provides a second level of protection to the release of radionuclides.

3.3.5 Cements

Cements are inorganic materials that set and harden as a result of hydration reactions. Cements microencapsulate wastes (Table 3.1), although there is recent evidence that during hydration three binding mechanisms can also occur between the cement and metal ions in the waste (Cocke and Molla, 1993; Cougar et al., 1996; Glasser, 1997):

- Precipitation of metal ions into the alkaline matrix as an oxide, mixed oxide, or as another discrete solid phase.
- Adsorption or (co-)precipitation of metal ions onto the surface of cement minerals.
- Incorporation of metal ions into hydrated cement minerals as they crystallize.

These processes are not mutually exclusive.

The most common type of cement, Portland cement, consists of calcium silicates, other aluminum and iron containing phases, and additives such as gypsum to control set time. Portland cement, when mixed with water and aggregates, hydrates to form concrete. Grout, a mixture of Portland cement and various sand mixtures, is commonly used to encapsulate radioactive wastes. DOE-EM is filling emptied HLW tanks at SRS and INL with grout to immobilize waste heels and provide structural support.

Cements are used to immobilize waste having relatively low levels of radioactivity (i.e., low- or intermediate-level radioactive wastes). Higher-activity wastes can result in radiolysis and production of hydrogen gas from the breakdown of water or hydroxyl groups in the cement (Bibler, 1980). To minimize radiolysis, the use of concrete formed under elevated temperature and pressure (FUETAP), which reduces the amount of entrapped water to about 2 percent, was considered for the immobilization of HLW (McDaniel and Delzer, 1988; Moore, 1981). This idea was eventually abandoned because of the complexity of processing. To the committee's knowledge, no waste processing programs are pursuing this technology today.

Modeling has shown that cements can be "designed" to retain radioactive and hazardous constituents (McPhee and Glasser, 1993). In fact, much research has focused on improving the effectiveness of grout in adverse environments associated with the disposal of radioactive waste (Ghattas et al., 1998; Mattus, 1998; Merz and Khalil, 1992). As discussed in these references, a variety of cement-polymer composites have been investigated as a means of making grouts more compatible with the radioactive and chemical constituents in waste.

For example, the addition of blast furnace slag to Saltstone,[7] which is being used to dispose of low-activity waste at SRS (see Chapter 2), provides a chemical reductant [iron(II)] and a precipitating agent (sulfide) that chemically binds contaminants such as chromium and technetium as insoluble species, thus reducing their tendency to leach from the waste form. Experimentation has shown that leaching of chromium and technetium was effectively reduced to levels that would allow all projected future salt solution compositions to be processed into Saltstone (MMES et al., 1992). These experiments showed that the addition of slag essentially stopped technetium-99 leaching, although it did not reduce nitrate leaching.

3.3.6 Geopolymers and Hydroceramics

Less mature technologies have been investigated for low-activity waste disposal since the mid-1990s. These include geopolymers and hydroceramics, which are described in the following subsections.

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[7] The Saltstone that is being used to immobilize low-activity waste at Savannah River contains 5 weight percent cement, 25 weight percent fly ash, 25 weight percent blast furnace slag, and 45 weight percent salt solution.

3.3.6.1 Geopolymers

Geopolymers are ceramic-like, inorganic polymers made from aluminosilicates cross-linked with alkali metal ions (Barbosa et al., 2000; Davidovits, 1994; Kriven et al., 2004). A low water content is used (H_2O/M_2O ~10-25 weight percent, where M denotes the alkali metals sodium, potassium, or cesium) so that an amorphous geopolymer forms instead of crystalline zeolites. A nominal composition of $4SiO_2{\bullet}Al_2O_3{\bullet}M_2O$ is often used to represent the geopolymer matrix, although Si:Al ratios can vary from 1 to 3 depending on the intended application. For cement- and concrete-like applications a ratio of 2:1 is nominally used (Sheppard, 2005). Geopolymers appear to be excellent low-temperature binders and are environmentally more acceptable[8] than cement waste forms.

Geopolymers are typically made by mixing an aluminosilicate such as metakaolinite ($Al_2O_3{\bullet}2SiO_2$) or Class F fly ash with a highly caustic hydroxide solution and an alkali silicate solution of the type $(Na,K,Cs)_2Si_2O_5$. Geopolymers can be formed under ambient conditions (Kriven et al., 2004) but often are autoclave cured between 80°C-120°C to produce an amorphous, cross-linked, three-dimensional structure. Curing of large-scale monoliths in a steam room at 40°C-45°C has been found to be adequate for stabilization of mining wastes (Davidovits, 1995; Hermann et al., 1999; van Jaarsveld et al., 1996).

Geopolymers and geopolymeric cements, including but not limited to fly ash-based geopolymeric concretes, are candidates for environmental applications, including permanent encapsulation of radioactive waste (Hanzlicek and Steinerova-Bopndrakova, 2006; Hanzlicek et al., 2006) and other hazardous waste (Perera et al., 2005), and also as sealants, caps, barriers, and other structures necessary for remediation of contaminated sites. Geopolymers have been used in pilot-scale demonstrations on both mining wastes and uranium mill tailings in Europe (Davidovits, 1995; Hermann et al., 1999; van Jaarsveld et al., 1996) and were also investigated in the mid to late 1990s for the disposal of radioactive wastes (Khalil and Merz, 1994; Zosin et al., 1998).

More recently, geopolymers have been investigated as a waste form for stabilization of Resource Conservation and Recovery Act metals; as binders for granular mineral wastes produced by fluidized bed steam reforming for low-activity waste at Hanford; and for the stabilization of cesium-137 and strontium-90 wastes.

Special geopolymer formulations, marketed under the name DuraLith,

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[8] Production of the raw materials used to make cement emits CO_2. Production of geopolymer materials emits only water vapor; moreover, geopolymers can be made from fly ash, a byproduct and waste from coal-fired power plants.

have been patented (Gong et al., 2006) by the Vitreous State Laboratory (VSL) in Washington, D.C. Testing of DuraLith formulation by Pacific Northwest National Laboratory (Gong et al., 2006) and VSL (W. Lutze, VSL, written communication) showed great promise for stabilization of technetium.

3.3.6.2 Hydroceramics

Hydroceramics are concrete-type materials that are made by curing a mixture of inorganic waste, calcined clay (metakaolin, $Al_2O_3 \bullet 2SiO_2$), vermiculite, Na_2S, and NaOH with water under hydrothermal conditions (60°C-200°C) to form a matrix containing crystalline tectosilicates (zeolites) embedded in a sodium aluminosilicate matrix (Bao et al., 2004). The solidification process occurs as a result of hydration reactions. The NaOH solution dissolves the metakaolin much the same as in geopolymers, but the presence of abundant water or hydroxide results in the production of crystalline silicates instead of an amorphous matrix. These silicates have sodalite and cancrinite structures, which can trap constituents and render them insoluble.

Hydroceramic waste forms have several potential applications to DOE-EM waste streams. They have been shown to be effective for immobilizing low-activity sodium-bearing waste at INL. Additionally, Scheetz and Olanrewaju (2001) have developed hydroceramic waste forms for HLW calcines at INL. However, the need for denitration and high-temperature curing will likely preclude the use of hydroceramics for immobilizing low-activity waste streams at SRS and INL.

3.3.7 Ceramicretes

Ceramicretes are phosphate-bonded ceramics, also known as chemically bonded phosphate ceramics. These materials are produced by reacting magnesium oxide, monopotassium phosphate, and the stoichiometrically required amount of water according to the reaction

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \bullet 6H_2O$$

This reaction is exothermic and occurs rapidly at room temperature. The reaction product, ceramicrete ($MgKPO_4 \bullet 6H_2O$), is a hard, insoluble phosphate ceramic (Wagh et al., 2003) that contains a considerable amount of bound water. Waste constituents react with the material to form insoluble phosphates or are encapsulated in the matrix.

A patented technology for producing ceramicretes (Wagh and Singh,

1997) has been licensed to treat mixed and low-level wastes and is being used for macroencapsulation and containerization of uranium. Phosphate ceramics are also used for road and highway repairs, and the oil industry is testing these materials for drilling casing and capping. The medical/dental industry is also using several phosphate-ceramic formulations.

DOE has also examined the suitability of this waste form for both micro- and macro-encapsulation of radioactive and hazardous waste streams, e.g., low-activity waste streams typical of Hanford and other sites. Testing of ceramicrete made with INL's sodium-bearing waste and Hanford Waste Treatment Plant Secondary Waste has been performed at Pacific Northwest National Laboratory.

3.4 DISCUSSION

As the discussion in this chapter illustrates, there are a wide variety of waste form materials that could potentially be used to immobilize radioactive and chemically hazardous wastes. Some waste form materials have been demonstrated in real-world applications on radioactive and hazardous wastes, whereas other have only been researched or demonstrated in the laboratory or at pilot scales.

The committee judges that there are many potential applications of new and improved waste form materials to DOE-EM waste streams. Table 3.7 illustrates the potential compatibility of the waste form materials described in this chapter to some of the DOE-EM waste streams that were described in Chapter 2. Note particularly:

- All eight classes of waste form materials that are described in this chapter are potentially compatible with one or more DOE-EM waste streams.
- Borosilicate glass is already being used by DOE-EM to immobilize HLW, and DOE-EM plans to use glass to immobilize low-activity waste at Hanford (see Chapter 2 and Appendix C). However, other waste form materials, in particular GCMs and crystalline ceramics, are potentially suitable for both of these applications.
- Glass, GCMs, and crystalline ceramic materials have the widest range of potential compatibilities with DOE-EM waste streams—in particular for HLW from tanks and high-sodium wastes, but also for cesium and strontium capsules (should DOE-EM decide not to dispose of those capsules directly) and excess plutonium.
- One or more of the encapsulant waste form materials (i.e., cements, geopolymer, ceramicrete, and hydroceramic waste forms) are potentially compatible with high-sodium wastes, cesium and strontium capsules, and wastes containing iodine-129 and technetium-99.

TABLE 3.7 Waste Form Compatibility with Selected DOE-EM Waste Streams

Waste Characteristics		**Waste Forms**								
Waste Types	Radionuclides	Borosilicate Glass	Other Glasses	Glass Composite Materials	Mineral Ceramics (Synroc)	Simple Oxides	Metal Matrix	Zeolites/Hydroceramics	Cements/Cermicrete	Geopolymers
HLW Tank Waste										
INL: Calcine	Cs, Sr, Tc, I	P[a]		C? /P	P					
SRS: Sludge (Al, Fe)		C		P[d]	P					
Hanford: Sludge (Al, Fe, Cr, Bi-P)		C	P[c]	P[e]	P					
High-Sodium Waste										
INL: Sodium-bearing waste	Fission Products (FP), low U, Pu	P		P	C			C	P	P
SRS: Low-activity waste/saltcake/supernate		P		P	P			P	C	P
Hanford: Low-activity waste/saltcake/supernate		C	P	P	P			P	P	P
Other										
Spent fuel and non-irradiated/irradiated	Pu, FP, TRU, U					P				
Cesium-strontium capsules	Cs, Sr	P	P	P	P			P		
Tank heels	FP, U								C	
Excess plutonium oxides	Pu	P[b]	P	P	P	P				

continued

TABLE 3.7 Continued

Waste Characteristics		**Waste Forms**								
Waste Types	Radionuclides	Borosilicate Glass	Other Glasses	Glass Composite Materials	Mineral Ceramics (Synroc)	Simple Oxides	Metal Matrix	Zeolites/Hydroceramics	Cements/Cermicrete	Geopolymers
EBR-2 (Experimental Breeder Reactor)	I, Cl			C			P	P		P
Melter recycle (Hanford)	I, Tc				P					
I and Tc^{99}	I, Tc				P		P	P		
Orphan wastes	?	?	?	?	?	?	?	?	?	?
Depleted Uranium	?	?	?	?	?	?	?	?	?	?

NOTES:
C = current application; P = possible application
[a] With blending, dissolving, low waste loading.
[b] Pu solubility low.
[c] With Bi-P or high SO_4.
[d] High waste loading.
[e] With high PO4, high waste or high Cr.

Of course, compatibility is just one of several considerations in selecting a waste form material to immobilize a specific waste stream. Other considerations include the ease of processing, cost, and risk. Processes for waste form production are described in the next chapter. The committee's finding on the fourth charge of its task statement (Box 2.1. in Chapter 2) is given in Chapter 1.

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4

Waste Processing and Waste Form Production

The focus of this chapter is on the fourth charge of the statement of task for this study (see Box 2.1 in Chapter 2), which calls for the identification and description of "potential modifications of waste form production methods that may lead to more efficient[1] production of waste forms to meet their performance requirements." Waste form production involves many complex operations, a comprehensive review of which is well beyond the scope of this study. Instead, this chapter presents some key unit operations/technologies that have been or could potentially be used to produce nuclear waste forms.

The following waste processing technologies are described in this chapter, and their key attributes are summarized in Table 4.1:

- Joule-heated melters
- Cold crucible induction melters
- In-container vitrification
- Self-sustaining vitrification
- Cold pressing and sintering
- Hot uniaxial pressing
- Hot isostatic pressing

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[1] A given waste processing technology is "more efficient" compared to a baseline technology when, for example, it enables higher material throughputs or higher waste loadings; accommodates higher levels of feed stream variability or liquid feed streams; accommodates higher levels of incompatible elements; results in reduced secondary wastes; is more operationally robust; or is less expensive.

TABLE 4.1 Waste Form Processing Technologies

Processing Technology	Processing Mode B=Batch C=Continuous	Treatment and Waste Stream Scale[a]	Waste Forms Produced
Joule-Heated, Melter (JHM)	C	Large	Borosilicate glass other glass types (LaBs, FeP, AIP, chalcognide, and others)
Advanced Joule Heated Melter (AJHM)	C	Large	Borosilicate glass, glass-ceramic materials, other glass types (LaBs, FeP, AIP, chalcognide, and others)
Cold Crucible Induction Melter (CCIM)	C	Large	Borosilicate glass, glass-ceramic materials, other glass types (LaBs, FeP, AIP, chalcognide, and others), crystalline ceramics/simple oxides, metal matrix
In-Container Vitrification (ICV) (also known as *bulk vitrification*)	B	Depends on container size (could be medium to large)	Borosilicate glass, glass-ceramic materials, other glasses (LaBs, FeP, AIP, chalcognide, and others)
Cold Press and Sinter	B	Small	Glass-ceramic materials, crystalline ceramic/simple oxides, metal matrix, zeolites, hydroceramics
Self-Sustaining Vitrification (SSV)	B	Small	Glass-ceramic materials
Hot Uniaxial Pressing (HUP)	B	Small	Glass-ceramic materials, crystalline ceramics/simple oxides, metal matrix, zeolites, hydroceramics
Hot Isostatic Pressing (HIP)	B	Small	Borosilicate glass (lab demonstration only), glass-ceramic materials, crystalline ceramics/simple oxides, metal matrix, zeolites, hydroceramics

Advantages	Disadvantages
Proven technology; typically operates with a "cold cap" to minimize volatility of species of concern	Materials of construction can be problematic for some wastes; solubility control of certain species (e.g., chromium spinels) critical; excessive spinels may seize-up melter; electrode erosion may be a problem
Increases throughput and melt rate compared to JHM	Operates with minimal or no "cold cap" with associated increases in volatility of species of concern
Allows the processing of corrosive glasses; no refractories; no metallic or oxide electrodes; water cooled; self-cleaning; high purity; can be stirred if needed; increases capacity compared to JHM and AJHM; can operate at higher temperatures than JHM and AJHM; operates with a "cold cap" to minimize volatility	Higher temperature operation can increase volatilization of species of concern but "cold cap" coverage minimizes these impacts
Relatively cheap and simple for low-activity wastes or contaminated soils; not applicable to high-level radioactive waste	Inhomogeneous waste forms produced; no temperature control so radionuclide vaporization is high; little to no convection in melt causes processing problems
Higher waste loadings; minimum disposal volumes	Usually small scale; may require precalcining or pretreating waste to an oxide form to avoid shrinkage of form
Low capital requirements, can be used to process small amounts of wastes at remote locations	May require some pre-processing, for example, grinding of the waste and pre-mixing
Higher waste loadings; minimum disposal volumes; mature flexible technology; mature industrial process	Usually small scale; may require precalcining or pretreating waste to an oxide form for shrinkage control
Zero off-gas emissions; higher waste loadings; minimum disposal volumes; mature flexible technology; no major secondary wastes; mature industrial process	Processes small quantities; can overpressurize if large amounts of volatiles (e.g., nitrates/hydrates) are present; may require precalcining or pretreating waste to an oxide form (shrinkage handled by bellows like canisters)

continued

TABLE 4.1 Continued

Processing Technology	Processing Mode B=Batch C=Continuous	Treatment and Waste Stream Scale[a]	Waste Forms Produced
Fluidized Bed Steam Reforming (FBSR)	C	Large	Crystalline ceramics/simple oxides, zeolites as formed, hydroceramics, geopolymers (as encapsulated)

[a] All processes characterized as "small" are batch processes. The size of the batch varies by technology. For example, HIP and SSV batches can range from less than a liter to several tens of liters in volume. The processing capacity depends on a multiplicity of factors, including the time scales of various physical process (e.g., time to charge, melt, and cool). Processes characterized as "large" are continuous processes that have the potential to handle several kilograms to several hundreds of kilograms of waste per hour. In HLW applications, for example, JHMs can typically process 3 tonnes per day per melter or 125 kilograms per hour; AJHMs can process up to about 4 tonnes per day. For LAW the production rate could be up to 25 tonnes per day. Similarly, a CCIM can double the capacity of waste processing. A fluidized bed, on the other hand, does not have the geometrical physical limitations imposed by JHMs or CCIMs and can process several hundred kilograms to several tonnes of waste per hour.

- Fluidized bed steam reforming
- Other thermal technologies
- Mix and set technologies

Cold crucible induction melters, hot isostatic pressing, and fluidized bed steam reforming technologies were discussed in the committee's interim report (NRC, 2010).

This list of technologies is not exhaustive. Rather, the committee selected technologies that it judged were potentially most relevant to the U.S. Department of Energy, Office of Environmental Management (DOE-EM) cleanup program.

4.1 JOULE-HEATED MELTERS

The term *Joule heating* refers to heating obtained by passing an electrical current through a resistively conducting material. The electrical resistance of the material causes the electrical energy to be converted to heat, with power dissipation following Ohm's Law.

A *Joule-Heated Melter* (JHM) is a refractory-lined container with nickel-chromium alloy electrodes, usually Inconel™. It is loaded with a

Advantages	Disadvantages
Industrially proven technology; acidic or basic tank wastes can be processed without neutralization; destroy organics and nitrates; convert aqueous components in a waste to stable, water-insoluble mineral products in single step; immobilize sulfur, chlorine, and fluorine in a stable mineral form with no secondary waste	Product is granular and requires a high-integrity container or encapsulation in a binder to make a glass ceramic material, a geopolymer, or a hydroceramic; radionuclide partitioning among the phases needs to be further studied

calcine or slurry containing waste and glass frit and is melted by applying voltage across the electrodes. The nominal melt temperature is 1,150°C, which is only 200°C lower than the melting point of the Inconel™ electrodes. A waste form is produced by pouring the molten material into a container and allowing it to cool. The melting and pouring processes can be operated in continuous or semi-continuous modes.

JHM technology is being tested or used successfully to immobilize high-level radioactive waste (HLW) in several countries, including Belgium, France, Japan, Russia, UK, and the United States (see Table 3.3 in Chapter 3). JHMs are part of the current DOE-EM baseline for immobilizing HLW at West Valley, Savannah River Site (SRS), and Hanford Site. Details on melter designs in use in different countries can be found in recent compendiums by Caurant et al. (2009), Jain (1998), Jantzen (in press), Ojovan (2011), and Ojovan and Lee (2005, 2007).

The size of a JHM is usually limited only by capacity of the cranes that are used to install and, if necessary, replace it; structural support is provided by a stainless steel shell of the melter, which contains the refractory. The Defense Waste Processing Facility (DWPF) at the Savannah River Site is the largest production JHM ever built. Larger JHMs are under construction for use at the Hanford Site; these large melters will be mounted on rails for ease of replacement.

Several improvements have been made to conventional JHM designs to increase throughputs and waste loadings. These improved designs are referred to as *Advanced Joule Heated Melters*, or AJHMs. These designs have been proven at the pilot scale with simulated wastes, as well as operated at the plant scale with mixed radioactive/hazardous waste at SRS where maintenance and repairs could be handled manually. They have not been operated with HLW where maintenance and repairs have to be performed remotely.

JHMs have production rates that are approximately proportional to the surface area of the melt; convection caused by the Joule heating is enhanced as the size of the melter is increased. So larger melters, with larger surface areas, have proportionately higher melt rates. The melt temperature is limited by the materials of construction of the electrodes, generally Inconel™ 690.

Melt rates can also be increased without increasing melter size through the following means:

- Adding lid heaters to increase the temperature of the melter plenum and enhance melting of the cold cap (i.e., the unmelted feed material on top of the melted mass).
- Adjusting the proportions of frit and cold chemical additions.
- Increasing the use of reducing agents (e.g., formic acid/sugar) to control oxygen foaming.
- Adding surface-active materials such as sulfates and halides.
- Increasing melter convection by using lower-viscosity glass, power skewing the bottom electrodes, or mechanical agitation (stirrer/bubblers/airlift pumps).
- Dry feeding instead of slurry feeding.
- Increasing the operating temperature.
- Bubbling to enhance feed to glass conversion.

Melt rates can also be increased by increasing melt temperatures. JHMs can be operated at ~1,200°C before different materials of construction are required. However, increased melt pool volatility, refractory corrosion, and electrode corrosion are to be expected at higher operating temperatures. In order to limit volatilization of radionuclides such as techentium-99 and ruthenium-104 in borosilicate melts, the melter can be operated with a cold cap and under reducing conditions to keep the technetium as sodium pertechnatate ($NaTcO_4$) and ruthenium as an oxide (RuO_2). The cold cap also helps minimize volatilization of cesium (as $CsBO_2$) and other alkali salts such as sodium chloride (NaCl), sodium fluoride (NaF), and sodium iodide (NaI) (Jantzen, 1991). The increasing production capability is offset by increasing complexity of the melter system.

The DWPF is considered to be a JHM with a few AJHM design features. It is round with a slightly sloped floor to avoid cold corners and improve melt pool convection. Wet feeding is used to avoid dusting and the need for a dust collection system. This melter also has lid heaters, adjusts the proportions of frit to waste, uses reducing agents to control oxygen foaming and convert nitrates to N_2, uses lower melting viscosity glasses, power skews the bottom electrodes, and uses an airlift pump to improve melt rate.

The planned Hanford HLW melter is a square AJHM melter.[2] It will allow the proportions of cold chemical additions to be adjusted, use of reducing agents to convert nitrates to N_2, and use of lower viscosity glasses. Additionally, it will allow use of power skewing of the bottom electrodes and use of bubblers[3] to improve melt rate and melt pool convection. Higher temperatures will be used. Partial dry feeding will also be used to improve melt rate.

The primary advantages of JHMs for waste immobilization are their high production rates and ability to produce waste form material of consistent quality. They can be designed with sloped bottoms and bottom drains with or without mixing to facilitate periodic draining of noble metals that may precipitate (as is done with the JHM in use at Tokai, Japan). The overall problems with noble metals in waste streams have been addressed by Bibler (2005) and some specifics of noble metals in a JHM have been treated by Jantzen and Lambert (1999).

JHMs also have several disadvantages: They are large compared to some other types of melters (see Section 4.2), and the electrodes and refractories require maintenance and periodic replacement. They are also intolerant of crystal growth in the melt, which causes slag formation. For example, the induction heating melter at Sellafield (Riley et al., 2009), which is not a JHM design, has shown the ability to increase waste loading from 25 weight percent to 38 weight percent by allowing spinel formation in the melt.[4] In comparison, the melter planned for Hanford will allow for only 1-2 percent crystallization of spinels; it is anticipated that these crystals will remain buoyant because of melt pool agitation by the bubblers. This strategy will likely work unless the crystals grow larger than can be sustained by the bubblers—as might happen, for example, during long maintenance outages.

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[2] Square melters have cold corners where glass can crystallize unless the melt pool is agitated. Round melters such as the DWPF and Japanese designs require no melt pool agitation except as needed to improve melt rate.

[3] The melter will be outfitted with eight twin-orifice melt bubblers that bubble air and thus improve melt rate and convection. The use of multiple bubblers with the capability for frequent replacements is considered to be an AJHM design.

[4] Transition metal-containing spinels form from the iron generated during fuel reprocessing and from corrosion products. Usually the least soluble component in the wastes is chromium, which readily precipitates in a melt as $(Fe,Ni)(Fe,Cr)_2O_4$ (Hrma et al., 2002).

4.2 COLD CRUCIBLE INDUCTION MELTING

The *Cold Crucible Induction Melter* (CCIM) consists of water-cooled tubes that are arranged to form a crucible, the contents of which are heated by induction. An inductor surrounding the crucible is energized by a high-frequency alternating current that induces eddy currents (and resultant Joule heating) of materials contained in the crucible. The melting process is usually initiated by inserting a resistive heating element into the crucible. This element couples with the fields to form an initial melt; the initial melt then couples with the electromagnetic field. At that point, the resistive element can be removed so that no foreign materials are in contact with the melt. A solid "skull" of quenched waste material, typically a few millimeters in thickness, forms along the inside crucible wall, protecting it from degradation and corrosion. The shell isolates the melt from the crucible so that the latter can be maintained at ambient conditions. This prevents molten materials from bonding to the crucible, allowing residuals to be removed at the end of the melting campaign. CCIMs are potential replacements for JHMs and AJHMs. As noted previously, JHMs with some AJHM features are now part of the current DOE baseline for production of high-activity and low-activity waste glass (see Chapter 2).

CCIMs have several advantages over both current-generation and advanced JHMs. They allow for higher throughputs and waste loadings. They are operationally simpler and allow for faster recoveries from system upsets.[5] The absence of internal electrodes and refractories allows for increased melter longevity and permits higher-temperature operation compared to current-generation JHMs. As a consequence, CCIMs can be used to process a wider range of waste compositions, including corrosive wastes that are incompatible with current-generation JHMs. Additionally, they can more easily accommodate differing glass compositions, including iron phosphate glasses, that are incompatible with many types of electrodes used in JHMs. CCIMs can be cycled frequently with varying feed compositions without thermal damage or loss of compositional control. And they are capable of producing crystalline ceramics through controlled or spontaneous crystallization. They can be fitted with stirrers to facilitate melt pool convection and homogenization so that crystals do not accumulate in one location in the melt pool.

CCIMs can also be used in conjunction with other technologies. For example, an integrated process that combines an oxygen plasma and induction-heated cold crucible is reported by Vernaz and Poinssot (2008). This process, which is still under development, is referred to as the Advanced

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[5] Simpler and more robust processing technologies are generally preferable because system upsets can pose critical bottlenecks for operations that must be conducted in hot-cell environments to protect workers from high radiation fields.

Hybrid System for Incineration and Vitrification (SHIVA). It consists of a single reaction vessel that has three functions: (1) incineration, (2) vitrification, and (3) gas post-combustion. This is a promising technology for processing mixed wastes containing radioactive, organic, and other hazardous chemical constituents that are difficult to separate by other processes. The plasma decomposes organic material, significantly reducing its volume, and produces a high-quality containment material (glass in this instance).

CCIM development began in France and Russia in the 1970s (Elliott, 1996). Russia is currently using CCIMs to process radioactive waste at the Mayak Plant (Demine et al., 2001; Kushnikov et al., 1997; Lifanov et al., 2003; Polyakov et al., 1997; Stefanovsky, 2009; Toumanov, 2003), and the French are using a CCIM to vitrify HLW at an industrial scale at the La Hague plant. DOE-EM is currently investigating CCIM technology for possible use in its HLW immobilization programs.

CCIM is an emerging technology for the vitrification of fission product solutions and decontamination waste streams. It also has potential applications for processing metallic waste streams (Vernaz, 2009). The underlying technology is proven, but operational experience in large-scale waste stream processing environments is limited in comparison to JHMs. Its deployment in DOE-EM applications may require some up-front development work to ensure its compatibility with specific process flow sheets, but no basic research is likely to be required. Of course, a CCIM system must be engineered for safety, for example, to prevent the loss of coolant. Gombert and Richardson (2001) have discussed such safety aspects for CCIM design.

Because CCIMs are smaller per unit of throughput and operationally more robust than JHMs, they could potentially be back-fitted to the Defense Waste Processing Facility at SRS (Barnes et al., 2008) and the Waste Treatment Plant at Hanford. For example, the DOE Independent Project Evaluation Team (IPET, 2003) examined the feasibility of replacing the JHMs in the Waste Treatment Plant at Hanford with CCIMs. It concluded that two CCIMs could be retrofitted into each of the two melter cells in the plant. If the melters were installed before the plant was hot commissioned, only about four months would be required to modify the melter cells and install the new equipment (IPET, 2003, p. 4.70). Additional time would be required to install the melters after hot commissioning—either to decontaminate the melter cells prior to installation of the new equipment or to construct a new melter facility.

Although CCIMs have a track record of successful deployment internationally, the experience and understanding for DOE applications are limited. Furthermore, the design of these melters is challenging in that, for example, one needs to understand the material properties, particularly the electrical resistivity of the melt, for determining the optimal operating conditions for a given crucible diameter. Some of these design challenges are summarized by Gombert and Richardson (2001). However, these are the kinds of challenges that are normally faced when implementing any new technology, and they can be overcome with appropriate development work.

4.3 IN-CONTAINER VITRIFICATION

In-Container Vitrification (ICV) (Thompson et al., 2003) is a batch process by which contaminated soil, liquid waste mixed with soil, and glass formers are vitrified *in situ* in a refractory-lined steel vessel. The energy for melting is generated by passing an electrical current through graphite electrodes installed in the vessel. The vitrified waste can be disposed of with or without the container; in the latter case the container can be reused. A similar concept for immobilizing contaminated soil in the ground, *In-Situ Vitrification*, was developed earlier (Thompson et al., 1992).

ICV requires soil- or glass-formers to establish the melt and create a stable, vitrified waste form. Therefore, soil or soil-like materials must be added to the waste stream being processed. (The silica and alumina contained in the soil are the glass formers for the process.) Because neither soil nor frit is a good electrical conductor at ambient conditions, melting is initiated by placing a conductive pathway between the electrodes.[6] The heat generated from graphite electrodes provides the electrical current in the vicinity of the conductive pathway and melts the soil or frit, which increases its electrical conductivity and establishes Joule heating. The melted zone gradually grows outward toward the refractory liner, and eventually the entire vessel contents become molten. The temperature of the melt varies between 1,400°C and 1,800°C depending on the composition of the soil and waste materials. It usually takes up to three days to melt and process a single batch.

The melting process destroys organic contaminants contained in the soil/waste mixture by pyrolysis or dechlorination. ICV can be equipped with an off-gas treatment system to capture any residual organic or other volatile materials released from the melt. The removal efficiency of the organics is typically greater than 99.9999 percent (Thompson et al., 2003).

The retention efficiency of most metals and radionuclides in the melt is greater than 99.99 percent for non-volatile species (Thomspon et al., 2003). The residuals released with the off-gas stream are captured either by filtration or scrubbing; radionuclide volatility is high because of the high processing temperatures and the inability to monitor melt temperatures. This is one of the major drawbacks of the process.

The vitrified product usually consists of a mixture of glass and crystalline materials. Convective currents generated during melting help mix the

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[6] A thin layer of graphite is added to the top of the waste-glass former mixture and touches the graphite electrodes to initiate Joule heating.

melt. In theory, if the melt is well mixed, the high content of glass-former materials such as SiO_2 and Al_2O_3 contained in the starting mixture can produce a durable waste form. However, compositional non-uniformities may exist that may greatly reduce durability.

The ICV technology was considered to treat low-activity waste (LAW) at Hanford and has been piloted at the Demonstration Bulk Vitrification System (DBVS), a full-scale test facility at the site. The process used soil from the Hanford Site and glass-former additives as the starting mixture. Several problems were encountered during the demonstration: High melting temperatures caused vaporization of all of the technetium into the off-gas stream. The Fe_2O_3 in the soil was reduced to Fe metal, which penetrated the ceramic liners and the outer metal shell of the container. These operational challenges are currently under review (Gerdes et al., 2007), and the project is on hold (GAO, 2007).

4.4 SELF-SUSTAINING VITRIFICATION

Self-Sustaining Vitrification (SSV) utilizes exothermic chemical reactions to produce glass, glass-ceramic, or ceramic waste forms. This technology was initially developed in the Soviet Union for producing high-quality ceramics and other refractory compounds (Borisov et al., 2002). The application of this technology to radioactive waste immobilization is discussed in Ojovan and Lee (2007).

The exothermic chemical reaction can be obtained by mixing waste and powder metal fuels (PMFs) such as Mg, Al, Si, or Ca. The oxidation of these fuels releases heat. The process is controlled by waste and PMF compositions, which are established based on computer simulations. A number of pre-processing steps may be required to develop the appropriate starting compositions and properties. For example, water removal is required to avoid excess gas generation and ensure the uniformity of the resulting waste form.

Because it does not require expensive equipment, SSV can be particularly useful for immobilizing small-volume waste streams or wastes that are difficult to immobilize by other methods. The feasibility of producing glass-ceramic waste forms using this technology has been demonstrated for a number of waste materials, for example, contaminated clay soils and ashes, spent inorganic ion exchangers, and calcined HLW (see Ojovan and Lee, 2007; Ojovan et al., 1999).

4.5 COLD PRESSING AND SINTERING

Cold Pressing and Sintering (CP&S) is one of the earliest technologies used for forming technical crystalline ceramics. The technology itself is simple; it involves pouring ceramic powder, often with small amounts of organic binders, into a die. The simplest die geometry consists of a cylindrical body with top and bottom plungers. The application of uniaxial compressive stress along the axis of the plungers leads to compaction of the powder into a cylindrical pellet. The pellet is ejected from the die and then sintered in a conventional kiln.

Alternatively, cold pressing can be done in an isostatic press. The powder is loaded into an elastomer mold, which is sealed and inserted into a liquid bath (generally oil). The liquid is then pressurized to compact the powder, then the pressed part is removed from the mold and sintered. The mold can be reused or discarded.

Uniaxial pressing is susceptible to die wall friction, which can result in density gradients in unsintered pellets. Sintering can produce distortions in the shape of the pellet or cracking. Isostatic pressing has the advantage of avoiding density gradients, thereby leading to more uniform and predictable shrinkage during sintering. The use of organic binders and lubricants with the powder will also minimize density gradients but requires processing of the waste stream to introduce these materials and thermal treatment of the pressed products to remove the organic components.

For the development of waste forms, the CP&S offers several advantages: it uses inexpensive equipment, is easily adaptable to small batches of waste, and is particularly well suited to laboratory studies of potential phases for waste forms such as glass ceramic material (Juoi et al., 2008; Staples et al., 2007) or crystalline ceramic material (Meyers et al., 1998; Oversby and Vance, 1994; Ringwood et al., 1988).

4.6 HOT UNIAXIAL PRESSING

Hot Uniaxial Pressing (HUP) has been in common use in the ceramic processing industry for decades and is often referred to simply as *hot pressing*. It involves loading of powder into a die, much as in CP&S. However, the die and plungers are inserted into a furnace and heated while pressure is applied. The process can produce high-density ceramics at lower temperatures than the two-step CP&S process described previously. However, the process is relatively slow because the die set and sample must be heated before pressing. Also, the dies can be expensive and, depending on the degree of reaction between the dies and powders, they can have a limited life.

HUP has been investigated as a technology for producing nuclear waste forms (Oversby and Vance, 1994; Ringwood et al., 1988; Staples et al., 2007). As with CP&S, the process is frequently used for laboratory evaluation of potential waste forms. For large-scale production of waste forms, however, consideration must be given to the volume of waste resulting from worn and damaged dies, which could be relatively large.

4.7 HOT ISOSTATIC PRESSING

Hot Isostatic Pressing[7] (HIP) also produces waste forms through the simultaneous application of heat and isostatic pressure. The waste and other materials to be processed are loaded into a metal can, typically stainless steel, which is sealed by welding and placed into a pressure vessel inside an electrically heated furnace. Pressure is then applied by compressing a gas such as argon, either by heating or by pumping, which compresses the waste isostatically while sintering into a solid monolithic waste form.

The HIP process, originally referred to as gas-pressure bonding, was first developed by Battelle Memorial Institute in the mid-1950s (ASME, 1985). Its initial use was for manufacturing nuclear fuels, but it is now a well-established technology used by a wide range of industries for castings, tool making, and manufacturing of ceramic components. The Australian Nuclear Science and Technology Organisation has developed and demonstrated HIP for immobilizing radioactive wastes from medical isotope production; it plans to commence the commissioning of a HIP facility for this purpose at the end of 2011. In January 2010, DOE announced its formal decision to use HIP to convert HLW calcine at the Idaho Site into “ceramic-like” waste forms (DOE, 2010). However, the technology readiness assessment is still in progress, the details of which had not been released by the time that this report was being finalized. Additionally, a safety assessment also had not yet been completed.

HIP is a mature and safe technology as demonstrated by its wide use outside the nuclear industry. The pressure vessels are designed with stringent codes such as those developed by the TÜV (Technischer Überwachungs-Verein [Technical Inspection Association], a German product safety and quality assurance testing firm) and the American Society of Mechanical Engineers (ASME). The conservative ASME code and inspection regime are designed to ensure that vessel integrity is maintained over its service life. Other safety features include active and passive over-pressure control systems and safety shields.

HIP also has many potential advantages for processing nuclear waste. Notably, it produces monolithic waste forms with substantially reduced volumes compared to untreated waste streams. Because the waste is processed in a sealed can, there are no volatile emissions. (If volatiles are produced they may not be retained in the solid.) There is no direct contact between the waste and the HIP apparatus, so secondary waste generation is minimized. HIP is compatible with a wide range of waste compositions, although it has a limited tolerance for gases and volatiles—for example, if copious amounts of hydrates or nitrates are present they will cause over

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[7] See http://www.synrocansto.com/Download/files/synrocANSTO_HIP_FactSheet.pdf.

pressurization unless the waste is calcined before HIPing. The HIP technology can produce glass (Harker et al., 1984), glass composite, and crystalline ceramic waste forms.

Unlike many other consolidation technologies, HIP does not require stringent control of physical properties such as viscosity, melt temperature, or melt conductivity, therefore permitting significantly higher waste loadings. However, for making ceramic waste forms, waste form additives must be tailored to sequester radionuclides in specified host phases. For production of SYNROC,[8] for example, redox conditions must be controlled to form the desired phase assemblages. In addition, processing conditions (pressure and temperature) must be closely controlled.

Although HIP is a flexible technology it does have some limitations. Crystalline ceramic waste forms produced by HIP (as well as conventional press and sinter technology) may contain intergranular glassy phases, especially when incorporating waste containing alkali or alkaline earth species in the presence of glass formers such as silicon or boron. Also, the distribution of volatiles in the can (when present) is not well understood. This intergranular glass can limit product stability and durability (Clarke, 1981; Cooper et al., 1986; Zhang and Carter, 2010). Additionally, HIP has been demonstrated only at small scales to date. The small size of the waste cans and long times required for heating currently limits the application of this technology to volumetrically small waste streams.

Given its flexibility, HIP is potentially applicable to a range of DOE-EM waste streams, including orphan waste streams and metallic waste streams whose diversity requires versatile methods for treatment and immobilization, as well as waste streams that are difficult or inefficient to process by other technologies because of physical or chemical heterogeneity. However, additional studies are needed to demonstrate the safety and compatibility of this technology with specific waste streams and also to address its scalability to high-volume waste streams.

4.8 FLUIDIZED BED STEAM REFORMING

A bed of granular material can be made to exhibit fluid-like properties by passing a liquid or gas through it. This process is referred to as *fluidization*, and the apparatus that supports this process is referred to as a *fluidized bed*. An 1879 patent appears to be the first instance to describe this phenomenon and its advantages. However, fluidization came of age during World War II, when the urgent need for aviation gasoline in the United States led to the development and construction of the first Fluid Bed Cata-

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[8] SYNROC (Synthetic Rock) is a monolithic crystalline ceramic containing hollandite, zirconolite, perovskite, and other minor constituents.

lytic Cracker (FCC). The fluidized bed offered an easy way of circulating the catalyst between regeneration and reaction cycles and was much easier to operate than the conventional process. Today, there are more than 400 FCCs operating worldwide. In addition to gasoline production, fluidization technology is broadly used in coal gasification and combustion, mineral processing, food processing, pharmaceuticals, soil washing, manufacturing of polymers, waste treatment, and environmental remediation. Its applications include several unit operations such as drying, heating/cooling, particle coating, and chemical reactions.

Applications of fluidized bed technology in nuclear fuel production, recovery, and waste processing date back to the late 1950s and early 1960s. For example, fluidization was used for the reduction and hydrofluorination of uranium concentrates (Sutton et al., 1966) and fluidized bed calcinations of high-level radioactive waste (Buckham et al., 1966). In the calcination process, liquid wastes are sprayed using atomizing nozzles into a fluidized bed of heated spherical calcine particles, evaporating water and nitric acid in the wastes and leaving behind solid-phase metal oxides. Two calcination facilities were successfully operated at the Idaho National Laboratory from 1961 to 1981 and from 1981 to 2000 (Newby and O'Brien, 2000). The calcine product is being stored in bins at the site. It may undergo further processing, possibly by HIP, to put it into a form that is suitable for disposal.

Fluidized Bed Steam Reforming (FBSR) is being used commercially for processing nuclear waste. A commercial facility to continuously process organic radioactive wastes at moderate temperatures in a hydrothermal steam environment was built by Studsvik in Erwin, Tennessee, in 1999. The Erwin facility uses a steam reforming technology, referred to as THermal Organic Reduction (THOR®), to pyrolyze organic resins loaded with cesium-137 and cobalt-60 from commercial nuclear facilities. The Erwin facility has the current capability to process a wide variety of solid and liquid streams including ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions at radiation levels of up to 400 rads per hour (Mason et al., 1999).

FBSR is a thermal treatment technology and therefore must comply with a number of regulations. The process has been shown to be Clean Air Act (CAA) compliant. It has also been shown to be Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) compliant for mercury, chlorine, carbon monoxide, total hydrocarbons, and heavy metals (Soelberg et al., 2004). A significant benefit of the FBSR process is that liquid secondary wastes are not produced (Mason et al., 1999). (Secondary waste solids such as fines from high-temperature filters and the bag house can be mixed with the bed product and monolithed for disposal.) Many years of operating and design experience with fluidized beds in the chemical industry and the availability of computational fluid dynamics tools significantly reduce development and operating risks for potential DOE-EM applications.

Depending on the starting material feeds, FBSR produces a range of waste form compositions. If kaolinite is added to an alkali-rich waste (e.g., neutralized HLW) during processing,[9] a crystalline ceramic waste form is produced that is composed of sodium-aluminum-silicon feldspathoid mineral analogues (e.g., sodalite) that serve as potential hosts or a number of radionuclides (see Appendix 4.A and Chapter 3). Bench-scale, pilot-scale, and engineering-scale tests have all produced this mineral assemblage using a variety of DOE waste simulants as feed materials. Additionally, an illite-type clay additive has been tested at the bench scale and shown to form dehydroxylated mica, which is a good host for lanthanides, cesium, strontium, barium, rubidium, and thallium (Jantzen and Williams, 2008; Keppler, 1990). It is reasonable to expect that these mineral assemblages would also serve as hosts for the radioactive forms of these elements that are present in DOE-EM waste streams.

DOE-EM plans to apply FBSR to some of its waste streams. An FBSR facility is being designed and constructed at the Idaho Site for treatment of decontamination solutions (referred to as *sodium-bearing waste*) for potential disposal in the Waste Isolation Pilot Plant (Marshall et al., 2003). Another facility is being designed for use at the Savannah River Site to process HLW in Tank 48, which contains nitrates, nitrites, and organic sodium tetraphenyl borate (NaTPB). This process will produce carbonate or silicate phases, which can possibly be fed to the DWPF for vitrification. DOE-EM has also carried out pilot-scale testing on a variety of simulated wastes to produce aluminosilicate ceramic waste forms (Jantzen, 2003).

As noted in the committee's interim report (NRC, 2010), there are at least two potential types of applications of FBSR in the DOE-EM cleanup program:

1. As a front-end process for conditioning waste feed streams:
    - For accelerating liquid evaporation at the front end of the HLW vitrification process. This could enable increased waste throughputs to the JHMs and increased production rates of high-activity and low-activity waste forms.
    - For processing waste streams, including resins, containing large quantities of organic materials and nitrates. The planned application of FBSR to process Savannah River tank waste containing high concentrations of NaTPB is an example of such an

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[9] The addition of kaolinite in the FBSR process is somewhat analogous to the addition of glass-forming materials (i.e., glass frit) in the vitrification process.

application. FBSR also has potential applications for processing waste streams containing organic solvents and radionuclide-loaded organic resins, for example, the technetium-99-loaded resins generated by groundwater cleanup efforts at the Hanford Site.

2. As a process for production of crystalline ceramic waste forms:
    - For processing alkaline HLW with bulk aluminosilicate additives (e.g., kaolinite clay), which could produce waste forms with good radionuclide retention properties and increased waste loadings relative to borosilicate glass (Jantzen, 2006). This process could also reduce or eliminate the need for recycling of melter off-gas condensates and is potentially applicable to both high-activity and low-activity waste streams.
    - For processing recycle liquids from HLW waste processing operations. This application has already been demonstrated at pilot scale for low-activity secondary waste simulants at Hanford.

FBSR is a mature technology in many industrial applications, including for the treatment of radioactive waste. Its deployment in specific DOE-EM applications may require some up-front development work to tailor it to specific waste streams, but relatively little basic research is likely to be required. Possible needs for basic research include the elucidation of key material structural characteristics (see Chapter 3) and waste form durability (see Chapter 5). Development work might also be required to better understand and ameliorate the attrition of granular bed material present in FBSR. Such attrition can be reduced through the proper design of internal components, dust collection equipment, operating conditions, and selection of additive materials. All of these have well-known solutions in chemical or petroleum industry applications of fluidized beds, and there are many available computational dynamics tools that minimize the risk of scale-up.

Waste forms produced by FBSR are granular and therefore may not be suitable for direct disposal in all cases. If necessary, they can be processed into high-integrity containers or further encapsulated in cement, geopolymers, hydroceramics, or glass to meet waste acceptance criteria (see Chapter 8) to be suitable for disposal.

4.9 OTHER THERMAL TECHNOLOGIES

There are several other technologies for immobilizing nuclear waste. Some of these are established procedures in other industries, whereas others have been demonstrated only at smaller scales. The committee provides brief overviews of these technologies in the following sections. For further details the reader is referred to Noyes (1995).

4.9.1 Gas-fired Technologies

In these technologies heat is produced by burning waste and/or fuel. Consequently, they produce large volumes of non-condensable off-gas products. In some cases, secondary tanks may be required to hold the waste form products that are produced. They can also pose safety issues because of open flames and large quantities of fossil fuels used within remote/enclosed facilities.

- *Cyclone Furnaces* can be used to immobilize highly contaminated wastes containing heavy metals and organics (and low-volatility radionuclides such as strontium and transuranics) in oil and sludge. Fuel and waste are fed in a spiral manner into a combustion chamber for maximum combustion and contacting efficiency. The waste form, a vitrified slag, can be withdrawn from the bottom of the cyclone.
- *Rotary Kilns* are slightly inclined, cylindrical, refractory-lined vessels that rotate about their axis. They find applications in a variety of industries to produce materials (e.g., Portland cement) or dry solids. Fossil fuel-fired glass furnaces have also been used in the glass industry. The same technology may be applicable for producing vitrified waste products. For a rotary kiln to produce a vitrified product it has to operate in a slugging mode. At high temperatures the kiln material becomes amorphous, and molten slag can be withdrawn from the kiln (Noyes, 1995).

4.9.2 Electric Arc Furnaces

Electric Arc Furnaces are primarily used in metallurgy and can also produce vitrified waste forms (O'Connor and Turner, 1999). They consist of refractory-lined vessels, usually water-cooled in larger sizes, covered with retractable roofs through which one or more graphite electrodes enter the furnaces. They can operate either by DC or AC current. The electric arc provides energy for heating and melting the material contained in the furnace. The DOE Albany Research Center in Oregon operated an electric arc furnace demonstration unit with simulated low-level radioactive, high combustible-bearing mixed wastes, and simulated low-level radioactive liquid tank wastes (O'Connor and Turner, 1999). The operation temperature was around 1,600°C, necessitating significant gas treatment equipment to scrub particulate matter and volatile radionuclides.

4.9.3 Plasma Heating

Plasma Heating is an electrical heating process in which plasma is created by passing a gas, commonly containing nitrogen, oxygen, or noble gases, through an electrical arc. It is suitable for processing low-level mixed waste to produce a vitrified waste form. One such process, the Plasma Hearth Process (PHP) (McFarlane et al., 1997), uses an ultrahigh temperature plasma (in excess of 5,000°C) generated by a direct current torch, which is remotely directed at containers of waste materials that are fed into a refractory-lined processing chamber.

Plasma heating results in oxidation, pyrolysis, and volatilization of the waste. Combustible pyrolysis gases generated in the primary process are oxidized in a propane-fired secondary combustion chamber. The remainder of the off-gas is filtered through HEPA filters. Non-volatile materials, such as metals, ash, and inert materials are then melted in the plasma chamber to produce a molten pool of metal and oxidized materials that form a slag. The molten material is captured in a shallow, refractory-lined hearth.

There have been pilot-scale tests of this technology (DOE, 1998; Wahlquist, 1996), but to the committee's knowledge there have been no large-scale demonstrations. The electrodes used to produce the plasma have short life times, which can be a significant drawback to this technology.

4.9.4 Microwave Heating

Microwave Heating takes place in dielectric materials because of losses from the polarization effect of electromagnetic radiation at frequencies between 300 MHz and 300 GHz. The successive distortion of the molecules causes heating. Microwave melting has been developed as a batch process and thus has a limited throughput. In this process drums of waste are heated in microwave chambers that function as ovens. Because of the nature of the process, uneven heating within the volume of the drum may occur, producing unacceptable waste form characteristics. Process scale-up of this technology has not been demonstrated at the scale necessary to process large amounts of wastes.

4.10 MIX AND SET TECHNOLOGIES

Waste forms can be generated by mixing wastes with materials that cure and solidify, encapsulating the waste and also binding some waste constituents in hydration product phases. Several binding materials can serve as waste forms.

4.10.1 Cement

Cement is an inorganic binder that sets and hardens to produce a rock-like material. Portland cement, which is the most commonly used cement type, is mainly comprised of lime, silica, alumina, and ferric oxide. Other oxides such as magnesia and sulfur are also introduced during various manufacturing processes. Portland cement comes in a variety of compositions.

Supplementary cement materials are sometimes added to Portland cement for either cost or availability reasons. These additions may significantly affect the properties of the resulting composite. Typically, cement in nuclear waste forms comprises much less than 50 percent of the total cementitious matrix with other materials, for example fly ash, blast furnace slag, and sand, comprising the remainder.

Two technologies are used for preparing waste-cement mixtures: (1) in-container mixing and (2) in-line mixing. In facilities designed for in-container cement production, the cement and additives are stored in silos and are usually pneumatically transferred to a batching station where they are added to the container. The waste liquid is metered to the container and the material is mixed and allowed to cure. For in-line mixing, the cement and liquid waste are mixed and then pumped into containers as thick slurries.

Cementitious waste forms are being used for the immobilization of radioactive waste in the DOE-EM cleanup program; two noteworthy examples are the Saltstone process at Savannah River Site, where waste salt solutions are mixed with fly ash, slag, and Portland cements and pumped into cement vaults for disposal. The other is the tank closures at Idaho National Laboratory, where the tanks are first washed to remove residues and then filled with grout made of sand, fly ash, blast furnace slag, and Portland cement. An overview of the cementation technology is given in Noyes (1995) and Ojovan and Lee (2007).

Some examples of the more commonly used cement technologies are described in the following sections. Fuhrmann (1981) provides a summary of other cement technologies that may be of utility for minor waste streams. These include sulfur-polymer, urea-formaldehyde, and polymer-impregnated cements.

4.10.2 Geopolymers

Geopolymers are ceramic-like, inorganic polymers made from aluminosilicates cross-linked with alkali metal ions (M_2O), nominally $4SiO_2 \cdot Al_2O_3 \cdot M_2O$. Clay (heat treated to render it amorphous) or amorphous fly ash are used as the aluminosilicate starting material. Alkali or alkaline earths in the waste (or added as sodium hydroxide or sodium silicate) "activates" the amorphous aluminosilicate structure to reorganize it into a cross-linked inorganic polymer.

Geopolymers are made using methods similar to the processing of cement waste forms. One such process is the Geopolytech® (Hermann et al., 1999). In this process, the geopolymer, cement, and additives are mixed with waste and water (if necessary) then transferred into molds. If desired, the geopolymer can be removed from the mold in 2 hours; the waste form cures to its final compressive strength in 28 days.

4.10.3 Hydroceramics

Hydroceramics are predominantly crystalline waste forms. They derive their name partially from the fact that they are directly related to the synthesis of zeolites from metakaolin and sodium hydroxide, and also from the fact that a hardened hydroceramic looks and breaks (exhibiting brittle behavior) like a ceramic. The term hydroceramic is used to distinguish this material from the much broader class of geopolymers, which as noted above are alkali-activated cements rather than zeolites.

A hydroceramic waste form (Bao et al., 2005) is formulated in the same fashion as zeolites (i.e., from metakaolinite and sodium hydroxide) except that less volume but more concentrated sodium hydroxide is used. A typical process for making the hydroceramics involves mixing of low-nitrate wastes with metakaolin in a pug mill (or similar mixer) and then extruding the mixture into a suitable container; the mixture sets up and hardens when precured at slightly elevated temperatures (ambient to 40°C) and is then hydrothermally[10] cured at 90°C-180°C for varying periods of time using an autoclave.

For application to wastes with high concentrations of sodium, the nitrate content of the waste needs to be below 25 percent mol NO_x (calculated as the ratio of moles of NO_x to moles of Na) for hydroceramics to solidify. Waste that has higher nitrate contents must be pre-treated to reduce them to an acceptable range before incorporation into hydroceramic waste forms.

There are currently no large-scale processes for making hydroceramic waste forms.

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[10] Hydrothermal synthesis is a method for producing of mineral and inorganic oxide phases in an aqueous system. Reactants are allowed to react in a closed vessel at temperatures of 100°C-250°C. Reaction vessels are generally autoclaves that allow temperature gradients to form, solution to supersaturate at different temperature zones, and crystallization product to form.

4.10.4 Bitumen

Bitumen, a viscous hydrocarbon and a major component of asphalt, has been used in Europe and Canada and to a lesser extent in the United States to solidify and stabilize radioactive materials. Bitumen immobilizes waste by encapsulation; it does not bind the waste chemically. The advantages of bitumen as a waste form are simplicity of production, low operating cost, and leach resistant characteristics. However, bitumen does not perform well with dehydrated salts, such as sodium sulfate, sodium nitrate, magnesium chloride, and aluminum sulfate (Noyes, 1995). It can also be a fire hazard (Zakharova and Masanov, 2000), especially when oxidizing wastes like nitrates are involved.

There are several processes for solidifying bitumen with waste streams (Ojovan and Lee, 2005). The most common are the use of a screw extruder or a rotary thin-film evaporator. The screw extruder, which is commonly used to mix pastes and plastics, consists of a screw, barrel, drive mechanism, bitumen, and waste feed point. The constantly turning screw augers the waste and bitumen through the heated barrel where it is heated to form a homogeneous melt. The volatile gases are allowed to vent.

The thin-film evaporator consists of vertical vessel with a rotated shaft at its center equipped with wiper blades, which help create a thin film on the wall and help mix the bitumen-waste mixture. Preheated bitumen and partially evaporated liquid waste are fed to the top of the evaporator, a distributor spreads the mixture around the inner wall of the vessel where heat is supplied, while the action of the wiper assemblies create a thin liquid film on the wall and also help to mix the molten material. The evaporated liquid passes through a series of condensers, and a molten bitumen waste mixture is discharged from the bottom of the evaporator.

4.11 DISCUSSION

This chapter has provided a brief overview of processing technologies used to produce a variety of waste forms, emphasizing technologies that are currently used, planned to be used, or in development stage that may be considered advancements. These technologies are generally well established through their use in other industries. The attributes, the advantages, and disadvantages of these processes are summarized in Table 4.1.

The committee highlighted the advantages of three technologies in its interim report (NRC, 2010): fluidized bed steam reforming, cold crucible induction melting, and hot isostatic pressing. These waste form production technologies are being used commercially in both nuclear and/or non-nuclear applications, as described elsewhere in this chapter, and appear to be applicable for processing and immobilizing a range of DOE-EM waste streams, especially HLW streams, which are summarized in Table 4.2. DOE-EM is already planning to apply these technologies to some of its waste streams, as discussed in the interim report and elsewhere in this chapter. The committee concurs with DOE-EM about the applicability of these technologies in the cleanup program. Even though these are mature technologies and have applications in different industries, some development work will be needed to use them in processing nuclear waste as described in the interim report (NRC, 2010) and in this chapter.

TABLE 4.2 Waste Form Production by Various Processing Technologies

		Borosilicate Glass	**Other Glasses (LaBs, FeP, AlP, chalcogenide, and others)**	**Glass-Ceramic Materials (GCMs)**	**Minerals/ Crystalline Ceramics/ Simple Oxides**
THERMAL	Joule-Heated Melters (JHMs)	Y	Y	Y	N
	Advanced JHMs	Y	Y	Y	N
	Heated Melters (bubblers, etc.)				
	Cold Crucible Induction Melters (CCIM)	Y	Y	Y	Y*
	Press + Sinter	N	N	Y	Y
	Hot Isostatic Pressing (HIPing)	N	N	Y	Y
	Fluidized Bed Steam Reforming (FBSR)	N	N	Y	Y
	Calcining	N	N	N	Y
	Hydrothermal Processing	N	N	Y	Y
NONTHERMAL	Mix and Set	N	N	N	N

Metal Matrix	Zeolites Hydro-ceramic	Cements (OPC, Ceramicrete, and Others)	Bitumen	Geopolymers
N	N	N	N	N
N	N	N	N	N
Y	N	N	N	N
Y	Y	N	N	N
Y	Y	N	N	N
N	Y	N	N	N
N	N	N	N	N
N	Y	Y	N	Y
N	N	Y [to include use of as waste forms and as binders (macro-encapsulation)]	Y (heating necessary to melt bitumen)	Y [to include use of as waste forms and as binders (macro-encapsulation)]

APPENDIX 4.A
FLUIDIZED BED STEAM REFORMING

The Fluidized Bed Steam Reforming (FBSR) of nuclear waste is a relatively new technology, though the fluidization phenomenon and steam reforming are well established in the chemical engineering field. Steam reforming is a method for generating hydrogen by reacting fossil fuels with water. For example, for natural gas:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

If coal is used as a carbon source, it first undergoes pyrolysis or devolatilization then the char (C) reacts with steam according to the following reaction:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

The H_2 is combined with O_2 so that no excess H_2 exists in the system at any one time. This combination is exothermic and provides energy in the form of heat for the autocatalytic operation of the FBSR.

The FBSR consists of two fluidized beds. The first one operates in a reducing environment, and its function is to evaporate the liquid nuclear waste stream; destroy organics; reduce nitrates, nitrites, and nitric acid to nitrogen gas; and form a stable solid waste product. The first-stage fluidized bed of the FBSR process is referred to as the Denitration and Mineralization Reformer, or DMR. The DMR uses superheated steam as the fluidizing media. The bed material consists of granular solid additives and co-reactant(s), such as carbon, clay, silica, and/or catalysts. Liquid waste is directly fed to the fluidized bed after minor pretreatment (e.g., to concentrate or dilute solubles) except the addition of clay.

By analogy to the above steam reforming chemistry, the carbon fed to FBSR (coal in this instance) produces H_2 and CO. For organic compounds in the waste stream, which undergo pyrolysis to form various hydrocarbons, the reducing environment is generated by the following reaction:

$$C_nH_m(g) + nH_2O(g) \rightarrow nCO(g) + (n + m/2)H_2(g)$$

Similarly, the nitrates contained in the liquid waste are reduced to

$$2NaNO_3(g) + 3C(s) \rightarrow 2NO(g) + 3CO(g) + Na_2O(s)$$

In the steam environment, the sodium oxide is transferred to sodium hydroxide:

$$Na_2O(s) + H_2O(g) \rightarrow 2NaOH(s,l)$$

yielding the overall reaction

$$2NaNO_3(g) + 3C(s) + H_2O(g) \rightarrow 2NO(g) + 3CO(g) + 2NaOH(s,l)$$

$$2NaNO_3(g) + 2C(s) + H_2O(g) \rightarrow 2NO_2(g) + 2CO(g) + 2NaOH(l,s)$$

The NO and NO_2 are further reduced to nitrogen gas by the reaction of CO, C, or H_2 generated from the reaction of the organic material with steam as shown above. The nitrates can also be reduced by the addition of a catalyst or a metal. For example:

$$2NaNO_3(g) + 5Fe(s) + H_2O(g) \rightarrow N_2(g) + 5FeO(s) + 2NaOH(s,l)$$

The second fluidized bed of the FBSR process operates in an oxidizing environment and is referred to as the Carbon Reduction Reformer, or CRR. The fluidizing gases are the off-gas from the first stage and added oxygen. Its function is to gasify carbon fines carried over in the process gases from the DMR, oxidize CO and H_2 to CO_2 and water, and convert trace acid gases to stable alkali compounds by reacting these acids with the bed media consisting of calcium carbonate and/or calcium silicate particles.

The addition of bulk aluminosilicates to the fluidized bed results in the production of various phases including anhydrous feldspathoid mineral analogue phases such as sodalite. The sodalite family of minerals (including nosean) are unique because they have cage-like structures formed of aluminosilicate tetrahedra. The remaining feldspathoid mineral analogues, such as nepheline, have a silica “stuffed derivative” ring-type structure. The cage structures are typical of sodalite and/or nosean phases where leach testing has indicated that the cavities in the cage structure retain anions and/or radionuclides, which are ionically bonded to the aluminosilicate tetrahedra and to sodium cation.

Sodalite has the formula $Na_8[Al_6Si_6O_{24}](Cl_2)$. In sodalites and analogues with sodalite topologies, the cage is occupied by two sodium and two chlorine ions. When the 2NaCl are replaced by Na_2SO_4, the mineral phase is known as nosean, $(Na_6[Al_6Si_6O_{24}](Na_2SO_4))$. Because the Cl, SO_4, and/or S_2 are chemically bonded and physically restricted inside the sodalite cage structure, these species do not readily leach out of the respective FBSR waste form mineral phases. Thus, FBSR waste forms can be useful for immobilizing these species to prevent their leaching into groundwater.

Other minerals in the sodalite family, namely hauyne and lazurite, which are also cage-structured minerals, can accommodate either SO_4^{2-} or S^{2-}. They are potential products of the steam reforming depending on the

REDOX of the sulfur during the process. Sodalite minerals are known to accommodate Be in place of Al and S_2 in the cage structure along with Fe, Mn, and Zn, e.g., helvite ($Mn_4[Be_3Si_3O_{12}]S$), danalite ($Fe_4[Be_3Si_3O_{12}]S$), and genthelvite ($Zn_4[Be_3Si_3O_{12}]S$). These cage-structured sodalites were minor phases in HLW supercalcine waste forms and were found to retain Cs, Sr, and Mo into the cage-like structure, e.g., Mo as $Na_6[Al_6Si_6O_{24}](NaMoO_4)_2$. In addition, sodalite structures are known to retain B, Ge, I, and Br in the cage-like structures. Indeed, waste stabilization at Idaho National Laboratory currently uses a glass-bonded sodalite ceramic waste form (CWF) for disposal of electrorefiner wastes for sodium-bonded metallic spent nuclear fuel from the EBR II fast breeder reactor.

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5

Waste Form Testing

The third charge of the statement of task for this study (see Box 2.1 in Chapter 2) calls for the identification and description of "state-of-the-art tests and models of waste forms used to predict their performance for time periods appropriate to their disposal system." This chapter describes waste form testing and the use of test results to inform the development of models for evaluating the long-term (10^3-10^6 year) *performance* of waste forms and their associated disposal systems.[1] The application of such models to waste forms and disposal environments is discussed in Chapter 7.

In the context of this report, a *test* is a laboratory procedure for measuring short-term (days to months) *release rates* of radioactive and chemical constituents from a waste form material and the formation of reaction products. It typically involves the *leaching* of a monolithic or crushed specimen of a waste form material under carefully controlled conditions. Release rates reflect the *durability* of a waste form material, that is, its resistance to physical and chemical alteration.

A large number of *standard test protocols* have been established by the American Society for Testing and Materials (ASTM) and other organizations; some of the principal tests that are used to investigate waste form materials for disposal applications are described in this chapter.

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[1] Box 5.1 provides definitions for a number of specialized terms that are used in this chapter.

BOX 5.1
Key Terms and Concepts

Experiment:	The application of tests to a waste form material to gain a better understanding of its degradation behavior and the release of radioactive constituents.
Dissolution:	A process (or processes) by which mass transport from a solid waste form to a liquid takes place (see ASTM C1308, ASTM C1220). Dissolution is the result of mechanistic reactions in which chemical bonds are broken and constituents are released from a material and become solvated in a test solution (see ASTM C1662).
Dissolution rate:	The rate of mass removal per unit time normalized to surface area of the material.
Durability:	The resistance of a waste form material to chemical and physical alteration and the associated release of contained radioactive and hazardous constituents.
Leaching:	The loss of radioactive or chemical constituents from a waste form by diffusion or dissolution.
Performance:	The ability of a waste form (waste form performance) or a disposal system containing the waste form (disposal system performance) to sequester radioactive and chemical constituents.
Release mechanisms:	The process that controls the rate of mass transport out of a specimen during dissolution (see ASTM C1308).
Solubility:	The thermodynamically limited saturation state or equilibrium concentration limit of species in solution.
Standard test protocols:	A standardized procedure for testing a specific type of material to generate a clearly defined test response. In principle, any test can be applied to any material to generate a response. However, a response will be meaningful only when the test and material are matched appropriately (see Section 5.1).
Waste form qualification:	Demonstration that a waste form material will have acceptable performance in a specific disposal facility and can be fabricated with acceptable performance control.
Waste form test protocols:	Standard tests developed by organizations such as the American Nuclear Society, American Society of Testing and Materials, International Atomic Energy Agency, and the International Organization for Standardization (see Section 5.3).

5.1 PURPOSE OF WASTE FORM TESTING

Laboratory testing of waste form materials is undertaken for several purposes, including to:

- Conduct experiments to elucidate the release mechanisms of radioactive and chemical constituents from a waste form material.

- Control waste form production.
- Ensure that production results in an acceptable waste form material.
- Provide the information needed to model the performance of waste forms in disposal systems.

These applications are described briefly in the following paragraphs.

Experiments involve the application of tests to waste form materials to gain a better understanding of their degradation behavior and release of constituents. These experiments may or may not be developed as standard protocols, but rather they are designed to address and challenge specific hypotheses about the behavior of waste form materials. Such experiments can also involve modeling and other types of measurements, for example, compositional analyses of alteration products that are formed on the surfaces of waste form materials during release.

Radioactive and chemical constituents can be released from a waste form material by one or more of the following three mechanisms:

- Reaction affinity-controlled release: Release is controlled by the difference in Gibbs free energy between the thermodynamically stable state and the metastable reactants.
- Solubility-controlled release: Release is bounded by the use of the maximum saturation of a constituent species from the waste form in the given leachant (solution) environment.
- Diffusion-controlled release: Release is controlled by the diffusion of a constituent in the waste form material, including diffusion through an encapsulant and/or through surface layers containing reaction products, if present.

In some cases a change in oxidation state of the constituent may occur prior to its release.

Laboratory experiments on *natural analogues* of waste form materials (e.g., basalt glass as a natural analogue for borosilicate glass) allow one to gain insights into the similarities and differences in release mechanisms. Short-term studies of natural analogues can also be extended to investigate other material properties, for example, for comparing radiation damage in actinide-doped materials with damage in uranium- and thorium-bearing minerals (Weber et al., 1994).

Testing for *production control* is used to determine how the production of a waste form material affects (or controls) its performance, and also to identify the ranges of processing variables that produce acceptable waste forms. The primary role of production control testing is to verify that the properties of a specific waste form product are consistent with the waste form material deemed to be acceptable for disposal, either by direct measurement or through process control.

Waste form *acceptance testing* is intended to show that the waste form produced within production control limits will have acceptable performance in a disposal facility. The performance of a waste form in a disposal facility depends on the environmental conditions in that facility (see Chapter 6). Waste form acceptability also depends on the performance requirements for that disposal facility (Ebert, 2008; see Chapter 8).

The acceptability of a waste form material for disposal is determined through predictive modeling studies (Chapter 7). These models use various thermodynamic and kinetic approaches, but most models used in the United States are based on irreversible thermodynamic (or steady state) transition state theory (TST). The information derived from laboratory tests can be used to parameterize these predictive models (e.g., Grambow, 1985; Grambow and Muller, 2001).[2] In some cases, it may be necessary to accelerate releases from a waste form material to obtain the necessary information. This can be done by altering the parameters of a laboratory test, for example, surface area (SA), time (t), temperature (T), or a combination such as (SA) × (t). This is a useful approach so long as the alterations do not change the release mechanisms.

The testing of a waste form material in the laboratory can be related to acceptable performance of that material in a disposal facility by the following linking relationships (Ebert 2008; Plodinec and Ramsey, 1994):[3]

$$\begin{gathered}\text{process control} \leftrightarrow \text{composition control} \leftrightarrow \\ \text{release rate control}^{4} \leftrightarrow \text{performance control} \leftrightarrow \\ \text{acceptable performance}\end{gathered} \tag{5.1}$$

These linking relationships provide a logical technical approach for identifying an acceptable range of processing and composition controls based on the range of waste form release rates and level of disposal system performance deemed acceptable by regulators. In other words, these relationships provide a technical basis for identifying an acceptable waste form release rate under particular test conditions because those test conditions can be related to performance.

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[2] The tests described in this chapter provide the fundamental information shown at the base of the Performance Assessment Pyramid (see Figure 7.2) that enables such modeling.

[3] Other approaches could be used, depending on the process for producing the waste form. For example, one could combine careful control of processing conditions with a frequent sampling procedure to ensure that the proper product has been produced.

[4] Dissolution rate control is achieved by modifying the composition and or waste-loading of the waste form.

For high-level waste (HLW) glass (i.e., alkali borosilicate glass) this linking relationship was established in a stepwise fashion:

- Develop an acceptable waste form durability specification based on HLW performance modeling. As discussed in Chapter 8, acceptable fractional release rates for waste forms in a generic geologic repository were determined to be between 10^{-4} to 10^{-6} parts per year[5] (Crandall, 1983). Because early versions of 10 CFR Part 60.113[6] specified fractional release rates of 10^{-5} parts per year, which was in the middle of the range determined by HLW performance modeling, this rate was adopted as the waste form specification.
- Select a waste form material that had the potential to meet this specification. As discussed in Chapter 8, borosilicate glass was selected as a waste form material for several reasons, including its potential ability to meet this performance specification.
- Develop an understanding of borosilicate glass durability mechanisms from a combination of ASTM test protocols (ASTM C1220, ASTM C1285, ASTM C1662), which were then a suite of tests under development by the Materials Characterization Center (MCC) (see Appendix 5.A for a history of test development). These test protocols are described in Appendix 5.C.
- Develop a glass standard, the Environmental Assessment (EA) glass, which bounded the upper release rate found to be acceptable from HLW performance modeling and 10 CFR Part 60.113.[7]
- Generate a substantial database for modeling the maximum radioactive release rate(s), which happens to be for technetium-99, iodine-129, and cesium-135,[8] by the release of non-radioactive species such as sodium, lithium, and boron, which release at the same rate (i.e., congruently; see Box 5.2).
- Develop a standard test for ensuring that every glass produced has a release rate less than that of the EA glass based on sodium, lithium, and boron, which in turn ensures performance control and acceptable performance.
- Using this standard test, continue to periodically verify that the durability of the production glass meets performance specifications.

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[5] That is, the waste form would take 10^4 to 10^6 years to completely dissolve.

[6] Waste Package Performance Objective; see Chapter 8.

[7] This acceptable release rate was based on a bounding calculation for a generic repository. The actual dissolution rate of a waste form material after emplacement in a disposal facility will depend on the specific geochemical and hydrological characteristics of that facility.

[8] Technetium-99, iodine-129, and cesium-135 are not solubility limited; consequently, these radionuclides are released at maximum forward (initial) rates of dissolution.

BOX 5.2
Congruent vs. Incongruent Dissolution

The term *congruency* describes the dissolution behavior of atomic species (including radioactive species) in a waste form material as that material reacts with a solution.

If species dissolve in proportion to their presence in a waste form material (i.e., in stoichiometric proportions), then dissolution is said to be *congruent*. In such cases, the rate of release of species from the waste form is proportional to both the dissolution rate of the waste form and the relative abundance of those species in the waste form. For materials that exhibit this behavior, for example borosilicate glass in a high pH under-saturated solution, the dissolution behavior of non-radioactive species such as sodium, lithium, and boron can be conveniently used to monitor the releases of radionuclides such as technetium-99, iodine-129, and cesium-135. Decades of research have provided the basis for this relationship to be used for HLW borosilicate glass (Bates et al., 1983; Bazan et al., 1987; Bibler and Bates, 1990; Bibler and Jurgensen, 1988; Bradley et al., 1979; Ebert et al., 1996; Fillet et al., 1985; McGrail, 1986; Ojovan et al., 2006; Vernaz and Godon, 1992).

If some species in the waste form material dissolve preferentially to others, then dissolution is said to be *incongruent*. Incongruent dissolution is often diffusion-controlled and can be surface reaction affinity-limited under conditions of near saturation or mass transport-controlled. Preferential phase dissolution, ion-exchange reactions, grain-boundary dissolution, and dissolution-reaction product formation (surface crystallization and recrystallization) are among the more likely mechanisms of incongruent dissolution. Precipitation of a secondary phase or phases can also lead to incongruent dissolution.

Apparent incongruent dissolution can occur in complex monophase or polyphase crystalline ceramic waste forms. For example, a multiphase ceramic waste form may contain sodium in more than one phase, whereas species such as technetium-99 are only sequestered in one of the sodium-containing phases. In this case, each phase undergoes congruent dissolution, but technetium-99 and sodium will not be released into solution at the same rate.

This approach was the basis for qualifying HLW glass from West Valley and the Savannah River Site in the Yucca Mountain Total System Performance Assessment–License Application (TSPA-LA) (Ebert, 2000). It was also the approach used in the Hanford performance evaluation for low-activity waste (LAW) glass intended for shallow-land burial (Mann et al., 2001) and to qualify glass-bonded sodalite for disposal in a deep geological repository (Ebert, 2005). A similar approach was also taken by Ebert (2005) to qualify a metallic waste form.

The HLW EA glass (Jantzen et al., 1993, 1994) standard does not necessarily apply to other types of glasses. For example, another glass standard, the LAW Reference Material (LRM) glass standard,[9] was developed for Hanford's Immobilized LAW (ILAW) glass. The LRM contained the glass components anticipated to be present in the Hanford low-activity waste streams as well as those that may be added to facilitate vitrification or improve the durability of the ILAW waste products (Ebert and Wolf, 1999). Extensive testing was again used to demonstrate that the most soluble radionuclides (i.e., those that are not solubility limited) were released congruently (Box 5.2) to sodium, lithium, and boron in the glass to qualify it for near-surface disposal.

5.2 TEST SELECTION

A suite of standard laboratory tests have been developed (Appendix 5.C) to measure the release behavior of waste form materials. The selection of a particular test for a particular waste form material depends on that material's release mechanism (Table 5.1). Standard tests established for use on materials that release by one mechanism, such as glass that preferentially releases its constituents by reaction affinity-control under non-saturated conditions, cannot necessarily be applied to materials that release by a different mechanism, such as cement that releases constituents by diffusion (e.g., Ojovan and Lee, 2005). Similarly, one cannot apply standard tests for borosilicate glasses to non-borosilicate glasses, because it is not known whether constituents in the latter material release congruently (Box 5.2) by the same mechanism(s). In these cases, new standard tests need to be developed, or existing standard tests need to be qualified, once the release mechanisms for a new material are determined.

The recent determination of the release mechanisms for silicate glasses and minerals provide a good illustration of this point. The rate-limiting step in silica-water reactions in a glass or mineral is breakage of the structural Si–O bonds (Oelkers, 2001; Oelkers et al., 1994; Rimstidt and Barnes, 1980). Oelkers (2001) has shown that the release mechanisms for single-phase minerals and glasses are similar. Thus, modeling of the dissolution of glass has paralleled the modeling of mineral-solution dissolution. Kinetic treatments have systematized the effects of pH, temperature, saturation state, ionic strength of the leachant, and inhibition on the overall release rate by developing models that treat each effect individually (Lasaga and Luttge, 2004). The kinetic effects of saturation state as a function of pH, temperature, and ionic strength have primarily been handled by the application of combined thermodynamic and kinetic TST models and the free energy dependence of basic irreversible dissolution reactions (Aagaard and

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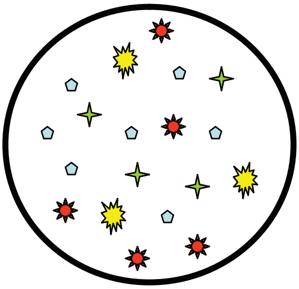
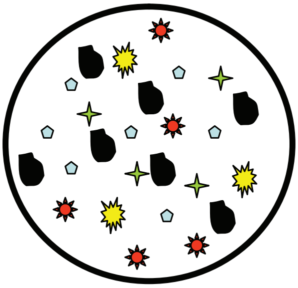
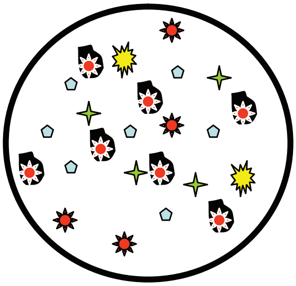
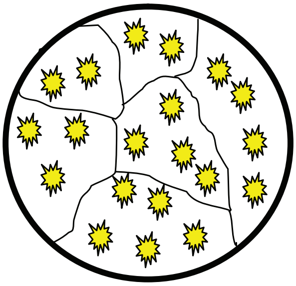
[9] This glass was originally developed as a standard for test method responses and later became a standard for glass durability (see Ebert and Wolf, 1999; Wolf et al., 1998).

TABLE 5.1 Summary of Waste Form Durability Response and Tests

Waste Form Class	Retention Mechanism
Single-Phase Glasses Constituents[b] are atomically bonded in the glass structure, usually to oxygen that is also bonded to other matrix elements (e.g., Si, Al, B, P) by short-range order (SRO) and medium-range order (MRO).	Chemical incorporation
Glass-Ceramic Material Constituents are present in the glass matrix and benign crystals such as spinels (Cr, Ni, and Fe species) are allowed to crystallize (●). These crystals do not contain radionuclides but may contain hazardous constituents (e.g., Cr, Ni).	Chemical incorporation
Glass-Ceramic Material Constituents are present in the glass matrix and in the crystalline phases. Example shows Cs in the glass and in a secondary phase (●). Secondary phase may be more soluble than glass (e.g., $(Na,Cs)_2SO_4$) or more durable than glass (e.g., pollucite $(Cs,Na)_2Al_2Si_4O_{12}$).	Chemical incorporation and encapsulation
Single-Phase Oxides/Minerals/Metals Consists of only one main crystalline phase, which contains the same radionuclide(s). May be granular or monolithic.	Chemical incorporation

Graphical Representation	Durability Behavior	Appropriate Durability Test/ Standards[a]	
	single phase source – homogeneous glass	ASTM C1220 ASTM C1285 ASTM C1662 ASTM C1663 PUF	EA, ARG-1, LRM, work for borosilicate-based GCMs; testing and standards must be developed for non-borosilicates
	single phase source—homogeneous glass as long as crystalline phases do not sequester constituents	ASTM C1220 ASTM C1285 ASTM C1662 ASTM C1663 PUF	EA, ARG-1, LRM, work for borosilicate based GCMs; testing and standards must be developed for non-borosilicates
	multiphase source—glass and multiple crystalline phases and grain boundaries	ASTM C1220 ASTM C1285 ASTM C1662 ASTM C1663 PUF	EA, ARG-1, LRM, work for borosilicate-based GCMs; testing and standards must be developed for non-borosilicates
	multiphase source—single crystalline phase and grain boundaries	ASTM C1220 ASTM C1285 ASTM C1662 ASTM C1663 PUF	Testing and standards must be developed

continued

TABLE 5.1 Continued

Waste Form Class	Retention Mechanism
Multiphase Oxides/Minerals/Metals Individual phases contain one or multiple constituents (e.g., solid solution indicated between UO_2 and ThO_2). Some phases do not incorporate any constituents (gray shading). May be granular or monolithic.	Chemical incorporation
Multiphase Granular Oxides/Minerals/Metals Granular waste forms must be monolithed for disposal if not containerized. The monolithing agent does not incorporate constituents (gray shading). Also known as composite waste forms.	Chemical incorporation and encapsulation
Cementation/Hydroceramics Geopolymers Hydrated phases incorporate constituents weakly or retain them by sorption. Encapsulation is by solidification or precipitation of constituents on grain boundaries where non-constituent phases hydrate or crystallize. Example shows Tc sequestered by C-S-H hydrates and sequestered by secondary fly-ash granules.	Encapsulation

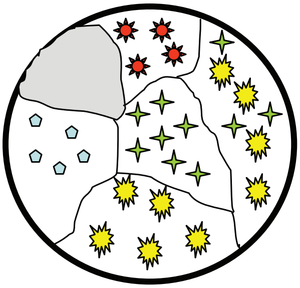
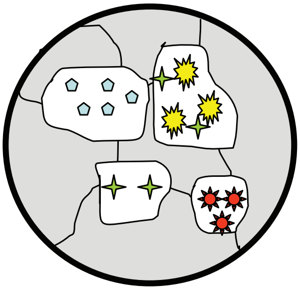
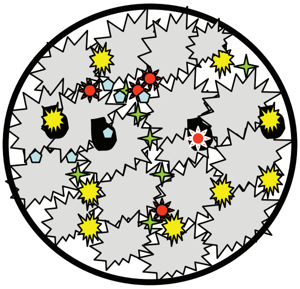
NOTES: EA = Environment Assessment Glass; ARG-1 = Analytical Reference Glass-1; LRM = Low-Activity Waste Reference Material.

[a] Standards are only appropriate if mechanisms and radionuclide releases are shown to be the same. The tests are described in Appendix 5.C.

[b] Can include both radioactive and chemical constituents.

Key:

✹ Cs ✸ U ⬠ Tc ✦ Pu

Graphical Representation	Durability Behavior	Appropriate Durability Test/ Standards[a]	
	multiphase source—multiple crystalline phases and grain boundaries	ASTM C1220 ASTM C1285 ASTM C1662 ASTM C1663 PUF	Testing and standards must be developed
	multiphase source—multiple crystalline phases but binder and grain boundaries contain no constituents	ASTM C1220 ASTM C1285 ASTM C1662 ASTM C1663 PUF ASTM C1308 or ANSI 16.1 or EPA 1315	Testing and standards must be developed
	multiphase source—multiple crystalline phases but phases encapsulate the constituents which exist primarily on the grain boundaries	ASTM C1308 or ANSI 16.1 or EPA 1315	Radionuclides or simulants must be measured or a standard developed

Helgeson, 1982; Apted, 1982; Grambow, 1985; Helgeson et al., 1984; Lasaga, 1984). These kinetic effects may not be the same for phosphate glasses or phosphate mineral waste forms, and surface-layer effects may also be different in these materials.

The TST and irreversible reaction models for mineral dissolution are being used to predict long-term dissolution of HLW glass in Yucca Mountain (Ebert, 2000) and release kinetics for the ILAW performance assessment at Hanford (Mann et al., 2001). In the TST treatment of durability of minerals and glasses, the rate-limiting step is considered to be the destruction of the slowest breaking metal-oxygen bonds, e.g., those that are essential for maintaining the mineral or glass structures such as $(SiO_4)^{-4}$, $(AlO_4)^{-5}$, and $(FeO_4)^{-5}$ (Oelkers, 2001; Oelkers et al., 1994).

The mechanisms of single-phase borosilicate glass dissolution are better defined now than 20 years ago. Advances have been made in understanding glass structure and how it controls release of radionuclides by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. The access of water to the atomic sites through percolation channels (which are created by medium-range order; see Box 3.1) has only recently been determined. The role of the leached layer on controlling the long-term durability is still under investigation.

Some initial studies of glass structural control for non-borosilicate glasses (e.g., for phosphate glasses) have been published. The structural model for these glasses (Day et al., 1997) suggests that the sodium iron phosphate glasses can be visualized as consisting of PO_4 tetrahedra joined together in various ways by oxygen polyhedra, which contain Fe^{2+}, Fe^{3+}, and/or sodium ions (if present). The structural model does not include percolation channels or evidence that iron phosphate glass releases constituents by a similar mechanism to borosilicate glass. Although the same testing protocols can be used on phosphate glass, the same glass durability standards may not be used unless the mechanistic interpretation of the test results are shown to be appropriate and/or the selection of a standard glass is shown to be an appropriate surrogate. The use of such a benchmarking material may not be necessary if the waste form test response can be related directly to its performance, but testing of radioactive release rates from iron phosphate glasses have yet to be completed and compared to borosilicate releases.

The qualification of a waste form for which the release mechanism is not known and existing standard tests have not been demonstrated to be appropriate is a detailed and laborious process. See, for example, Appendix 5.B, which illustrates the time and effort required for the qualification of borosilicate glass for immobilization of HLW at West Valley and the Savannah River Site. The process for qualifying new waste form materials is described in Section 5.4.

5.3 STANDARD TEST PROTOCOLS

Waste form tests have been under development for decades. A brief discussion of the history of testing is provided in Appendix 5.A. A suite of standard tests, referred to as *waste form test protocols*, has been developed by the ASTM Subcommittee C26.13 on Spent Fuel and HLW[10] and Subcommittee C26.07 on Nuclear Waste Materials:

- C1174: Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste
- C1285: Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)
- C1662: Standard Practice for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method
- C1663: Standard Test Method for Measuring Waste Glass or Glass Ceramic Durability by Vapor Hydration Test
- C1220: Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste
- C1308: Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms

Additionally, three other standard tests also used for waste form testing:

- PNNL Pressurized Unsaturated Flow (PUF) Test
- ANSI 16.1: Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure
- EPA 1315: Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Test

Several new ASTM test protocols are also under development; for example, a version of C1662 is being developed for spent nuclear fuel (SNF).

These tests are typically applied to small (kilogram mass or less) specimens of waste form materials. The material may be tested as a monolith or crushed to accelerate the test response. Testing protocols must be suitable

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[10] The charter of ASTM Subcommittee C26.13 is to develop consensus standards in support of the national HLW disposal program.

for the material to be tested. For example, for waste form materials that sequester constituents by encapsulation, crushing would partially destroy the encapsulation and produce a meaningless test response.

ASTM C1174 is a roadmap to waste form qualification and is discussed in detail in the next section. The remaining test protocols and their applicability to various waste form materials are described in Appendix 5.C.

5.4 WASTE FORM QUALIFICATION

The purpose of the ASTM C1174 practice is to guide the development of materials-behavior models that can be used to predict alterations in materials over the very long time periods (tens of thousands of years and more) pertinent to the operation of an HLW repository. Under the very extended periods relevant to geological disposal—much longer than those encountered in normal engineering practice—equilibrium or steady state conditions can be achieved, and models for reaction kinetics can be replaced by models describing equilibrium extents of alteration. The development of such models is an important step in qualifying new waste form materials for disposal.

ASTM C1174 has been under development and revision since the mid-1970s. It describes test methods and data analyses used to develop models for the prediction of the long-term behavior of materials, such as EBS materials and waste forms, used in the geologic disposal of SNF and HLW in a geologic repository. The alteration behavior of waste forms and EBS materials is important because it affects the retention of radioactive and hazardous constituents in a disposal system. The waste form and EBS materials provide barriers to release either directly, as in the case of waste forms in which the constituents are initially immobilized, or indirectly, as in the case of containment materials that restrict the ingress of groundwater or the egress of species that are released as the waste forms and EBS materials degrade. The waste form materials include, but are not limited to, glass, glass-ceramic, crystalline ceramics, oxides, and metallic waste forms.

ASTM C1174 lays out a roadmap (Figure 5.1) that shows the steps involved in predicting long-term behavior. The key steps are (1) problem definition, (2) testing, (3) modeling, and (4) model confirmation. An important aspect of C1174 is reiteration between testing and modeling, so these steps are intended to be carried out iteratively. The predictions are based on models derived from theoretical considerations, expert judgment, interpretation of data obtained from tests, and appropriate analogues. For the purpose of this practice, tests are categorized according to the information they provide and how such information is used for model development and use. These tests may include but are not limited to the following:

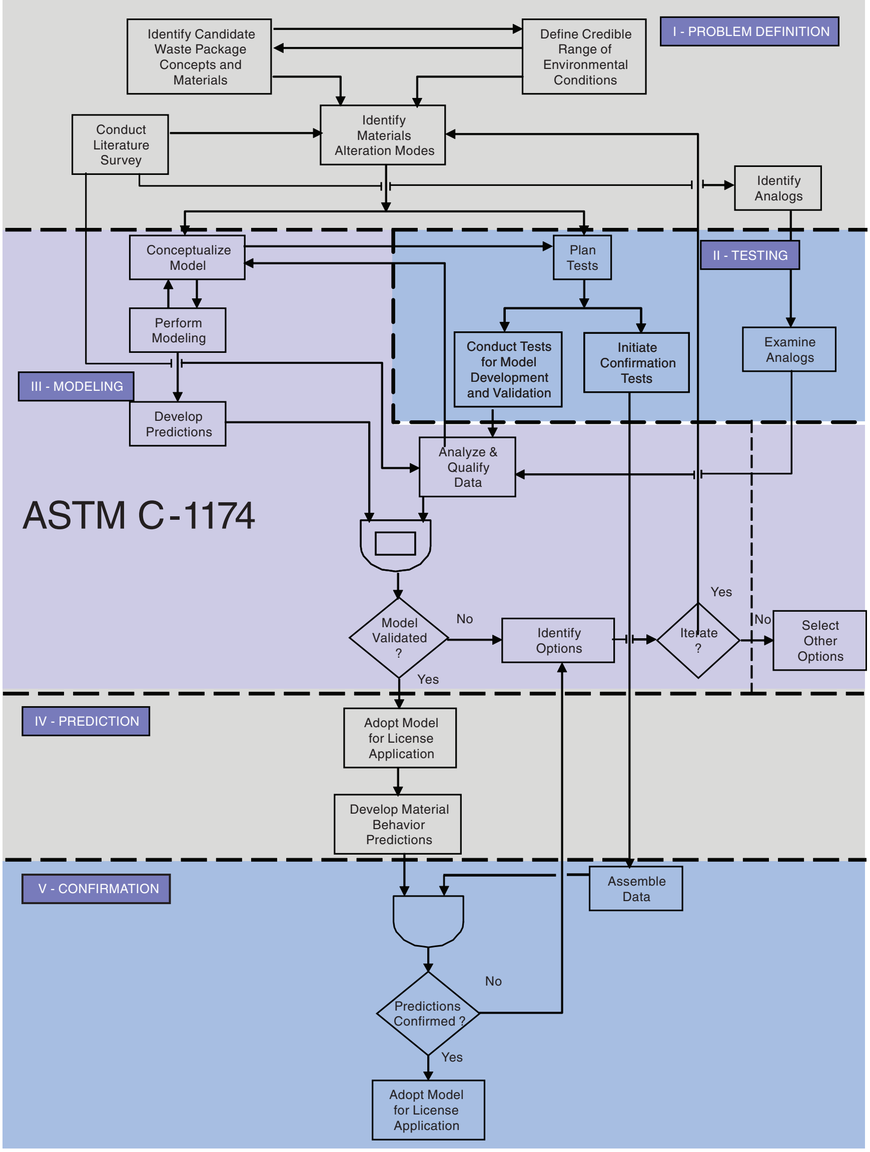

FIGURE 5.1 Logic roadmap to qualification of a waste form in a licensed geologic repository in the United States.
SOURCE: From ASTM C1174-07.

- Attribute tests to measure intrinsic materials properties.
- Characterization tests to measure the effects of material and environmental variables on behavior.
- Tests to accelerate alteration and determine important mechanisms and processes that can affect the lifetime performance of waste form and EBS materials.
- Service condition tests to confirm the appropriateness of the model and variables for anticipated disposal conditions.
- Confirmation tests to verify the predictive capacity of the model.
- Tests or analyses performed with analogue materials to identify important mechanisms, verify the appropriateness of an accelerated test method, and to confirm long-term model predictions.

ASTM C1174 identifies what type of information is needed from various test methods and how that information should be applied. For most waste forms, it is expected that several test methods will be needed to understand the degradation mechanism(s) well enough to develop a performance model. Many of the tests and analyses address multiple information needs.

For example, many tests provide insights into the waste form matrix degradation mechanism and radionuclide release mode (Ebert, 2008):

- Identify the radionuclide release mechanism—tests must determine if the radionuclide is released congruently with the matrix or incongruently (Box 5.2). In most cases, these tests will serve to confirm the release mode based on an understanding of the matrix material and how the individual radionuclides are incorporated. Testing must determine if the release of various radionuclides is by diffusion (ion exchange), congruent dissolution of the matrix, or dissolution of the matrix to expose the phase containing the radionuclide, which then may dissolve or be released as a colloid.
- Determine the matrix degradation mechanism—it is anticipated that radionuclides will be released by degradation of the waste form matrix, either physically or chemically. Dissolution of the matrix may be required before a radionuclide can be released, or it may simply need to be physically or chemically altered. Removal or reaction of a particular component in the matrix may be required to provide a pathway for release of the radionuclide. For some multi-phase waste forms, dissolution of an encapsulating material may be required before water can contact and react with the phase bearing the radionuclide. The durability of both the matrix and the radionuclide-bearing phase will then affect its release, and these may occur by different mechanisms.

Many of the accelerated durability tests developed by ASTM have been in support of the testing block in Figure 5.1 with the purpose of accelerating the alteration of a waste form and determining the important release mechanisms. As noted previously, no one test gives all the information about alteration parameters and mechanisms; hence, various tests were developed to be used in conjunction with each other and with modeling.

5.5 DISCUSSION

State-of-the-art tests on waste form materials are used for a number of purposes, ranging from the investigation of degradation behavior and release of constituents to the parameterization of predictive models for waste form and disposal system performance. A large number of standard test protocols have been developed over the past three decades for these purposes. A key take-away message from this chapter is that these tests are material-specific, and no one test gives all the information needed to understand waste form properties or performance; indeed, a battery of tests must be used to understand waste form properties or performance.

Standard tests have been developed and qualified for use with borosilicate glass, glass-ceramic, and some crystalline ceramic materials. These tests can be applied to other waste form materials as part of experimental studies to investigate their degradation behavior. A standard testing protocol (ASTM C1174) has been established to qualify new waste form materials for use in disposal applications. However, the use of this protocol to qualify a waste form material for which the release mechanism is not known and existing standard tests have not been demonstrated to be appropriate is a detailed and laborious process.

APPENDIX 5.A
HISTORICAL DEVELOPMENT OF WASTE FORM TEST PROTOCOLS

In the early 1980s, the Office of Nuclear Waste Isolation (ONWI) under the Nuclear Waste Terminal Storage (NWTS) Program developed draft performance specifications and data requirements for mined geologic disposal of nuclear waste (ONWI 1981). Many of the requirements were for safe transportation of waste forms from their production sites to a geologic repository. The draft specifications required the following minimum information for waste forms:

- Waste loading, including isotope inventory and heating rates
- Radionuclide solubilities in various ground waters
- Dissolution rates
- Thermal properties
- Mechanical strength properties
- Radiation stability
- Gas generation rates
- Physical properties
- Phase identification and composition

It was judged that this data would be sufficient to demonstrate the contribution that the waste form makes to the performance of the entire waste package (ONWI, 1981). ONWI required standardized, reproducible testing based on sound statistical principles to ensure high data quality.

In October 1979, DOE established the Materials Characterization Center (MCC) at the Pacific Northwest Laboratory (now the Pacific Northwest National Laboratory). The MCC developed tests (Mendel, 1983) for high-temperature vaporization of radionuclides (MCC-8), impact behavior (MCC-10), tensile strength (MCC-11), and chemical durability (MCC-1 through MCC-5) (see Table 5.A.1). Some of the durability protocols were static to mimic the slow flow of water in a flooded repository; some were dynamic to define a forward rate of maximum dissolution. Most were performed in three standard leachants: distilled water, WIPP Brine A, and a tuff groundwater representative of Yucca Mountain, Nevada. Results were always reported as normalized elemental mass loss in grams of test material per square meter of waste form surface area.

MCC-1 and MCC-2 have become ASTM C1220 (Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste), MCC-3 has become ASTM C1285 (Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test

TABLE 5.A.1 MCC Test Methods

Waste Form	
Chemical durability	MCC-1, 2, 3, 4, 5
Aging effects (thermal and radiation)	MCC-6, 7, 12, 13
Volatility	MCC-8, 9, 16
Physical strength	MCC-10, 11, 15
Canister Container	
Corrosion resistance	MCC-101, 102, 103, 104
Repository Interactions	
Canister/container corrosion	MCC-105[a]
Waste form durability	MCC-14[a]

[a] The repository interactions tests are divided into site-specific subcategories, e.g., MCC-105.1 (basalt).

(PCT)), MCC-4 has become ASTM C1662 (Standard Practice for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method), and MCC-5 is the Soxhlet durability test often performed in Europe to evaluate waste form durability. Additionally, the International Atomic Energy Agency has recommended for durability testing the International Standards Organization standard ISO 6961 (Long-Term Leach Testing of Solidified Radioactive Waste Forms). This leaching test was developed by the ISO and is similar to MCC-1 at normal (room) temperature.

Additional test protocols have been developed by the American Nuclear Standards Industry (ANSI) and by the U.S. Environmental Protection Agency (EPA). Some of the EPA leach protocols are designed to test the waste form response under adverse conditions[1] to provide confidence that the release of hazardous species will meet the Universal Treatment Standards (UTS) under the Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDR) regardless of whether the waste form was made from characteristically hazardous or listed wastes (see Chapter 8).

Although no specific test protocols exist for radiation damage, the existing leaching protocols can be used to test a waste form's durability response both before and after radiation damage at a variety of doses. However, this approach may not reveal subtle effects, such as preferential etching, if the waste form dissolution rate is too rapid. In addition, the existing thermal stability protocols can be used in conjunction with the existing durability protocols to test a waste form's durability before and after thermal treatment.

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[1] Acetic acid is used to simulate leaching under acidic conditions, such as what might occur in a landfill.

APPENDIX 5.B
QUALIFICATION OF HLW BOROSILICATE GLASS AND HLW GLASS PRODUCTION AT THE SAVANNAH RIVER SITE

1973	Waste form and process alternatives evaluation—concrete and glass
1975	Savannah River Site decision to use borosilicate glass for HLW immobilization
1976	Waste form and process selection-continuous glass production process
July 1982	DWPF Environmental Assessment released for public comment
Nov. 1983	Groundbreaking for the Defense Waste Processing Facility (DWPF)
1983	Initiated validation of glass performance (international burial testing)
Aug. 1984	DWPF construction began
1986	First waste compliance plan completed
1987-1994	Established reproducible glass performance test protocol (product consistency test)
Aug. 1988	Major DWPF construction efforts complete
Aug. 1989	DWPF operations began—component testing
1990	Established performance benchmark glass (EA Glass)
April 1994	Non-radioactive operations began—established control of the DWPF glass production process
1996	Radioactive operations began of DWPF
2010	Fourteen years of HLW glass production

APPENDIX 5.C
DURABILITY TEST PROTOCOLS

The test protocols listed in Section 5.3 are described in this appendix.

ASTM C1220 (MCC-1 AND MCC-2)

This test method provides a measure of the reactivity of a material in a dilute solution in which the test response is dominated by reaction of the specimen. The specimen is normally a monolith[1] polished to 600-grit finish. The test is normally performed at temperatures of 40°C, 70°C, and 90°C in either deionized water or groundwater (actual or simulated). If multiple temperatures are tested the activation energy for dissolution can be measured for a given reaction time. Test durations vary; nominal is 28 days, but shorter periods of time (1, 3, 5, and 7 days) can be measured and used to determine a forward rate of reaction (Ebert, 2005), or longer-term tests up to several years can be conducted.

This test method can be used to compare the dissolution behaviors of candidate radioactive waste forms and to study their reactions during static exposure to dilute solutions in which solution feedback effects are small. Data from this test may form part of the larger body of data that is necessary in the logical approach to long-term prediction of waste form behavior, as described in ASTM C1174. In particular, solution concentrations and characterization and altered surfaces may be used in the testing of geochemical modeling codes. This test method can be used as either a "characterization" or "accelerated" test under the protocol of ASTM C1174 (see main text). Although it is not a formal part of the test method, the specimen can also be examined for surface alteration products to correlate with the solution results and study the reaction mechanism.

This test method is sensitive to the dissolution behavior of the waste form. The geometric surface area of a specimen can be measured to allow accurate calculation of the specific dissolution rate. The test is easy to run, can be conducted under a wide range of conditions, provides a large solution volume for analysis, and is economical. Short-term tests can be used to measure the effects of temperature, pH, and components in the leachant on the dissolution rate of materials that degrade by dissolution. Longer-term tests become affected by the affinity term and can be used to estimate the solubility of the waste form by regressing data with the rate expression.

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[1] This test method excludes the use of powdered specimens and organic materials.

ASTM C1285 (MCC-3)

This durability test method, commonly known as the Product Consistency Test (PCT), has two parts: PCT-A and PCT-B. The specimen is normally crushed to increase the surface area exposed to the test solution, which accelerates the evolution of the solution chemistry toward saturation (see Figure 5.C.1).[2] PCT-A is a seven-day chemical durability test performed at 90°C in a leachant of ASTM-Type I water. The test method is static and conducted in stainless steel vessels. PCT-B is a durability test that allows testing at various test durations, temperatures, mesh size, mass of sample, leachant volume, and leachant composition, including simulated or actual groundwaters. This test method is static and can be conducted in stainless steel or Teflon vessels.

Together, PCT-A and PCT-B provide data for evaluating the chemical durability of glass waste forms as measured by elemental release. The glass waste forms are defined in the procedure as homogeneous glasses, phase separated glasses, devitrified glasses, glass ceramics, and/or multiphase glass-ceramic waste forms. Although this test has not been qualified for other types of waste form materials (e.g., cements), it is often used to determine dissolution mechanisms for other waste form types or used as a scoping test to compare waste forms or interpret mechanisms.

PCT-A can specifically be used to obtain data to evaluate whether the chemical durability of glass waste forms has been consistently controlled during production via the linking relationships discussed in Section 5.1 of this chapter. In the case of homogeneous borosilicate HLW glasses, acceptable performance is defined as an acceptably low dissolution rate, which is controlled by maintaining the glass composition within an acceptable range. The approach can be represented in terms of the linking relationships shown in Equation 5.1.

This linkage is appropriate for glass waste forms because the radionuclides are chemically bound within the glass structure and are released congruently as the glass dissolves. In general, for any waste form it must be established that control of performance in a laboratory test (i.e., the PCT) predicts acceptable control of performance in a disposal system based on performance tests, known mechanisms, and modeling.

PCT-B accelerated tests have been developed to provide data on longer-term performance of HLW borosilicate glass waste forms. PCT-B can specifically be used to measure the chemical durability of glass waste forms under various leaching conditions, for example, by increasing test durations, crushing of the solid waste form to increase the ratio of sample surface

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[2] Acceleration by increasing the surface area (SA) to volume (V) of leachant or the time duration of the test (t) is a common practice in waste form durability testing.

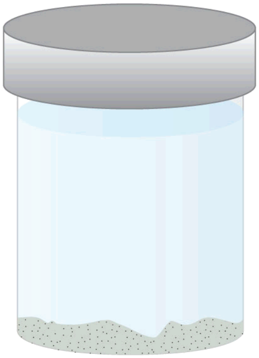

FIGURE 5.C.1 Example of static container for PCT.
SOURCE: Eric Pierce, Oak Ridge National Laboratory.

area (S) to solution volume (V), and using a variety of simulated or actual groundwater compositions. In addition, the temperature of the PCT-B type test can be increased to any temperature that does not alter the long-term dissolution mechanism to increase the dissolution rate and advance the overall progress of the waste form-groundwater reaction (Steefel et al., 2005).[3]

PCT-B tests can be used to determine radionuclide solubilities in various groundwaters; as an accelerated test to determine long-term dissolution rates of waste form materials; and to determine when solubility-limited concentrations for some radioelements are reached. The measurement of such concentrations provides crucial inputs to performance assessment of disposal systems. Thermodynamic databases are typically used to derive solubility-limiting phases for radioelements for all types of radioactive wastes in disposal systems (e.g., ANDRA, 2005; DOE, 2008; Nagra, 2002; NRC, 1996, 2005).

Such derivations are, however, complicated by factors such as metastability of precipitated radionuclide-bearing phases as well as the potential for co-precipitation of radionuclides as trace components in clay, zeolites, or other alteration phases (e.g., Apted, 1982; Bruno et al., 1997). Measurements from accelerated waste form testing of actual equilibrium or

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[3] With increasing temperature, it becomes critical that well-sealed test vessels are used so that no loss of water occurs arising from enhanced rates of evaporation. For test temperatures above 100°C, the internal water pressure of such sealed test vessels will move along the liquid-vapor (boiling) curve for water as defined by the imposed temperature, unless some external method (e.g., thin-walled, deformable metal "bags"; see Apted, 1982) are used to independently impose and control a higher test-system pressure to match pressure prevailing at appropriate repository depths.

steady-state concentrations of radionuclides can provide an important confirmation to the application thermodynamic databases. This raises the importance of continuing the development of advanced state-of-the-art solids and solutions analytical techniques in support of accelerated waste form testing (e.g., Pierce, 2008).

Data from PCT-B tests may form part of the larger body of data that are necessary for long-term prediction of waste form behavior (see Figure 5.1). PCT-B tests are useful for generating concentrated solutions to study chemical affinity effects on the dissolution rate. Tests at high temperatures and high glass/solution mass ratios can be used to promote the formation of alteration phases to (1) identify the kinetically favored alteration phases, (2) determine their propensity to sequester radionuclides, and (3) evaluate the effect of their formation on waste form dissolution rate. This information can be used to support the development of waste-form alteration models that can be coupled with relevant aqueous transport models to predict the release rate of radionuclides over the very long time periods pertinent to the operation of an HLW repository.

As noted previously, equilibrium or steady-state conditions may be achieved under the very extended service periods relevant to geological disposal. The same build-up of dissolved species that leads to a reduction in borosilicate dissolution rate also leads to saturation of the groundwater, with potential precipitation of both stable and radioactive dissolved species. At this point, the initial control of radionuclide release by reaction kinetics of the waste form would be replaced by solubility limits to radionuclide concentrations imposed by the initial crystalline waste form matrix, or by formation of new alteration products. The extended capabilities and flexibility of the PCT-B tests are intended to establish the various processes and associated data that control the release of radionuclides from disposal systems as waste forms react with groundwater over thousands of years and more.

ASTM C1662 (MCC-4)

This durability test method, known as the Single-Pass Flow-Through (SPFT) Test Method, is used for the measurement of glass dissolution rates. This test is most frequently used on homogeneous glasses, including nuclear waste glasses, in various test solutions at temperatures less than 100°C. The test procedure allows for inhomogeneous glasses (i.e., those that are phase separated or crystallized) to be studied provided the test response from each phase can be determined. The SPFT test is best suited for use with crushed materials, but tests can be conducted with monolithic specimens (Tole, 1982; Tole et al., 1986).

The SPFT test has been used for decades by geologists to measure the dissolution of minerals. It is commonly used for single-phase crystalline ceramics but has also been used for multiphase mineral waste forms (Icenhower et al., 2003; Jantzen et al., 2007; McGrail et al., 2003a,b; Zhao et al., 2000). Data interpretation is more complex with multiphase mineral waste forms because there are different source terms coming from the different mineral phases, unless comparisons can be made to the dissolution of single-phase natural analogue minerals and/or single-phase pure standards that have been tested for comparison. However the SPFT test is the most informative for characterization of a material's leaching parameters and is recommended for determining the long-term dissolution of glass (Strachan, 2001).

SPFT tests may be conducted under conditions in which the effects from dissolved species on the dissolution rate are minimized to measure the forward dissolution rate at specific values of temperature and pH, or to measure the dependence of the dissolution rate on the concentrations of various solute species. This test can be used to characterize various aspects of corrosion behavior that can be utilized in a mechanistic model for calculating long-term behavior of a nuclear waste glass. Many of the parameters determined from this test, such as the activation energy of dissolution and the reaction progress, are used in the TST and irreversible intrinsic models developed for mineral dissolution (Helgeson et al., 1984; Oelkers, 2001; Oelkers et al., 1994).

The composition of the leachant solution can be controlled precisely, and dissolution rates can be measured fairly precisely (see Figure 5.C.2). The effects of the solution flow rate and sample surface area are taken into account when determining the dissolution rate using the rate equation for glass/mineral dissolution. The test method is appropriate for other materials that dissolve by the same mechanism, such as aluminosilicate minerals (Ebert, 2008). The test can be used to measure effects of various leachant components when waste solution volume is not a limitation (e.g., with non-radioactive materials).

The reacted sample recovered from a test may be examined with surface analytical techniques, such as scanning electron microscopy, to further characterize corrosion behavior. Such examinations may provide evidence whether the waste form is dissolving stoichiometrically or if particular leached layers and secondary phases were formed on the specimen surface. These occurrences may impact the accuracy of the glass dissolution rate that is measured using this method.

ASTM C1663

The vapor hydration test (VHT) (Ebert et al., 1991) is a static test in which a monolithic specimen is suspended in a sealed vessel with a small amount of water. When heated, the vapor phase becomes saturated, and a

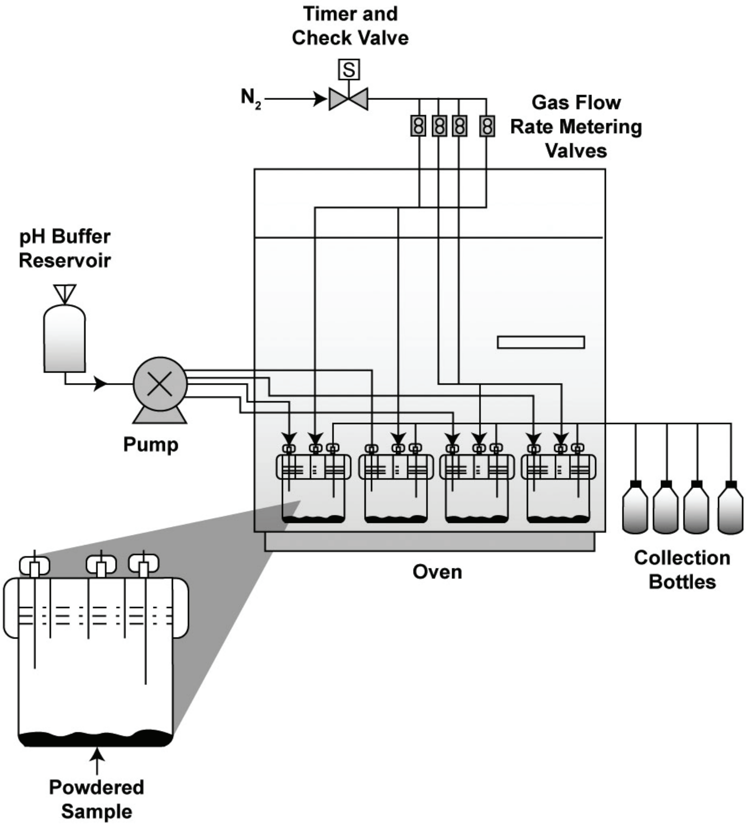

FIGURE 5.C.2 Schematic of the SPFT test method.
SOURCE: Eric Pierce,Oak Ridge National Laboratory.

thin film of water condenses on the specimen. The amount of water in the vessel is carefully controlled so that no liquid remains. This is done to prevent solution from dripping off the specimen and establishing a reflux cycle and to maintain a static film of water on the specimen. Alteration phases formed on the reacted sample are analyzed, and thickness of the altered surface layer is measured on a cross-sectioned specimen.

The VHT can be used to study the corrosion of glass and glass ceramic waste forms under conditions of high temperature and contact by water vapor or thin films of water. This method may serve as an accelerated test for some materials, because the high temperatures will accelerate thermally activated processes. A wide range of test temperatures have been reported in the literature, from 40°C (e.g., Ebert et al., 2005) to 300°C (e.g., Vienna et al., 2001). It should be noted that with increased test temperature comes the possibility of changing the corrosion rate-determining mechanism and the types of alteration phases formed from those that occur at lower temperatures such as in a particular disposal environment (Vienna et al., 2001).

The VHT can be used as a screening test to determine the propensity of waste forms to alter and for relative comparisons in alteration rates between waste forms. This test provides useful information regarding the alteration phases that are formed,[4] the disposition of radioactive and hazardous components, and the alteration kinetics under the specific test conditions. This information may be used in performance assessment (e.g., Mann et al., 2001).

In a modification of the VHT, enough water is added to promote refluxing, and the solution is analyzed periodically to track the release of constituents. This provides very high specimen surface/volume ratios in a test with a monolithic specimen. This modification is similar to the Soxhlet test, except that the sample itself is used to condense the water vapor and maintain an adhering layer of water. Thus, the modified VHT method serves as a simplified flow-through test or Soxhlet test at elevated temperatures.

PNNL PUF TEST

The pressurized unsaturated flow (PUF) test (McGrail et al., 1997a) was developed at Pacific Northwest National Laboratory (PNNL) to simulate the flow of water/air mixtures in a hydrologically unsaturated environment. The test method is similar to the SPFT test in that the water/air mixture flow through a crushed sample and the effluent is collected periodically for analysis. The leachant can be pre-conditioned by placing other materials upstream of the sample, for example, to simulate interactions with geologic or engineering materials; interactions of released species can be simulated by placing other materials downstream of the sample. Reacted sample materials can be extracted and analyzed at the end of the test.

This test can be used to directly incorporate materials interactions in the test and simulate integrated hydrologically unsaturated systems. Leachant composition is controlled prior to contacting the specimen and the solution chemistry resulting from corrosion can be tracked during the test. Altered specimen and alteration phases can be collected for analysis after testing. This test is appropriate for confirmation testing of waste form corrosion mechanism in an integrated environment, regardless of whether it is hydrologically saturated or unsaturated. The method is not well-suited

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[4] The alteration phases that form in this test can be used as indicators of phases that might form under repository conditions.

for tests with monolithic specimens because of uncertainties in the water flow path and specimen contact.

The PUF test has not been standardized and is currently not conducted anywhere but PNNL, which has patented it (McGrail et al., 1999a). Some key uncertainties in the test are surface area of the crushed samples, preferential solution flow paths through sample, and possible modifications of the effluent prior to collection. The data resulting from several processes occurring in parallel or series can be difficult to relate to each specific process (McGrail et al., 1996, 1997a,b, 1999b).

ASTM C1308

ASTM C1308 accelerated leach test (ALT) is a modification of the ANS/ANSI 16.1 test method (see Figure 5.C.3) that can be used to (1) determine if the release of a component is controlled by diffusion and (2) determine the effective diffusion coefficient based on a model for diffusion from a finite cylinder. It is applicable to any matrix material that does not degrade or deform during the test, including cements and other monolithic waste forms. It is a semi-dynamic test in which a monolithic specimen of prescribed dimensions is immersed in a large volume of leachant in a sealed vessel for a relatively short interval. The leachate solution is periodically removed for analysis, and the sample is placed in fresh leachant to continue the test. The cumulative amounts of the species of interest released in successive test intervals are fitted with the diffusion equation for a finite cylinder. The test results can be used to qualitatively determine if the release of a component is controlled by diffusion alone, partitioned into a non-leachable fraction, or affected by solution saturation effects. Although evaluation of the diffusion coefficient requires use of a monolithic specimen having right cylinder geometry, the test method can be modified for use with crushed materials to determine (qualitatively) if releases are being controlled by diffusion.

This test provides for the determination of an effective diffusion coefficient using a mechanistic model. The method provides a procedure to determine if release from small or irregular specimens is controlled by diffusion or matrix dissolution, even though the specimens cannot be modeled to determine a diffusion coefficient from the test data. Very large volumes of waste solution can result from testing.

ANSI 16.1

This standard is similar to EPA Draft Method 1315 as well as ASTM C1308 (in fact, ANSI 16.1 preceded the ASTM C1308 standard). It provides for less frequent replenishment of the leachate and the calculation of a leaching index for various radionuclides (see Figure 5.C.3). The test

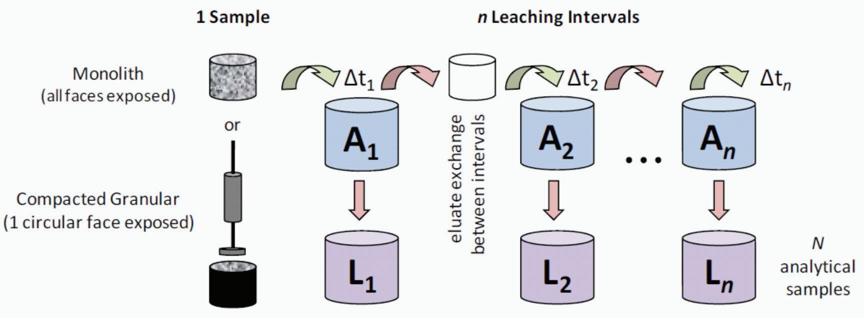

FIGURE 5.C.3 Schematic representation of the ANSI/ANS 16.1 test method. ASTM C1308 and EPA 1315 are similar but have more frequent replenishment frequencies. SOURCE: EPA, 2009.

procedure is used to measure and index the release of radionuclides from waste forms as a result of dissolution in demineralized water for five days or longer. The results of this procedure do not apply to any specific environmental situation except through correlative studies of actual disposal site conditions. The test has by now become familiar to those working in the radioactive waste form development field.

EPA 1315

This test protocol (EPA, 2009) is a relatively new procedure that is still undergoing round robin testing. It is designed to provide the mass transfer rates (release rates) of inorganic analytes contained in a monolithic or compacted granular material under diffusion-controlled release conditions as a function of dissolution time. Observed diffusivity and tortuosity may be estimated through analysis of the resulting dissolution test data. The test is suitable to a wide range of solid materials, which may be monolithic (e.g., cements, solidified wastes) or compacted granular materials (e.g., soils, sediments, stacked granular wastes) that behave as a monolith in that the predominant water flow is around the material and release is controlled by diffusion to the boundary.

This test provides intrinsic material parameters for release of inorganic species under mass transfer-controlled dissolution conditions. It is intended as a means for obtaining a series of eluants, which may be used to estimate the diffusivity of constituents and physical retention parameter of the solid material under specified laboratory conditions.

EPA 1315 is a characterization method and does not utilize solutions considered to be representative of field conditions. This method is similar in structure and use to predecessor methods ANSI/ANS 16.1 and ASTM C1308. However, this method differs from previous methods in that: (1) leaching intervals are modified to improve quality control, (2) sample preparation accounts for mass transfer from compacted granular samples, and (3) mass transfer may be interpreted by more complex release models that account for physical retention of the porous medium and chemical retention at the pore wall through geochemical speciation modeling.

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6

Waste Forms and Disposal Environments

The first charge of the statement of task for this study (see Box 2.1 in Chapter 2) calls on the National Academies to identify and describe "Essential characteristics of waste forms that will govern their performance within relevant disposal systems. This study will focus on disposal systems associated with high-cost waste streams such as high-level tank waste and calcine but include some consideration of low-level and transuranic waste disposal."

The most essential characteristic of a waste form that governs its performance[1] in a disposal system is *durability:* that is, the resistance of a waste form material to physical and chemical alteration and associated release of contained radioactive and hazardous constituents[2] (see Chapter 5). Durability depends partly on intrinsic material properties, as described in Chapter 3, but also on the physical and chemical conditions in the disposal facility into which the waste form has been emplaced. Consequently, the durability of a waste form in a disposal environment can be optimized by matching it with the appropriate physical and chemical conditions that foster long-term stability.

The focus of this chapter is on waste form performance in disposal facilities. Given the emphasis of the study charge on high-cost waste streams, this chapter focuses primarily on waste form performance in disposal facili-

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[1] That is, the ability of waste forms to sequester radioactive and hazardous constituents.

[2] As noted in previous chapters, radioactive waste can contain both radioactive and hazardous constituents.

ties for spent nuclear fuel (SNF), high-level radioactive waste (HLW), and transuranic (TRU) waste.

6.1 DISPOSAL OF WASTE FORMS

Waste forms containing radioactive waste are intended for disposal in engineered facilities constructed in stable geologic formations. *Geologic repositories* are designed for the disposal of higher-hazard wastes[3] such as SNF, HLW, and TRU waste. These facilities are constructed in geologic formations located hundreds of meters below Earth's surface. *Shallow-land disposal facilities* are designed for the disposal of lower-hazard wastes such as low-level radioactive waste (LLW). These facilities are typically excavated into sediments located within 10 meters or so of the Earth's surface (Figure 6.1).

Given the focus of this report on HLW, the discussion in this chapter focuses on geologic repositories. However, many of the environmental processes that govern waste form performance in geologic repositories would also apply to shallow-land facilities.

Geologic repositories are designed with multiple barriers to isolate waste from the environment (NRC, 2003; OECD-NEA, 2003). They contain both *engineered barriers*, which include the waste form, disposal canisters, and backfills, if present, and *natural barriers* such as the host rock. These barriers are intended to work in concert, passively providing different safety functions at different levels of effectiveness and reliability and at different times into the future for long-term isolation of radioactive waste (Figure 6.1). Barrier *safety functions* can overlap, providing so-called *latent safety functions*, with each barrier contributing to waste isolation at varying levels and times. Taken collectively, the barriers and their safety functions define the *safety concept* for the disposal system.

There are two basic isolation strategies to achieve long-term (10^3-10^6 years) safety of multiple-barrier disposal facilities (Apted and Ahn, 2010):

- *Containment* of radionuclides within the engineered and natural barriers of the disposal facility. Containment allows time for radioactive decay, which reduces the hazard of the radioactive component of the waste.
- *Attenuation of the concentrations* of radionuclides that are released from the disposal facility. This strategy may, for example, rely on

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[3] Hazard depends on several factors, including the types and concentrations of radioelements and their mobility in the environment. The classification of radioactive wastes in the United States is based on waste origin rather than hazard. Nevertheless, wastes destined for geologic disposal generally have a higher hazard than wastes disposed of in shallow facilities.

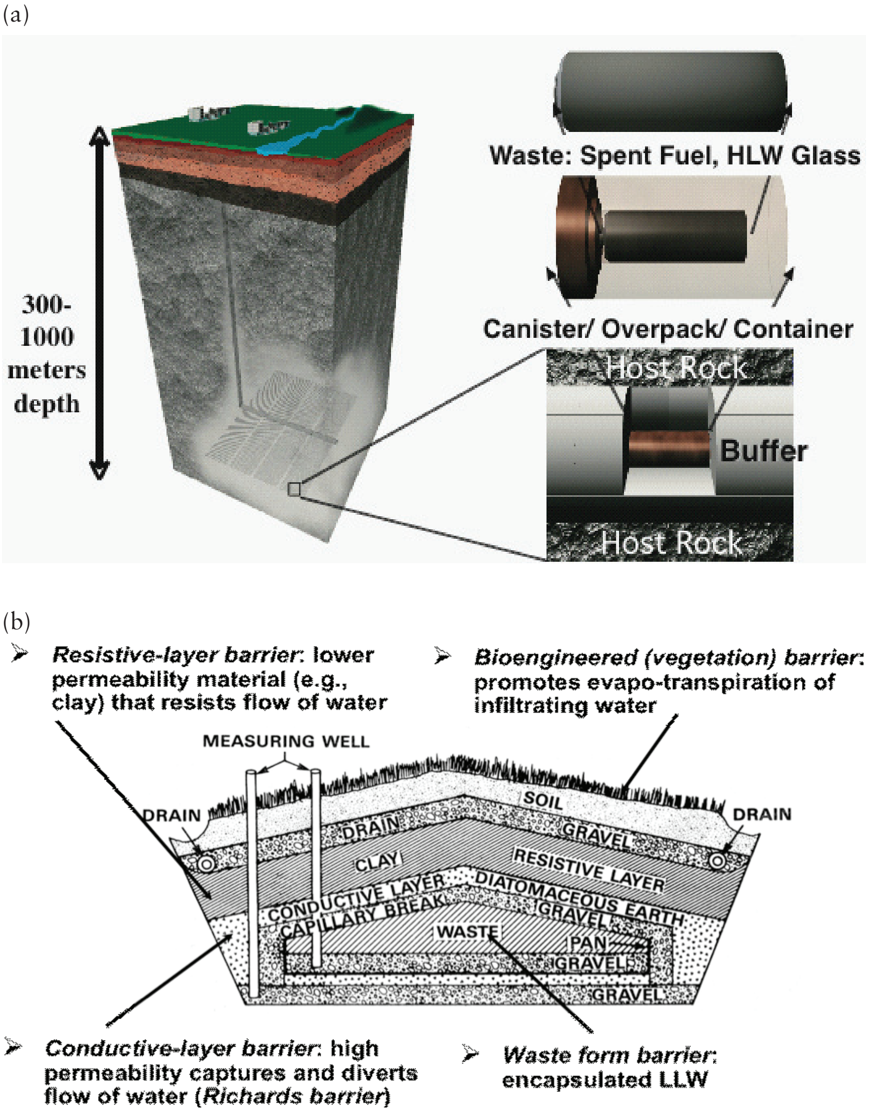

FIGURE 6.1 Examples of multiple-barrier disposal facilities for (a) SNF/HLW (b) LLW.
SOURCES: Apted and Ahn (2010); Schulz et al. (1992).

extremely slow waste form dissolution rates; on solubility limits for radionuclides in groundwater contacting the waste forms; on dispersion of radionuclides as they migrate through the barriers in the disposal system; on dilution, which can be volumetric (by mixing contaminated and uncontaminated groundwater) or isotopic (by mixing radioactive and stable isotopes of the same elements; see Section 6.3.8); and on long transport times from the disposal facility to the biosphere.

A number of concepts have been developed both in the United States and internationally for geologic repositories that utilize different barriers and rely on different processes to provide containment and attenuation (e.g., NWTRB, 2009; Witherspoon and Bodvarrson, 2006). A full review of these alternative concepts is beyond the scope of this report. It is important to understand that such concepts are typically tailored to work in concert with the environmental conditions that have been measured and characterized for specific disposal sites.

6.2 GEOLOGIC ENVIRONMENTS

The desirable geologic characteristics of repositories have been well-delineated. According to Bodansky (1984):[4]

> A good repository site is one for which the location and type of rock (a) prevent or limit the flow of water into the repository, (b) provide geochemical conditions favorable for a low rate of corrosion of the waste package and low solubility of radionuclides in the event of entry of water, (c) slow the outward migration of water to the biosphere, (d) retard the motion of major radionuclides so that they move more slowly than the water, and (e) are at low risk of future disruption by earthquake, volcano, erosion, or other natural phenomena. Together, these attributes provide a series of natural barriers.

Decades of research nationally and internationally have created a wealth of world-wide accumulated experience concerning the disposal of radioactive waste in various geologic environments (Table 6.1). Studies have examined the merits of developing disposal facilities in salt, basalt, granite, tuff, clay, shale, and metamorphic rocks. Detailed studies, in some cases supporting planning and construction of disposal facilities, have been executed for clay, tuff, salt, and granite. Some important characteristics of these materials are described in the following sections.

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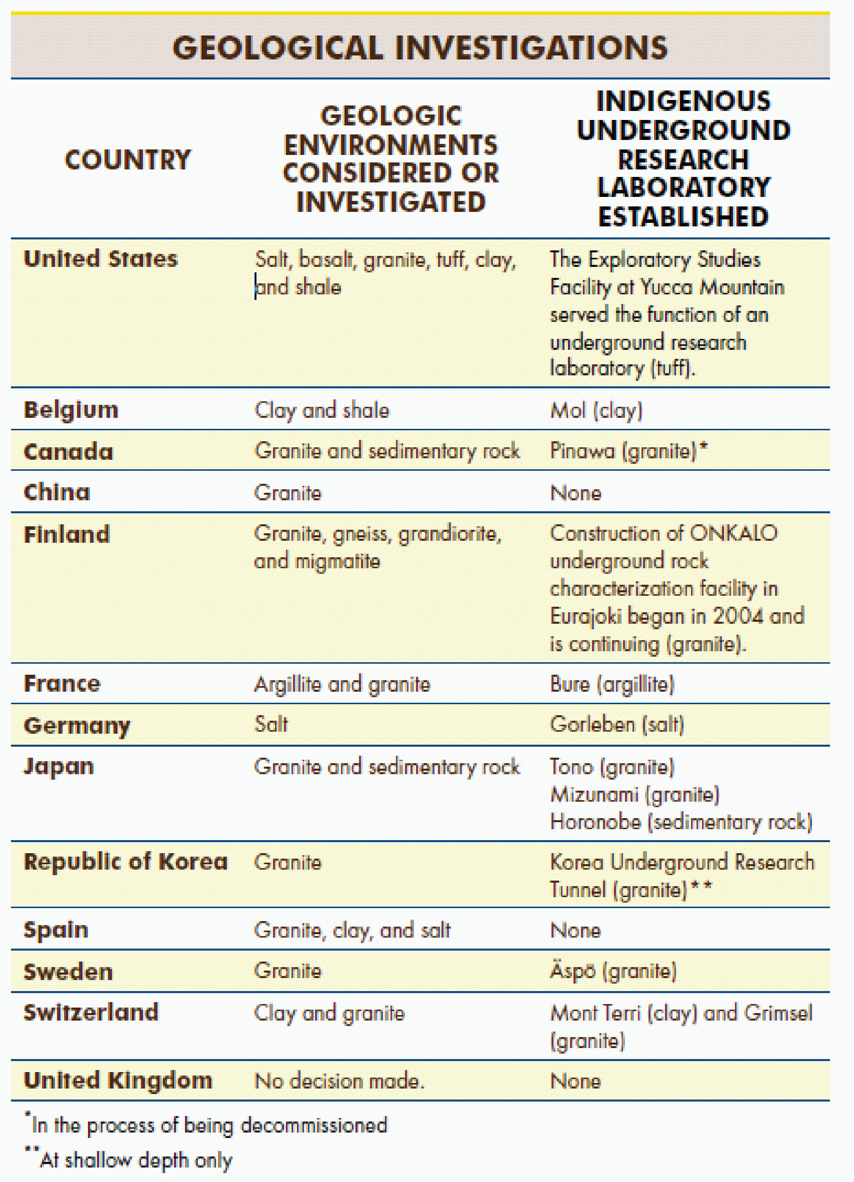
[4] Bodansky (1984) also provides a discussion of geologic environments for disposal facilities.

TABLE 6.1 Geologic Investigations of Potential Sites for Disposal of SNF/HLW



GEOLOGICAL INVESTIGATIONS

COUNTRY	GEOLOGIC ENVIRONMENTS CONSIDERED OR INVESTIGATED	INDIGENOUS UNDERGROUND RESEARCH LABORATORY ESTABLISHED
United States	Salt, basalt, granite, tuff, clay, and shale	The Exploratory Studies Facility at Yucca Mountain served the function of an underground research laboratory (tuff).
Belgium	Clay and shale	Mol (clay)
Canada	Granite and sedimentary rock	Pinawa (granite)*
China	Granite	None
Finland	Granite, gneiss, grandiorite, and migmatite	Construction of ONKALO underground rock characterization facility in Eurajoki began in 2004 and is continuing (granite).
France	Argillite and granite	Bure (argillite)
Germany	Salt	Gorleben (salt)
Japan	Granite and sedimentary rock	Tono (granite) Mizunami (granite) Horonobe (sedimentary rock)
Republic of Korea	Granite	Korea Underground Research Tunnel (granite)**
Spain	Granite, clay, and salt	None
Sweden	Granite	Äspö (granite)
Switzerland	Clay and granite	Mont Terri (clay) and Grimsel (granite)
United Kingdom	No decision made.	None

*In the process of being decommissioned

**At shallow depth only

SOURCE: NWTRB (2009).

6.2.1 Salt

Salt deposits form where water is evaporated, typically over thousands of years. Evaporation of a shallow inland sea or lake can give rise to large deposits composed primarily of the minerals halite (NaCl) and sylvite (KCl) and secondarily of the minerals gypsum ($CaSO_4(H_2O)_2$), anhydrite ($CaSO_4$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and various borate minerals.

Two general types of salt deposits have been investigated for disposal of SNF/HLW and TRU waste: bedded salt deposits and salt domes. Bedded salt deposits consist of thick layers of salt with significant lateral extent. In contrast, salt domes are the result of buoyancy-driven migration of salt into overlying rocks to form large diapir structures. Salt deposits of either type may have associated oil and gas or other mineral resources, the existence of which may increase the probability of human intrusion (by drilling or excavation) into disposal facilities located within those deposits.

The halide minerals[5] that constitute the bulk of salt deposits are water soluble and easily deformed under moderate pressure. Permeability in such a rock is essentially non-existent because deformation readily closes pore spaces and seals fractures. Some water is trapped as fluid inclusions in the salt crystals, and pockets of saline brines trapped during formation of the salt deposits often persist for geologic times (i.e., tens to hundreds of millions of years). Such inclusions have been observed, for example, within the Salado Formation at the Waste Isolation Pilot Plant (WIPP) in New Mexico (Stein, 1985). These saline brines are high ionic strength chloride solutions.

A waste form emplaced in a salt deposit well below Earth's surface will not contact flowing water unless a disruptive geologic event such as a meteorite impact or human intrusion takes place. Groundwater flow is thus not a factor in determining waste form performance in salt. Because salt deposits are easily deformed, however, materials placed within them can physically move over the course of time if they are more or less buoyant than the salt itself. Buoyancy-driven transport of materials can be enhanced at elevated temperatures (e.g., Nunn, 1996; Speight, 1964); brine inclusions in salt will preferentially move toward heat sources (i.e., up the thermal gradient) in the salt. (The brine will preferentially dissolve salt at the higher-temperature wall of the inclusion while simultaneously precipitating salt at the lower-temperature wall of the same inclusion.) Consequently, emplaced materials with significant heat loads can be problematic for disposal in salt.

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[5] Halide minerals contain one or more of the halogen anions bromine, chlorine, fluorine, or iodine.

6.2.2 Clay

Clay minerals[6] consist of sheets of silicate tetrahedra combined with layers of octahedra containing various metals surrounded by oxygen or hydroxyl ions; they may also contain water and various alkali and alkaline earth elements. Clay minerals are the major weathering products of silicate minerals such as feldspar; they can form in sedimentary deposits and where any silica-rich rock is weathered or altered by relatively low-temperature geologic fluids. Clay deposits can form *in situ* as a result of weathering of rocks such as volcanic ash or tuff, or accumulated in sedimentary deposits as a result of transport by wind, water, gravity, or ice. Clay deposits that form *in situ* can have significant lateral extent, whereas sedimentary deposits tend to be more restricted in area.

It is important to note that there are dozens of varieties of clay minerals with considerably varied chemical and physical properties. Some clay minerals, for example, readily exchange cations contained between the silicate sheets in their structures; others may swell significantly when they absorb water. The specific chemical and physical properties of a given clay deposit depend strongly on its mineralogy and the presence of organic matter. Organic matter is often present, sometimes in large quantities, and ensures that any water that is present does not contain dissolved oxygen. In the absence of radiolytic decomposition of water (see Section 6.3.7), its oxidizing potential is minimal.

Owing to the extremely small size of clay grains, clay deposits are readily compacted and have low porosity and extremely low permeability.[7] Clay minerals have been proposed both as the host rock for SNF/HLW repositories and for use as buffer/backfill materials. For example, swelling smectite clay has been proposed for use as an engineered buffer/backfill barrier in most planned repositories for SNF/HLW in Europe (NWTRB, 2009). However, not all clay deposits have desirable characteristics for emplacement of radioactive waste forms.

6.2.3 Other Sedimentary Rocks

Sedimentary deposits are produced as a result of transport and deposition of weathered rocks near the Earth's surface. The transporting agents include water, wind, gravity, and ice. Such deposits are initially unconsolidated, but they may later become consolidated as a result of compaction (if they are buried) and cementation by minerals precipitated from ground-

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[6] In geologic and engineering terminology *clay* also refers to minerals having small grain sizes regardless of their composition. They include clay minerals as well as small grains of quartz and feldspar.

[7] Permeability is the ability of a material to transmit fluids (such as water) by advective flow.

water flowing through them. Consolidation typically occurs over thousands to millions of years.

The physical and chemical properties of such deposits can be highly variable and depend both on the source material and the depositional environment. For example, materials deposited by ice (glacial tills) are typically unsorted, unstratified, and highly variable in composition. In contrast, sediments deposited by water (e.g., in a river or beach environment) are typically well sorted, stratified, and may contain a restricted range of mineral compositions (dominantly quartz) and grain sizes. Deposits from wind likewise exhibit restricted grain size distributions and also are dominantly quartz.

Unconsolidated sediments can experience very high groundwater flow rates because of their high permeability. The pore spaces within these sediments will be filled with both air and water above the groundwater table (the *unsaturated zone*, also referred to as the *vadose zone*). Below the groundwater table (in the *saturated zone*), the pore space is filled with water. Oxidizing conditions will prevail in the vadose zone in the absence of significant organic matter or microbial activity. At least locally oxidizing conditions are likely to prevail even in saturated unconsolidated sediments if they are near enough to the surface to be subjected a high influx rate of oxygenated water from the overlying vadose zone.

Thick alluvial deposits, especially in the Great Basin in the western United States, have attracted attention as potential sites for disposal of radioactive waste (Tyler et al., 1996). Disposal of radioactive waste forms in shallow unconsolidated sediments may be suitable for relatively low-activity materials when combined with appropriate supporting engineered barriers (see Figure 6.1b).

Sedimentary rocks with significant organic components present a strongly reducing geochemical environment. An example is oil shale, a fine-grained sedimentary rock that contains a number of solid organic compounds that can be thermally processed to recover oil. The permeability of such a rock may be low, and any groundwater that is present will be devoid of dissolved oxygen. The rock presents substantial reducing potential and may continue to buffer the redox potential of water for a very long time.[8]

6.2.4 Crystalline Rocks

The continental crust is composed primarily of crystalline igneous and metamorphic rocks containing aluminosilicate minerals such as quartz, feldspar, mica, and minor amounts of other minerals. These rocks are pro-

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[8] Such reducing shale formations account for the existence of the natural reactor at Oklo in Gabon (Janeczek, 1999).

duced by the cooling and crystallization of molten magma (igneous rocks) or by solid-state mineral reactions at elevated pressures and temperatures (metamorphic rocks). Extrusive igneous rocks (e.g., basalts), intrusive igneous rocks (e.g., granite), and metamorphic rocks (e.g., gneiss) have been or are being considered as potential environments for the disposal of SNF/HLW (see Table 6.1).

Extrusive igneous rocks form when molten lava is cooled at or near Earth's surface. Although there is essentially a continuum of silica concentrations in these rocks, ranging from felsic (silica rich) to ultramafic (silica poor), basalt (mafic) is the most abundant extrusive igneous rock on Earth. Fissure eruptions have created vast accumulations of basalt, known as flood basalts; notable examples of flood basalts include the Columbia River basalts in the western United States and the Deccan Traps in India. Fissure eruptions produce layers of basalt in a series of extrusive events. Such sequences of basalt flows may be several kilometers thick and provide a relatively homogeneous geochemical environment for a disposal facility.

Basaltic rocks are variably crystalline, often with glassy components, depending on their cooling history. These rocks commonly contain significant porosity because of the development of gas bubbles prior to solidification, but these void spaces are not well connected and therefore do not result in high permeability. However, basalt flows can contain extensive systems of vertical fractures that arise from contraction during cooling. An extreme example is columnar basalt in which the entire flow layer has fractured into vertical columns a few tens of centimeters in cross section. As sequences of basalt flows originate from a series of discrete eruptive events, horizontal rubble zones and buried soil horizons can also occur. Water can flow rapidly through these fractures, zones, and horizons in what would otherwise be an impermeable rock.

Lavas of felsic composition are more viscous than their mafic counterparts, and they are usually erupted more violently as a result of the explosive decompression of dissolved gases. These eruptions can eject substantial volumes of mineral, rock, and glass fragments (referred to as *volcanic ash*) that accumulate to form *tuff*. These fragments may be compacted and fused together to form *welded tuff*. Tuffs can contain significant porosity because of trapped air bubbles, but increased degrees of welding reduce porosity. The permeability associated with this porosity tends to be low. However, additional permeability can be produced by fracturing as the tuff cools and contracts, and additional fracturing can occur through subsequent tectonic processes. These fractures provide pathways for the flow of groundwater through the tuff, which can result in the formation of a suite of lower-temperature minerals, such as zeolites, with high ion-exchange capabilities.

Groundwater traveling through fractured rocks above the groundwater table contains dissolved oxygen and is therefore oxidizing. Such oxidizing environments may not be optimal for disposal of waste forms that are susceptible to oxidation, for example, SNF comprised of uranium/plutonium dioxide and some metal alloys. As will be discussed in more detail in Section 6.3.2, uranium, neptunium, plutonium, iodine, selenium, and technetium are more soluble in their oxidized forms.

Intrusive igneous and metamorphic rocks are characterized by interlocking crystals with little or no primary porosity. However, these rocks usually contain fractures due to some combination of cooling and tectonic processes, and these fractures provide pathways for groundwater flow. Groundwater flow rates in these rocks can vary significantly, from merely a few centimeters or less per year to rates exceeding several meters per year.

Groundwater in crystalline rocks below the water table may be oxidizing or reducing depending on the presence and reactivity of redox-active minerals (see Section 6.3.2). For example, water in a granitic rock containing significant magnetite (Fe_3O_4) and pyrite (FeS_2) or other reducing minerals will not contain dissolved oxygen in any appreciable quantities. Under these conditions dissolution rates of some waste forms may be much lower than in the presence of water containing dissolved oxygen. Moreover, the concentrations of actinides and some long-lived fission products will be lower under reducing conditions.

6.3 FACTORS AFFECTING WASTE FORMS IN DISPOSAL ENVIRONMENTS

A *disposal environment* is defined as the time-dependent physical and chemical conditions in a facility designed for the disposal of radioactive waste. An initially undisturbed geologic environment can be substantially perturbed by the development of a disposal facility. Factors that change the environment include the actual excavation, the addition of building materials (such as steel and concrete) for facility stabilization, and the emplacement of waste. The environment will also be impacted by the presence of engineered barriers such as buffer/backfill, overpacking materials, and canisters.

The disposal environment will change from the construction of underground facilities and emplacement of wastes. These changes continue over timescales of hundreds to thousands of years as physical and chemical conditions evolve and as the various components of the disposal facility—including the emplaced waste forms, other engineered barriers, and natural barriers—interact in a coupled fashion (see Chapter 7). In fact, interactions among these components under evolving environmental conditions of a repository will impact the stability and chemical durability of waste forms, as well as the mobility of any radionuclides released into the near-field host rock.[9] The complex interactions between the host rock of the facility, groundwater, and the waste forms, and engineered barriers make each disposal environment unique.

The stability of a waste form over time and its alteration products in a given repository environment dictate its performance. *Waste forms will perform optimally when matched with appropriate physical and chemical conditions that foster long-term stability.*

Given sufficient time, waste forms will eventually be contacted by groundwater and will begin to dissolve, releasing radionuclides into and through the near-field environment of the disposal facility, representing the *source term* for the facility. Degradation can occur through a number of physical and chemical processes, including *chemical corrosion* through reactions of the waste form with groundwater or *physical alteration* through buildup of radiation-induced damage or in growth of daughter products.

The following sections provide brief descriptions of some key processes and environmental factors that can affect waste form performance and radionuclide mobility in disposal environments.

6.3.1 Groundwater

The interaction of groundwater with waste forms in the near-field environment of the disposal facility is of paramount importance in determining waste form performance. The most important attributes of groundwater include volume and rate of flow, temperature, pH, presence of dissolved oxygen, ionic strength of dissolved constituents, and presence of inorganic and organic species that complex radioactive constituents or otherwise interact with the waste form in a deleterious fashion. Some of these factors are described in greater detail in subsequent sections.

As precipitation (rain, snow, hail), water contains comparatively few dissolved species, mainly atmospheric gases. Once in contact with soils and rocks, however, the chemical composition of the water will be altered as it passes through and over mineral surfaces. In fact, the total dissolved solids in groundwater are generally governed by the solubility of the mineral phases in the soil and rock through which it flows. The solubilization of major and trace constituents governs the ambient pH of the water and often the redox conditions of the environment.

The quantity of water moving through the vadose zone and into the saturated zone is directly dependent on rainfall, infiltration, and evapora-

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[9] As noted in Chapter 1, the *near-field environment* is generally taken to include the engineered barriers in a disposal system (e.g., waste canisters) as well as the host geologic media in contact with or near these barriers whose properties have been affected by the presence of the repository.

tion rates, which can change markedly over time. Groundwater flows are impacted by changes in recharge and withdrawal rates, water table gradients, and rock porosity and permeability because of changes in strain state and mineral precipitation/dissolution. The location of the groundwater table can change through time as a result of the interplays among these factors. As a consequence, a disposal facility constructed in the vadose zone or saturated zone near the groundwater table can cycle from saturated to unsaturated conditions.

Climate change has the most significant long-term impact on groundwater characteristics. Consider for example the Death Valley drainage basin in eastern California (Lowenstein et al., 1999). At present, Death Valley is a desert with minimal precipitation and a deep groundwater table. Toward the end of the last continental glaciation about 12,000 years ago, however, Death Valley contained several hundred feet of water. The Great Salt Lake in Utah is the remnant of the pluvial lake Bonneville, which existed at the same time and had a much greater areal extent and depth than the current lake. Climate changes that trigger such large variations can occur over the course of a few thousand years or less. There is substantial reason to believe that dramatic changes of the climate will occur in the future, as they have for millennia.

Consequently, a disposal facility in the vadose zone may experience significantly increased water flow rates and perhaps even fully saturated conditions in the future because of climate change. A disposal facility located below the water table would likely experience less variation as long as it remained saturated with water.

6.3.2 Redox Potential (Eh)

Redox potential (Eh) determines the activity of oxygen in geologic formations. It can be buffered by pairs of minerals containing an element, typically iron but also possibly manganese, sulfur, or carbon that can exist in two or more valence states. One mineral of the buffer pair contains the redox-active element in a more reduced valance state, and the other mineral contains the same redox-active element in a more oxidized valance state. Below the near-surface oxidizing zone (>100 m typically), oxygen has been removed by microbially mediated processes, which produces mildly to strongly reducing conditions depending on the mineralogical buffer-pair (Langmuir, 1997).

The prevailing buffered Eh state of a geologic formation can be perturbed by changing the availability of electron donors (reducing agents) or electron acceptors (oxidizing agents). Such changes can arise from numerous processes, for example, from introduction of atmospheric oxygen during construction of a repository or possibly from deep circulation of oxidizing waters during glacial periods. The mineral buffer-pair will act to restore the Eh to the ambient value unless the redox buffering capacity is exhausted (e.g., because all of the reduced mineral is converted to the oxidized-mineral).

Radioelements that occur in multiple oxidation states can exhibit variable chemical behavior depending on Eh, including carbon, selenium, iodine, technetium, plutonium, neptunium, and uranium. Each of these elements has accessible multiple (two or more) oxidation states under typical environmental conditions, for example iodine (–1 to +7); technetium (0 to +7); and plutonium, neptunium, and uranium (+3 to +6). The stability of phases containing such redox-active elements, and the subsequent transport behavior of such elements, will be strongly affected by redox conditions with disposal systems and host rock formations.

The oxidation state of the element can affect its mobility in the environment. For example:

- Technetium is relatively insoluble under reducing conditions (TcO_{2s}) (Chen et al., 2000) but forms the soluble pertechnetate anion (TcO_4^-) under oxidizing conditions. In contact with organic complexing agents[10] in solution, technetium can exhibit multiple valence states. At the Hanford Site, the presence of organic complexing agents in tank waste was seen to produce soluble technetium species that were not TcO_4^- (Icenhower et al., 2010).
- Iodine occurs in mobile forms whether conditions are oxidizing (IO_3^-) or reducing (I^-).
- Under conditions typically existing in subsurface environments, uranium, neptunium, and plutonium are relatively insoluble under reducing conditions (as AnO_{2s}, where An = actinide), moderately soluble (UO_2^{2+}/PuO_2^{2+}) but susceptible to hydrolysis/mobilization by complexation, or intrinsically soluble (NpO_2^+/PuO_2^+) in the presence of oxidizing agents. Hexavalent actinides interact strongly with natural complexing agents such as carbonate or humic materials and can exhibit substantial environmental mobility in this circumstance (Ewing et al., 2010).
- Anionic species are highly mobile and can transport from their point of release from a waste form with the water front.
- Cations with low charge (such as cesium (+1)) are measurably mobile, but less so than anionic species.

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[10] Such agents can include naturally occurring species such as citrate or oxalate or man-made reagents like EDTA.

6.3.3 pH

pH is a measure of the dissolved hydrogen ion (H^+ or H_3O^+) activity in a solution. Although there can be natural occurrences of relatively low pH (strongly acidic) and high pH (strongly alkaline) groundwater, these rather unfavorable pH conditions arise from known mineralogical factors and can be avoided through careful site characterization and selection. Many geologic formations are characterized by porewater that is buffered by mineralogical reactions to ambient pH values close to neutrality (Figure 6.2).

In the same way that Eh can be perturbed by events such as excavation of the rock during repository construction or deep circulation of surface water, pH can also be perturbed away from ambient values. For example, pH can be raised to high values by the introduction of cement-based materials into the repository, either as mechanical supports, flow barriers, or as a waste-form matrix. However, pH can also decrease to low values when groundwater contacts corroding engineered barriers (such as corroding waste canisters) in the repository. In the same manner as Eh buffering, the pH-active minerals of the rock formation will act to restore pore water pH to ambient values as long as the buffering potential of the minerals is not exhausted.

The presence of cementitious materials in concretes used in disposal facilities promotes alkaline conditions. This can lead to a significant increase in the dissolution rate of silica-based waste forms, such as borosilicate glass, attributable to the increased solubility of silica at $pH > 9$. This concern applies not only to conventional Portland-type cements, but also to recently developed so-called “low pH cements” as well slag- and fly ash-based concretes (Savage and Benbow, 2007).

Absent the presence of dissolved CO_2, alkaline conditions tend to precipitate polyvalent cations, including actinides, but will have minimal direct effects on cesium, strontium, technetium, or iodine solubility. Under alkaline and CO_2^- saturated conditions, the solubility of oxidized actinide species can be expected to increase substantially. On the other hand, the presence of phosphate minerals will tend to retard the mobility of actinides, but such retardation will probably be more effective under reducing conditions. High pH can also lead to rather rapid (few days) mineralogical alteration of swelling smectite clay, used as buffer/backfill in many disposal facilities (Figure 6.1a), to non-swelling illite clay (Eberl et al., 1993).

6.3.4 Anions/Salinity

Another important characteristic of groundwater affecting the performance of waste forms and disposal systems in general is the concentration

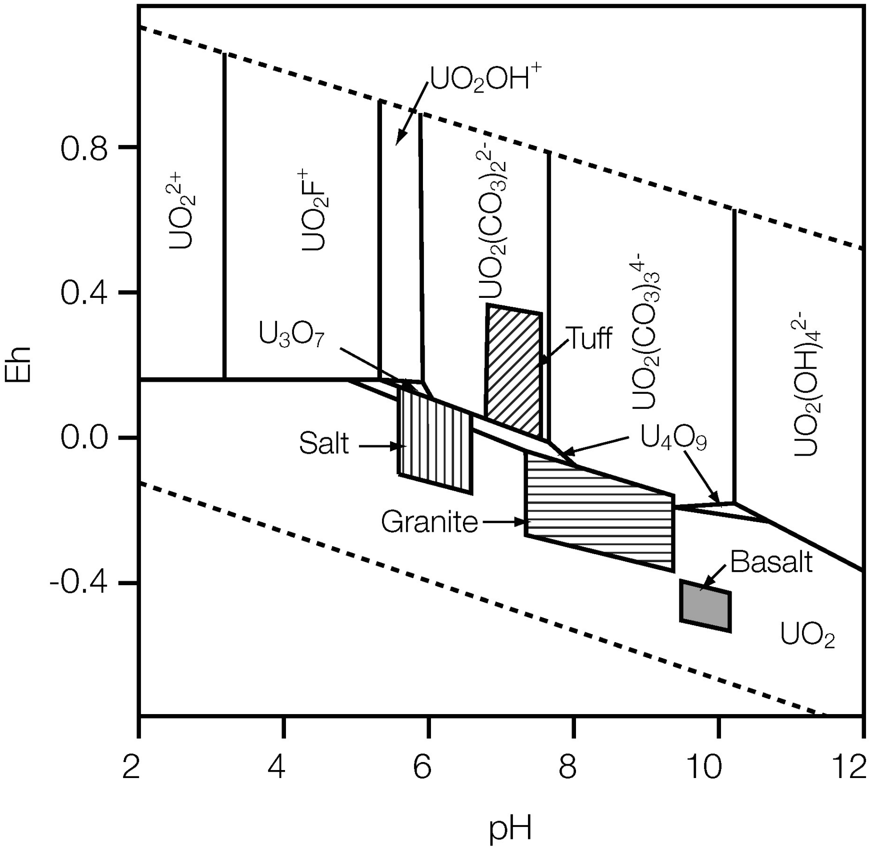

FIGURE 6.2 Stability diagram for UO_2 in various groundwaters at 25°C showing the pH-Eh stability fields for aqueous uranium species. The Eh-pH conditions for groundwaters in tuff (Yucca Mountain, Nevada), basalt (Hanford, Washington), granite (Sweden Stripa), and salt (Permian brine groundwater) are represented by the shaded areas. Note that basaltic and granitic groundwaters are reducing whereas tuffaceous groundwaters are oxidizing. Groundwater in shale (not shown) will likely be reducing, depending on its content of organic material, but pH would depend on rock composition and geologic setting.

SOURCE: Data from Jantzen (1992) and Johnson and Shoesmith (1988).

of anionic species.[11] These anions are important primarily because they can form stable aqueous complexes with radioelements, thus increasing radioelement solubilities in groundwater and modifying the transport characteristics of such radioelements through the near-field environment. Formation of anion complexes increases with increasing concentration of anions, so that high-salinity groundwaters can be a proxy indicator for anion complexation and its impact on radioelement solubilities.

For potable water, ionic strength is typically low, but highly saline waters are frequently encountered in the subsurface. The chemical properties of the water can be altered significantly by the presence of substantial amounts of dissolved salts.

6.3.5 Complexation

The solubilities of many radioelements can be significantly different in water containing complexing agents. For example, oxidized waters containing significant concentrations of carbonate will tend to support higher concentrations of uranium, neptunium, and plutonium but will tend to precipitate strontium (+2). High-sulfate waters should also lower the solubility of strontium (+2), although sulfate will have only a minimal effect on actinide mobility.

Organic complexing agents, if present, tend to increase the potential mobility of actinides; some may even suppress hydrolysis reactions that tend to precipitate such species. Examples have been reported of radionuclides being transported substantial distances from near-surface, LLW disposal sites through the agency of complexants like EDTA (Cleveland and Rees, 1976). The transport properties of cesium, iodine, and technetium will be minimally impacted by the presence of complexing agents (man-made or natural) unless the complexants also happen to be reducing agents. Humic and fulvic acids[12] can strongly complex polyvalent cations. Terrestrial humic materials are often polycyclic aromatic moieties[13] and may also reduce polyvalent metal ions, including actinides. Humic matter derived from aquatic sources tends to be more aliphatic[14] in nature and is less likely to produce reducing conditions. Many humic materials have colloidal dimensions and are thus capable of transporting complexed metal ions in

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[11] Anionic species include chloride, carbonate, sulfate, phosphate, and several other less abundant species.

[12] Humic and fulvic acids are the degradation products of naturally occurring complexants resulting most commonly from the decomposition of plant debris. These materials contain a wide variety of carboxylic acid, phenolic, alcoholic, and amino groups.

[13] That is, functional groups containing two or more simple aromatic rings that share carbon atoms. The carbon atoms in such rings are unsaturated.

[14] Aliphatic compounds contain fully saturated carbon atoms.

surface or subsurface waters. Humic colloids can also interact strongly with mineral surfaces to retard radionuclide mobility.

6.3.6 Colloid Formation

Radionuclides that are chemically sorbed to low-molecular-weight colloidal[15] materials have been observed to travel unexpectedly large distances in the subsurface environment. For example, radionuclides have been transported hundreds of meters in the subsurface via such transport methods at the Nevada Test Site and Mayak (Russia) Site (Kersting et al., 1999; Novikov et al., 2006).

Several materials can serve as a source of colloids including inorganic clay mineral degradation products and natural organic compounds such as humic acids. The latter can also serve as complexing agents. These compounds tend to be intrinsically reducing, but they are strong complexants for polyvalent metal ions and capable of transporting metals over substantial distances. Both humic and inorganic colloids can also interact strongly with mineral surfaces to retard radionuclide migration. Humic materials are ubiquitous in surface and near-surface environments and have also been reported to be present at low concentrations in deep groundwater. These complex polyelectrolytes can have substantial impact on cation transport in natural waters (Koppold and Choppin, 1987).

6.3.7 Radioactive Decay and Radiolysis

Radioactive decay and radiolysis may have profound effects on waste form performance in disposal facilities. The decay of radionuclides and formation of daughter products in a waste form can affect its stability. Additionally, radiogenic heating will create thermal, compositional, and radiation-field gradients that can alter thermodynamic equilibria and rates of chemical reactions in the engineered and natural barriers, including the waste form.

The radiolytic decomposition of water[16] produces an OH radical, H atom, and a hydrated electron (e^{-}_{aq}) as primary products, all of which are reactive and unstable species, whether oxidizing or reducing. The significance of radiolysis pertaining to waste form performance has been extensively studied (Shoesmith and Sunder, 1992). Radical recombination produces H_2O_2 (hydrogen peroxide), H_2O, and H_2. Reactions of the primary radicals or recombination molecules with other ions will produce

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[15] In the context of this report, a colloid is a sub-micron particle suspended in a liquid.

[16] Radiolysis is the dissociation of water molecules by alpha, gamma, and to a lesser extent beta radiation.

other radicals such as carbonate radical anion ($CO_3^{=}$) that can cause further redox changes.

Radical recombination reactions are most common in the energetic ionization tracks formed by alpha decay, the most common decay mode for heavy elements such as actinides. Most actinide isotopes emit alpha particles with 4-6 million electron volts (MeV) of kinetic energy, sufficient to break tens of thousands of chemical bonds. Hence, radiolysis can be an important process in actinide speciation; peroxide chemistry is an integral feature of this chemistry in systems containing water. Radioactive ion decay recoil represents another pathway for radionuclide release from waste forms.

In the near-field environment of a repository, ambient radiation fields will be substantial for hundreds to thousands of years (Roddy et al., 1986) after emplacement of the waste packages. In general, the waste packages are designed to minimize the potential impact of the radiolysis on the mobility of the wastes. However, it is possible that some percentage of the waste packages thus emplaced could experience a premature failure; consequently, the wastes could be subjected to a groundwater flow that has been impacted by the ambient radiolysis field. Redox active species (iodine, technetium, and actinides) released from the waste form will be most significantly impacted by this effect.

The near-field environment of a repository will be impacted by an ambient radiation field for millennia after emplacement of radioactive materials. Although the most intensely radioactive isotopes decay over a few tens of decades, long-lived radionuclides will cause a radiation field that persists essentially indefinitely. Evidence indicates that radiolysis impacts actinides even in natural uranium deposits (Kubatko et al., 2003). Once a waste form is exposed to groundwater, radiolytically derived species may impact redox active radionuclides such as the actinides, iodine, and technetium (Spahiu et al., 2004).

6.3.8 Natural Isotopic Dilution

Once a radionuclide leaves the waste form and enters the near-field environment of the repository it can be diluted naturally by stable isotopes of the same element. Such dilution can significantly reduce the biological hazard of the radionuclide.[17] For example, alluvial deposits in the Atacama desert (Chile) are sufficiently rich in iodine that several iodate

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[17] Although intentional dilution is generally considered to be inappropriate as a waste disposal strategy, natural isotopic dilution can serve as an important natural barrier in a disposal system. This further illustrates the importance of matching waste forms to disposal environments.

minerals (which are soluble) precipitate (Burns and Hawthorne, 1993). In such an environment introduction of radioactive iodine may have a negligible impact on the specific activity of the iodine in the environment. Other radioisotopes that can be affected by natural isotopic dilution are carbon-14, chlorine-36, and tritium.

As a specific example, Moeller and Ryan (2004) estimated the potential annual dose to adults from the intake of radioactive iodine-129 released from the proposed repository at Yucca Mountain, Nevada. According to their study, stable iodine-127 would dilute iodine-129 by a factor of more than 2 billion to 1. This natural dilution places an upper bound on the annual effective dose to adults from the release of iodine of about one millionth of the 0.15 mSv standard.

6.3.9 Biological Activity

Biological activity can also impact the transport of radionuclides. Biotransport mechanisms are likely to be minimized by high thermal gradients and high radiation fields during the first few decades after emplacement of waste, although extremophile microorganisms that are not adversely impacted by radiation are known to occur in nature. There is some information available about the biogeochemistry of some nuclides (iodine and possibly technetium), but comparatively little is known about actinide interactions with biological systems. It is known that cell debris can absorb and transport (as colloids) or retard mobility of some nuclides. Biological interactions with radionuclides in a repository environment are considered to be a frontier area for investigation, as there is so little information available.

6.3.10 Thermal Effects

Ambient temperatures increase with depth in Earth's crust, typically at a rate of 25-30°C per kilometer. Emplacement of waste forms that contain relatively short-lived radionuclides such as cesium-137 and strontium-90 (as is typical for spent nuclear fuel, for example) in a geologic repository will generate considerable heat from the decay of these isotopes. The impact on the thermal environment of the repository depends, among other factors, on the quantity of waste emplaced, the presence or absence of backfill, the waste configuration in the repository, and exchange of air between areas of the repository. Several of the factors affecting waste forms in disposal environments delineated in the sections above are temperature dependent, as are the complex couplings between such factors.

The boiling point of pure water in hydrologically saturated repository environments is about 220°C at a depth of 300 meters and is about 250°C at a depth of 500 meters. Typical maximum design temperature for saturated zone repositories is conservatively set between 80°C (e.g., SKB, 2006) and 120°C (e.g., Nagra, 2002), so no boiling of water will occur after resaturation of the repository. For unsaturated sites, groundwater boils at a temperature near 100°C, moderately affected by local atmospheric pressure and salinity. Promoting boiling conditions in an unsaturated site has been proposed to delay the contact of HLW/SNF by groundwater (e.g., DOE, 2008), although the maximum temperature was set below the thermal phase-transition for certain common rock-forming minerals such as silica.

Even below the boiling point of water, elevated temperatures will impact the reactivity of groundwater with a waste form (typically increasing reactivity), modify the solubility and complexation of radionuclides, and change the impact of radiolysis on waste form stability. Increased temperatures will also impact the chemical interactions of groundwater with the minerals present in the rocks, which may alter the salinity and dissolved gas content of the water. Furthermore, significant changes in the thermal regime surrounding a repository will modify the flow of both vapor and groundwater in the vicinity (Webb et al., 2003).

6.4 DISCUSSION

The focus of this chapter is on waste form performance with respect to the disposal of SNF, HLW, and TRU waste in repositories located several hundreds of meters below Earth's surface. The physical and chemical conditions in such repositories can be highly variable, depending on the rock type and subsurface conditions, especially with respect to groundwater. Furthermore, these conditions will evolve over time as a result of the construction of the facility, emplacement of radiogenic-heating waste forms, and natural events including climate change. Waste forms in such facilities will perform optimally in a repository when they are matched with the appropriate physical and chemical conditions that foster long-term stability. An important implication of this fact is that the suitability of a waste form for disposal depends crucially on the characteristics of the disposal facility into which it will be emplaced. The suitability of a particular waste form material for disposal in a particular repository can be assessed quantitatively, as discussed in the next chapter.

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7

Waste Form Performance in Disposal Systems

The third charge of the statement of task for this study (see Box 2.1. in Chapter 2) calls for the identification and description of "state-of-the-art tests and models of waste forms used to predict their performance for time periods appropriate to their disposal system." This chapter provides a discussion of the modeling portion of this charge, including waste form performance in disposal systems and models for evaluating waste form performance. Waste form testing is discussed in Chapter 5.

For the purposes of the discussion in this chapter it is important to distinguish between a *disposal facility* and a *disposal system*. The term disposal facility (see Chapter 6, Figure 6.1) refers to physical infrastructure; it typically includes tunnels (in the case of deep disposal) or surface excavations (in the case of shallow disposal), the surrounding host rock, and engineered barriers, including the waste form if present. A disposal system, on the other hand, refers to both physical infrastructure and how the natural and engineered barriers in that infrastructure function to sequester radioactive and hazardous constituents. The ability of a disposal system to sequester these constituents is referred to as *disposal system performance*. The performance of a disposal system can be evaluated using *performance assessment* (see Section 7.2).

7.1 WASTE MANAGEMENT SYSTEMS

As discussed in Chapter 2, waste processing and waste form production are key activities in the Department of Energy, Office of Environmental

Management's (DOE-EM's) cleanup program and, indeed, in any integrated waste management system. A conceptual diagram showing the important steps in DOE-EM's waste-management system is provided in Figure 7.1. There are interdependencies among the steps in this system; moreover, decisions at each step can affect waste management options and activities at subsequent steps.

The International Atomic Energy Agency (IAEA, 1995) addresses these interdependencies explicitly in *Principle 8. Radioactive Waste Generation and Management Interdependencies*, which states:[1]

> Since the steps of radioactive waste management occur at different times, there are, in practice, many situations where decisions must be made before all radioactive waste management activities are established. As far as reasonably practicable, the effects of future radioactive waste management activities, **particularly disposal** [emphasis added], should be taken into account when any one radioactive waste management activity is being considered.

In the context of the present report, this principle suggests the need to consider waste form development and selection in the context of disposal system performance. The principle also explicitly recognizes that, although there are many steps and activities that can optimize the safety, capacity, schedule, and cost of a waste management system, all paths eventually lead to final disposal.

7.2 DISPOSAL SYSTEM PERFORMANCE

The National Research Council (NRC) has published numerous reports bearing on the performance of disposal systems for spent nuclear fuel (SNF) and high-level radioactive waste (HLW) (e.g., NRC, 1995), transuranic (TRU) waste (NRC, 1996), and low-level radioactive waste (LLW) (e.g., NRC, 2005), as well as specifically on the performance of disposal systems (e.g., NRC, 1983, 1990, 2003). The NRC Committee on Technical Bases for Yucca Mountain Standards (NRC, 1995, p. 70) provided the following definition for disposal system performance, which, as noted previously, is usually referred to as *performance assessment* (PA):

> The only way to evaluate the risks of adverse health effects and to compare them with the [Environmental Protection Agency] standard is to assess the

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[1] This same principle to consider interdependencies in waste management operations and disposal is part of the Chapter 2, Article 4.iii of the Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management, of which the United States is a signatory.

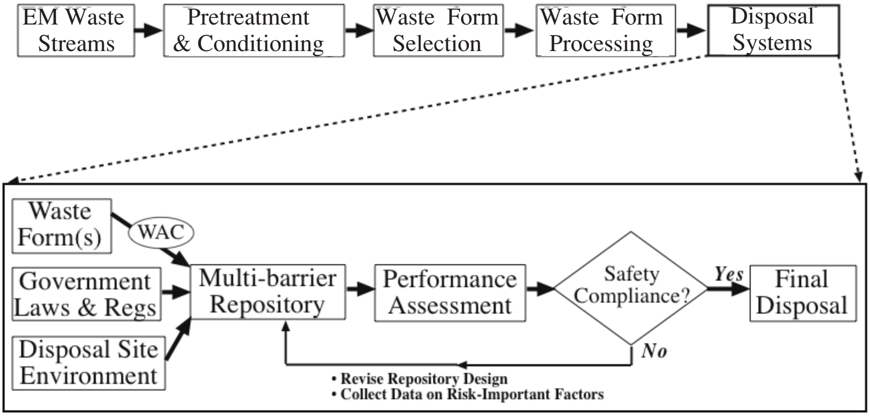

FIGURE 7.1 Schematic illustration of DOE-EM's waste management system. NOTE: WAC = waste acceptance criteria (see Chapter 8).

> estimated potential future behavior of the entire repository system . . . this procedure, involving modeling of processes and events that might lead to releases and exposures, is called performance assessment.

PA modeling has several useful applications in the design and licensing of disposal facilities, such as a repository for SNF/HLW; for example, PA can be used to:

- Demonstrate compliance with regulatory requirements, typically health-risk metrics such as dose rate to a critical group. Abstracted and simplified versions of PA can also be used to communicate with concerned stakeholders about disposal system performance. These applications are considered to be the conventional roles of PA.
- Identify system components and processes that strongly affect the isolation of radionuclides within disposal systems to coordinate and guide repository design, site characterization, and safety assessment activities.
- Evaluate the radiological safety of disposal systems in the larger context of costs, schedules, alternative options, and optimization of overall waste management policies.

This chapter focuses primarily on the first type of PA modeling: i.e., assessment and demonstration of compliance with regulatory guidelines. It describes a logical and systematic approach for carrying out PA modeling—an approach that is not always used in real-world applications.

When selecting a PA model, it is important to consider its fitness-for-purpose—that is, its suitability for the intended application. In many instances a "best estimate" analysis is warranted, especially with respect to establishing regulatory compliance. For exploratory purposes, conservative bounding analyses may be appropriate, although it must be cautioned that there is always a danger of compounding so many conservative assumptions and data values together that the resulting analysis becomes unrealistic and potentially misleading.

There are two important elements in a PA. First, the PA must consider the entire disposal system composed of multiple barriers and multiple containment processes. Modeling radionuclide releases and exposures requires consideration of the potential pathways by which radioactive constituents in the waste form could migrate through the disposal facility and eventually lead to future radiological exposures (health risks). Second, PA must consider the future behavior of these barriers (including the waste form) with respect to safety standards, such as those developed by the Environmental Protection Agency (see Chapter 8). The NRC (1995) recommended that a risk-based health standard should be applied as the appropriate metric for assessing the long-term safety of geological disposal for radioactive waste.

Repository programs typically employ a hierarchy of PA models to assess long-term safety, barrier design, and regulatory compliance of disposal systems containing radioactive waste. This hierarchy, referred to here as the *PA Pyramid*, is illustrated in Figure 7.2. The models of fundamental physicochemical processes affecting repository performance form the base of this pyramid. These models focus on processes such as chemical reactions among the waste form, other engineered barriers systems (EBS) in the disposal facility, and groundwater. Successively higher levels of PA models represent abstractions (with computational simplifications) of these underlying models. At intermediate levels in the PA Pyramid, the design and layout of EBS in the disposal facility are incorporated into the models. Models at the top of the pyramid represent abstractions with computational simplifications of the underlying models into a total system performance assessment, or TSPA (DOE, 2008; Whipple, 2006).

Uncertainties in assumptions, alternative conceptual models, and data are passed upward through the PA levels to ensure that all identified uncertainties are maintained at each level (e.g., DOE, 2008; Nagra, 2002). Likewise, sensitivity analyses made at an upper PA level can be used to identify specific risk-important factors or processes for which more detailed modeling and analysis at a lower PA level may be desirable. In other words, the PA Pyramid represents an iterative process for assessing the performance the waste form and its intended disposal system.

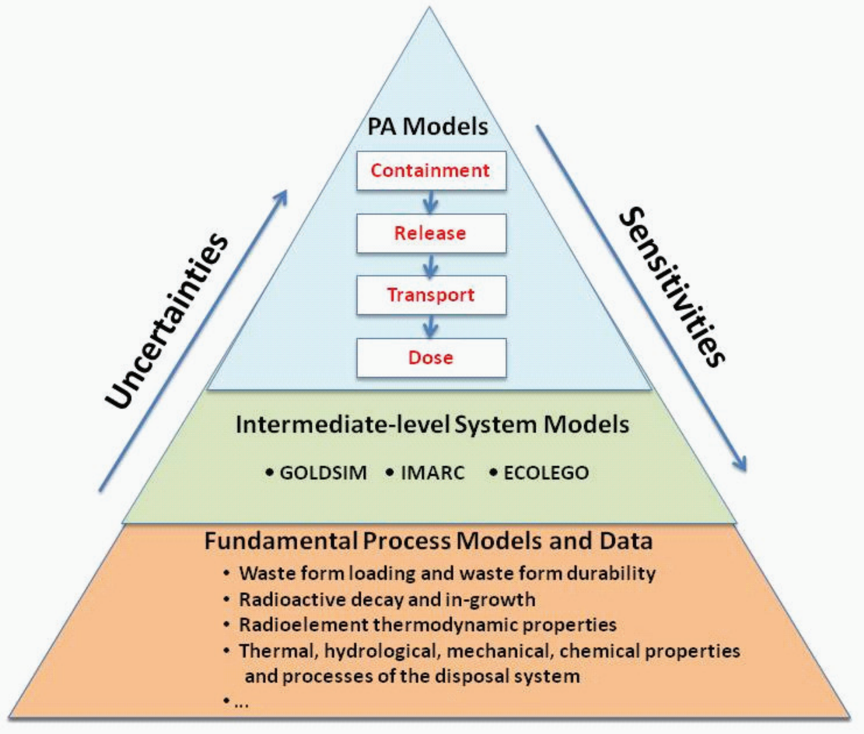

FIGURE 7.2 The PA pyramid showing the hierachical structure of PA models to evaluate the safety of disposal for radioactive waste. Uncertainties in assumptions, alternative conceptual models, and data are passed upward through the PA levels (upward arrow). Sensitivity analyses can be used to identify specific risk-important factors or processes for which more detailed modeling and analysis may be desirable (downward arrow).

7.3 MODELS FOR WASTE FORM PERFORMANCE IN DISPOSAL SYSTEMS

As noted in Chapter 6, the dominant potential pathway for radionuclide release from a disposal facility to the biosphere is via groundwater transport. Radioactive constituents may be released either as dissolved species or as suspended, radionuclide-bearing colloids. There is also the possibility of gaseous release of radionuclides that are volatile or form volatile compounds.[2] Because groundwater flow and radionuclide transport

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[2] A repository constructed in salt would likely have no aqueous, colloidal, or gaseous pathways for radionuclide release, unless there is some disruptive future human-based or natural event (NRC, 1996).

are primary concerns with respect to long-term performance of disposal systems for radioactive waste, the following conclusions from NRC (1990, pp. 14-15) are pertinent:

> Appropriate and successful models of groundwater flow and transport can range from simple analytical solutions for 1-dimensional flow in a homogeneous aquifer to highly complicated numerical codes designed to simulate multi-phase transport of reactive species in heterogeneous, 3-dimensional porous media. A useful model need not simulate all of the physical, chemical, and biological processes that are acting in the subsurface. The model that is appropriate for analyzing a particular problem should be determined primarily by determining the objective of the study. . . . Efforts should be made to avoid using models that are more complicated than necessary. Overly complicated models require information that cannot be obtained reliably from . . . measurements, which introduces unnecessary uncertainty into the modeling output.

Transport processes link waste form dissolution (Chapter 5) to disposal system performance and safety. Transport of dissolved and colloidal species released by the dissolution of a waste form may be controlled by either *advective flow* of the groundwater, or, if the engineered or natural barriers surrounding the waste form have sufficiently low permeability (Chapter 6), by *diffusion*.

The following three subsections provide more detailed descriptions of the PA model hierarchy illustrated in Figure 7.2 and the key physical and chemical processes that affect disposal system performance.

7.3.1 PA Models

The NRC's Waste Isolation System Panel (WISP) report (NRC, 1983) was the first multi-disciplinary study to integrate waste form dissolution and transport of dissolved radionuclides into a PA model for disposal systems. The WISP report applied well-understood, mass-transfer analytical models to elucidate the linkages between dissolution and transport in disposal systems. Independently, similar analytical mass-transfer models were being developed for international repository programs (e.g., KBS, 1983; Nagra, 1985; Neretnieks, 1978). The application of mass-transfer models to disposal system performance assessment is now routine for all types of radioactive waste (e.g., Andra, 2005; JNC, 2000; Nagra, 2002; SKB, 2006). Such simple mass-transfer models have, over time, been supported by more detailed and data-intensive physicochemical modeling (e.g., Steefel et al., 2005) in a manner consistent with the hierarchy of models shown in Figure 7.2.

7.3.1.1 Basic Release and Transport Processes that Control System Performance

To illustrate the linkage between waste-form dissolution and radionuclide transport, a simple but rigorous mass-transfer analytical model (NRC, 1983; Zavoshy et al., 1985) is cited here. The model is for a simplified geometry of a dissolving waste form surrounded by a diffusion barrier[3] (i.e., buffer/backfill) and is based on well-validated, mass-transfer principles. A so-called *flux ratio* R is defined as (Zavoshy et al., 1985):

$$R = \frac{\text{waste form dissolution rate}}{\text{steady-state diffusive flux}} = \frac{j_0 r_0}{\varepsilon D_e C^{SAT}} \tag{7.1}$$

where

j_0 is the dissolution rate (i.e., *chemical durability*) of the waste form, normalized for the mass fraction of radionuclide i in the waste form[4]
r_0 is the radius of the waste form
ε is the connected porosity of the buffer
D_e is the effective diffusion coefficient of dissolved radionuclide i in the buffer
C^{SAT} is the solubility limit for a solid phase incorporating radionuclide i.

For conditions where the flux ratio R is much greater than 1 (fast dissolution rate relative to diffusive transport flux), the long-term concentration of radionuclide i increases at the waste-form surface until the point that a solid phase containing radionuclide i precipitates; this precipitate sets a solubility-limited concentration (C^{SAT}) for radionuclide i at the waste form

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[3] In all concepts for the disposal of SNF/HLW in saturated rock, a low-permeability buffer or backfill engineered barrier is placed around the SNF/HLW containers (e.g., NWTRB, 2009; Witherspoon and Bodvarsson, 2006). Such a buffer has several important safety functions, including promoting diffusive transport of all radionuclides released from the dissolution of waste forms. Low-permeability buffers also promote the filtration of any radionuclide-bearing colloids that might form from dissolution of the waste form (Nagra, 1994; SKB, 2006). For a repository located in unsaturated rock, buffer/backfills (so-called Richards barriers) based on the principle of capillary-breaking have been tested and built. These barriers are designed to perform the twin safety functions of assuring diffusive transport and colloid filtration (e.g., EPRI, 1996; Gee et al., 2002).

[4] Mass fraction is the mass of radionuclide i (i.e., waste loading of radionuclide i) divided by the mass of the entire waste form.

surface. This is called *transport control*, and the same basic process has long been recognized and applied to the interpretation of diagenetic mineral dissolution in nature (e.g., Berner, 1979). Conversely, when the flux ratio R is much lower than 1, the long-term concentration of radionuclide i at the waste form surface is basically controlled by the dissolution rate of the waste form. This is called *surface-reaction control* and also is well known from studies of natural diagenetic systems.

Note that this simple model does not depend on any specific waste form, dissolution rate mechanism, or model; it is general to any waste form for which a long-term dissolution rate (or release rate of radionuclides) can be defined. Similar mass-transfer expressions that link waste-form dissolution rate and advective transport have also been developed (Pigford and Chambré, 1987). These mass-transfer analytical models provide the critical linkage between waste form fabrication and geological disposal (Figure 7.1).

The important characteristics of waste forms with respect to long-term (10^3-10^6 years) performance and safety of a disposal system depend on a number of factors:[5]

- Type of waste form (see Chapter 3)
- Radionuclide inventory and waste loading of the waste form
- Environmental conditions in the near field of the disposal facility (see Chapter 6)
- Long-term dissolution rate of the waste form under those environmental conditions (see Chapter 5)
- Solubility limits of dose-contributing radioelements
- Rate of diffusive or advective aqueous transport of dissolved and colloidal radionuclides
- Presence of engineered barriers (e.g., clay buffer, Richards barrier)

For SNF/HLW repositories that include a low-permeability buffer surrounding the waste form, it is the solubility limits of the solid phases that incorporate the radionuclides that (i.e., C^{SAT} in Equation 7.1) are the dominant factors in limiting the long-term release rates of most radionuclides (e.g., Andra, 2005; DOE, 2008; JNC, 2000; Nagra, 2002). Such solubility limits are also considered to be controlling factors for potential releases via human intrusion from the WIPP site for disposal of defense TRU waste (DOE, 1995; NRC, 1996). Performance analyses of LLW disposal systems also typically apply these solubility limits as controls on radionu-

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[5] The timeframe for regulatory compliance and the half-lives of key radionuclides present in the waste are also considerations; the dissolution rate of a waste form may limit radionuclide releases from disposal systems for an initial period before the onset of solubility limits imposed by precipitation of radionuclide-bearing solids.

clide releases (e.g., Andra, 2005; Nagra, 2002; NRC, 2005). Waste-form dissolution rates can, however, provide an important constraint on the release of highly soluble radionuclides, such as carbon-14, chlorine-36, and iodine-129, if such radionuclides are present in the waste form.

Application of PA models for disposal systems can place diverse factors such as waste-form dissolution rate, waste loading, and solubility limits of the solid phases containing radionuclides into a common system-level context for evaluation and optimization. Furthermore, such PA models can also provide guidance to future decisions on whether there is a safety-based reason for further development of advanced waste forms. The most notable application of system-level PA models to advanced waste form development relates to thresholds at which extremely low waste form dissolution rates would constrain (and simplify the calculation of) the performance of a given disposal concept.

NRC (1983, pp. 279-280) made a detailed analysis of the necessary fractional dissolution rate for waste forms performance to control the performance of disposal systems:

> The effect of low-solubility waste forms on radionuclide release rates is to decrease the number of radionuclides that may dissolve more slowly than the host, until, in the limit, all waste products will be released congruently or diffuse out and dissolve faster than the host. This limiting condition probably occurs at waste-form dissolution rates around 10^{-9} or 10^{-10}.

NRC (1983) further identified potential advantages of a low-solubility waste form with such exceptionally low fractional dissolution rates, including the following:

- Verification of the safety performance of the entire disposal system would depend largely on the laboratory measurements made under appropriate site-specific conditions (i.e., risk-based testing of waste forms),
- Release rates of an increasing number of radionuclides would become proportional to decreasing fractional dissolution rate,
- The need for estimating separate solubility limits would be greatly attenuated if not eliminated, and
- The number of sites that could serve as suitable repositories might increase.

A more recent analysis (SKB, 2006, Figure 10-44) of a deep geological repository for the disposal of spent nuclear fuel in granitic crystalline rock suggests the fractional dissolution-rate threshold for a waste form (in this case UO_2) might be as low as 10^{-6}/year for certain key radionuclides.

The exact threshold at which the waste-form dissolution rate controls the release performance of a disposal system (i.e., when the flux ratio *R* in Equation 7.1 becomes much less than 1) depends on a number of factors. In particular, waste loading and solubility limits, which typically vary among different radioelements over many orders of magnitude, influence this threshold value.

The sensitivity of factors affecting the threshold value at which waste-form fractional dissolution rate controls the release performance of a hypothetical disposal is illustrated in Table 7.1. This table applies Equation 7.1 to calculate flux ratios *R* for a several key, long-lived dose-contributing radioelements present in a standard HLW glass (Nagra, 2002) for reference waste loadings, solubility limits (C^{SAT} in Equation 7.1), and fractional dissolution rates.

For the reference fractional dissolution rate of 10^{-5} parts per year, the releases of selenium-79, technetium-99, and neptunium-237 from the disposal system would be constrained by their respective solubility limits,

TABLE 7.1 Sensitivity of Calculated Flux Ratios Using Equation 7.1 for Radioelements with a Key Long-lived Radionuclide Present in a Reference HLW Borosilicate Glass

Radioelement/ Key Radionuclide	Waste Loading (kg of radionuclide/ kg glass)[a]	Solubility, C^{SAT} (kg/m^3)[b]	Fractional Dissolution Rate (j_0, in parts per year)[c]	Flux Ratio, R
Selenium-79	1.63×10^{-4}	4.0×10^{-7}	10^{-5}	360
			10^{-7}	3.6
Technetium-99	2.79×10^{-3}	4.0×10^{-7}	10^{-5}	6100
			10^{-7}	61
Iodine-129	5.52×10^{-7}	130	10^{-5}	3.7×10^{-6}
			10^{-7}	3.7×10^{-8}
Neptunium-237	1.36×10^{-3}	1.2×10^{-6}	10^{-5}	990
			10^{-7}	9.9

NOTES: Diffusional transport from the waste-form surface is assumed, with $\varepsilon = 0.01$, $D_e = 3.15 \times 10^{-2}$ m^2/year, and $r_0 = 0.4$ m (Zavoshy et al., 1985). R values much greater than 1 indicate release performance of the disposal system would be constrained by radioelement solubility, whereas *R* values much lower than 1 indicate release performance of the disposal system for that radionuclide would be constrained by waste form dissolution rate.

[a] Waste loading for a Reference HLW Borosilicate Glass (McGinnes, 2002, Tables A.1-1 to A.1-4).

[b] Reference Case radioelement solubilities for reducing disposal conditions (Nagra, 2002, Table A2.4).

[c] The reported long-term dissolution rate of 5.5×10^{-4} kg/m^2 year for the Reference HLW Borosilicate Glass is stated to correspond to a fractional dissolution rate of 10^{-5} parts per year (Nagra, 2002, p. 144).

SOURCE: Nagra (2002).

whereas the release of highly soluble iodine-129 would be limited by the dissolution rate of the HLW glass. Even for a postulated fractional dissolution rate of 10^{-7} parts per year, the releases of selenium-79, technetium-99, and neptnium-237 from the disposal system would still be constrained by their solubility limits. It would require a speculative fractional dissolution rate on the order of 10^{-9} parts per year (i.e., the waste form would take 1 billion years to completely dissolve) for a waste form to control, and thereby lower, the release rates of these key radionuclides from the disposal system. This value is in basic agreement with the previous NRC (1983) estimate. The important point is that such sensitivity analyses provide a defensible basis by which to determine "how much better" an advanced waste form would have to perform to significantly enhance the safety of disposal systems compared to current HLW borosilicate glass, for example.

7.3.1.2 Integrated PA Models

The analytical models discussed above link the *release* and *transport* boxes shown in Figure 7.2. However, there are additional processes and barriers that affect the overall safety of disposal systems, including containment (i.e., barriers designed to delay contact between groundwater and waste forms), transport through the natural barrier (host rock) of the disposal facility, and finally the various pathways in which released radionuclides might migrate through the biosphere and lead to doses to humans. A system-level analysis is needed that incorporates all of the design aspects and properties of natural and engineered barriers that affect overall safety.

Numerical codes have been developed to allow more complete linkage among the models for the process boxes shown in the upper part of the PA Pyramid in Figure 7.2, such as the GoldSim code used in the recent license application for a SNF/HLW repository at Yucca Mountain (DOE, 2008) and the IMARC code (EPRI, 2009), which was also applied to the Yucca Mountain Site. Such codes provide great flexibility for evaluating uncertainties and sensitivities in model parameters; inclusion of alternative conceptual models for certain processes; detailed spatial expansion of important regions (compartments) of disposal facilities (especially the EBS); and relatively easy use of alternative data sets from pre-configured libraries.

Such top-level PA codes are now being used widely across DOE sites to provide a more accesible means for communicating about and addressing uncertainties and sensitivity about disposal system performance with nontechnical stakeholders. With the detailed models discussed in Sections 7.3.2 and 7.3.3, scientific and engineering understanding about the disposal system can be established. The top-level PA model is established with such fundamental understanding, while stylization for unverifiable assumptions, such as biosphere radionuclide pathway models, is introduced.

7.3.2 Intermediate Level Models

Significant insights on the performance of waste forms in disposal systems can be gained from the application of relatively simple performance assessment models described in the previous section. However, the abstractions in these models may not account for all of the important variables in the disposal system or changes in system conditions over time, especially during the initial period following facility closure. Consequently, there can be a need to develop engineering-type models that more fully incorporate the features of the facility design (e.g., EBS configuration, dimensions, and layout) and system conditions. Such models occupy the intermediate layer of the PA Pyramid in Figure 7.2 and bridge the fundamental process models at the bottom of the pyramid to the abstracted models at the top.

A facility for disposal of SNF/HLW will contain thousands of waste packages, usually in a two-dimensional array, each of which is surrounded by multiple engineered barriers. Some internal structure and heterogeneous radionuclide distribution will be present within each waste package. Consequently, the repository will display heterogeneity at different spatial scales. In conventional PA, radionuclide transport is modeled by reducing this heterogeneity to some extent (i.e., heterogeneity is homogenized). Packages are represented by several end-member types, and radionuclide transport in the repository is modeled without considering interferences from adjacent packages or the effects of the two-dimensional package-array configuration (Ahn et al., 2002).

The homogenization of spatial heterogeneity can obscure important processes that govern the performance of the disposal system, for example, the existence of advection-dominant flow paths. Radionuclide release from the near-field region to the far-field region is strongly influenced by the existence of these *fast paths*. The existence of fast paths can affect degradation of the engineered barriers, which in turn can affect fast-path geometry (Murakami and Ahn, 2008; Steefel et al., 2005).

Taking into account heterogeneity at all spatial scales requires a tremendous amount of computation. For instance, a relatively small-size simulated repository, containing fewer than 100 packages and millions of rock fractures in the near field, was the maximum size that could be simulated by the Earth Simulator supercomputer (Tsujimoto and Ahn, 2008). Compartmentalization is a logical modeling approach to improve computational efficiency because a repository contains thousands of packages surrounded by similar combinations of barriers. In a compartmentalization approach, modeling can be made at two levels: one at a local scale within a compartment and the other at a repository scale connecting compartments. For waste form performance, local-scale modeling is more urgently needed.

7.3.3 Fundamental Process Models

Fundamental process models, which occupy the base of the PA Pyramid shown in Figure 7.2, integrate the knowledge obtained in the experiments and tests described in Chapter 5. These process models can be used to estimate performance at "local" (i.e., sub-facility) scales. Such models can be used to obtain best-estimates of waste form performance in particular disposal environments; to select suitable combinations of waste forms and engineered-barrier configurations; and to evaluate system performance using metrics other than dose, which can aid in optimizing facility designs.

More complex models for waste form durability need to account for waste form material properties (Chapter 3), disposal environment (Chapter 6), and interactions with other engineered and natural barriers in the disposal system (Chapter 6). The importance of such interactions is highlighted in a recent summary of the GLAMOR[6] project (Van Iseghem et al., 2007, 2009). A specific focus of this project was to understand the long-term decrease in the rate of dissolution of glass waste forms (Figure 7.3), with two competing hypotheses considered:

1. The effect of silica concentrations in solution on the depression of the rate (the so-called "chemical affinity effect"[7]).
2. The role of surface layers that develop during the corrosion/dissolution process in limiting transport of reactive constituents to and from the primary glass phase, assuming that such layers do not spall off.

The rate of glass dissolution could be accelerated by placing it in proximity to a bentonite (clay) buffer or steel and iron canister corrosion products. Accelerated dissolution seems to be caused by the sorption and removal of glass reaction-products from solution, which if present would

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[6] A Critical Evaluation of the Dissolution Mechanisms of High Level Nuclear Waste Glasses in Conditions of Relevance for Geological Disposal; see ftp://ftp.cordis.europa.eu/pub/fp6-euratom/docs/euradwaste04pro_pos9-van-iseghem_en.pdf.

[7] *Chemical affinity* is defined as the log (Q/K_{sp}), where Q is the ion activity product of dissolved species in solution and K_{sp} is equilibrium constant for the waste form (Lasaga, 1979). Borosilicate glass is thermodynamically unstable and cannot be re-precipitated from solution, so a proxy K_{sp} is derived for it.

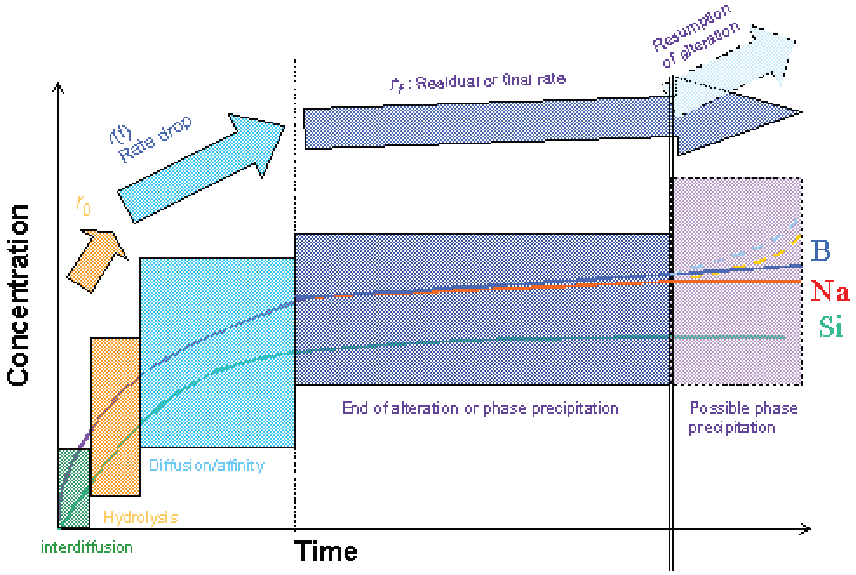

FIGURE 7.3 Schematic representation of predominant mechanisms and resulting kinetics affecting the concentration of glass alteration elements silicon (Si), boron (B), and sodium (Na).
SOURCE: Van Iseghem et al. (2009).

slow the rate of dissolution due to the chemical affinity effect. To understand the underlying mechanism it was necessary to conduct a series of experimental studies supplemented with detailed microscopic characterizations of the evolving glass surface layers. Similar studies will be necessary for any candidate waste forms considered by DOE-EM because a mechanistic understanding of the controls on waste form dissolution provides the basis for understanding waste form performance at long time scales.

Evaluation of the performance of waste forms in disposal systems may be required for periods ranging up to 1 million years, depending on the pertinent regulations (see Chapter 8). Figure 7.4 provides an illustration of important processes that can occur in the near-field environment of a disposal facility for SNF/HLW over these time scales. The durability of a waste form depends, in addition to its own properties, on several environmental factors:

- solution composition and pH
- flow rate
- temperature

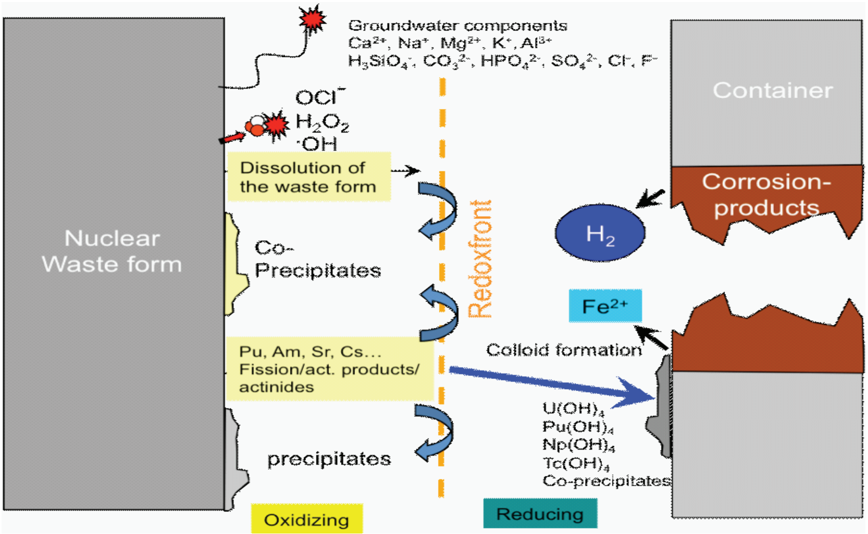

FIGURE 7.4 Simplified scheme of chemical processes in the near-field environment of a disposal facility.
SOURCE: Grambow et al. (2000), as modified by Horst Geckeis.

- redox conditions
- speciation in solution
- radiolysis
- interactions with corroded canisters and near-field geology
- formation and mobility of colloids

These individual factors often interact and are coupled in a repository environment. The dissolution of waste forms containing radioactive waste can be complex, particularly following the closure of a disposal facility when thermal, radiological, mechanical, hydrological, and chemical perturbations to the disposal system are highest. (This is a primary reason that radioactive wastes are typically placed in canisters with containment lifetimes of several thousands of years or more, which prevents groundwater contacting waste forms until these initial perturbations dissipate.)

Evaluating the complexity of disposal system performance can be accomplished using models that explicitly couple thermal, hydrological (transport), mechanical, and chemical processes in 3-dimensional representations of the barriers and spatial variation in properties. All of these processes occur against a backdrop of changing environmental conditions that may be externally imposed, including water infiltration rates, water chemistry, and decay of the thermal field. Local-scale mechanistic modeling based on understanding of near-field processes can be made by coupling thermal (T), hydrological (H), chemical (C), radiological (R), and mechanical (M) processes for evolution and transport of materials in the near-field environment, including the waste form and its radioactive constituents. Estimates are typically restricted to pair-wise analyses such as T-H, T-C, T-M, or R-T, under the assumption that such sub-set analyses capture the full system behavior. Attempts to develop such models have already been made (e.g., Steefel et al., 2005) but much more work is needed. The development of such models could provide the scientific basis for best-estimates of waste form performance.

The challenge for using coupled models to evaluate waste form performance in disposal systems is the identification of key processes in the near-field environment, including:

- Rate-limiting steps. These could include the dissolution mechanism of the waste form; the formation and decomposition of radiolytically produced species in solution; initial surface sorption/desorption reactions; or the nucleation and precipitation of secondary phases.
- Reaction mechanisms: Even when rate-limiting steps have been identified, reaction mechanisms can change in response to changing environmental conditions. The full range of possible mechanisms and the conditions under which these mechanisms control waste form reactions must be evaluated.
- Radiolysis effects: Radiolysis at the waste form/solution interface can have an important effect on dissolution processes, particularly for redox-sensitive elements such as uranium and plutonium (see Chapter 6). The long-term effects of radiolysis, for example the formation of H_2O_2, have barely been explored, although in nature U(VI) phases that contain peroxyl groups have recently been discovered (Kubatko et al., 2003).

For coupled models to be realistic and useful, relevant chemical and physical processes must be represented. Relevant chemical processes include the following:

- Kinetically controlled dissolution of the waste form
- Nucleation and kinetic controls on the growth and sequence of metastable phases
- Solid-solution (co-precipitation, see Figure 7.4) models for substitution of minor components
- Kinetic and equilibrium sorption via different mechanisms (ion exchange, surface complexation)
- Aqueous complexation

- Oxidation-reduction state of the waste form as influenced by transport, local reactions, and radiolysis
- Composition and chemical concentration of pore water chemistry caused by evaporation

The relevant physical processes include the following:

- Heat transport as a result of convection, conduction, and radioactive decay, which provides the time-dependent temperature field affecting relative humidity, reaction kinetics, and thermodynamics
- Water flow under variably saturated conditions
- Diffusive and advective transport of solutes in the aqueous phase
- Gas phase transport via advection and diffusion, especially for the reactive gases O_2 and CO_2

The application of advanced reactive transport modeling of the near-field environment (Steefel et al., 2005) can aid in the overall safety assessment of disposal systems by reducing unwarranted conservatisms in more abstracted PA models and by enhancing the comprehensiveness and confidence in the PA.

7.4 DISCUSSION

The PA of waste forms containing radioactive waste can only be meaningfully accomplished within the context of disposal system PA, in which health-risk consequences are the appropriate basis for evaluations. As shown in Figure 7.2, there is typically a hierarchy of PA models employed in assessing any waste form/disposal system, with each level of PA models having the appropriate fitness for purpose, for example, design optimization, identification of risk-informed R&D needs, or regulatory compliance.

The development of new or improved waste forms by DOE-EM could offer two potential benefits: (1) more efficient waste processing and immobilization; and (2) enhanced performance of the disposal systems into which the waste forms will eventually be emplaced. With respect to the first benefit, increasing waste loading and/or processing rates could lower production costs and accelerate cleanup schedules (see Chapters 2 and 4). With respect to the second benefit, enhanced performance of the waste form, established under relevant disposal system conditions, could eliminate unwarranted conservatisms and provide greater confidence in the overall performance of the disposal system.

It is important to recognize that repository performance is an optimization problem, and the waste form is one of several elements in the optimization. Other elements include the physical and chemical characteristics of the rocks hosting the repository as well as the design and characteristics of other engineered barriers. In other words, there is no single figure of merit for waste form performance.

PA can provide safety-based insights to guide future decisions on further development of waste forms. The most notable application relates to estimating thresholds at which extremely low waste-form dissolution rates would control (and simplify the calculation of) the release of all radionuclides for a given disposal environment and design concept. As noted elsewhere in this chapter, the necessary threshold value for waste form durability (expressed as a fractional dissolution rate) to control the performance of a disposal system might be on the order of 10^{-6} to as low as 10^{-10} per year, depending on factors such as disposal system design, environmental conditions, applicable radioelement solubility limits, and radionuclide loadings in the waste form.

It must be stressed, however, that such exceedingly low dissolution rates for waste forms under disposal conditions are not requirements. Current safety assessments of disposal systems (e.g., Andra, 2005; DOE, 2008; JNC, 2000; Nagra, 2002; SKB, 2006) for a wide variety of HLW and LLW waste forms in various geological formations (e.g., salt, granite, tuff, clay) generally show wide margins of compliance with applicable regulatory safety standards.

As presented in NRC (2003) and illustrated in Figure 7.1, the development of a multiple-barrier repository concept is initially based on (1) identification of waste forms meeting specific waste acceptance criteria (WAC, see Chapter 8); (2) establishment of national laws and regulations (Chapter 8); and (3) selection of a specific disposal site (Chapter 6). Based on this design and collection of field and laboratory data, a series of PAs can be made and the results used to adapt the design of the disposal facility and the iterative collection of additional data, as necessary. From such analyses, the disposal system concept can be adapted and new data collected in iterative stages as necessary. Flexible, staged-adaptation in disposal system development leading to eventual licensing is being implemented in numerous national programs worldwide (NRC, 2003).

This inherent adaptability would also apply to a situation in which a new waste form might be proposed. The waste form would need to pass WAC regarding its physical form, dimensions, and potential impacts on the site environment (e.g., no introduction of major chemical components that might compromise the safety functions of other barriers). As discussed in Chapter 8, there are no specific long-term waste form performance requirements in the WAC; short-term (seven-day) leach rates are used instead as a measure of quality assurance and product consistency. *The absence of such performance requirements on waste forms means that an adaptive repository program should readily accommodate new waste forms through* *the iterative process of modifying the repository design and updating performance assessment, as illustrated in Figure 7.1.* In the case where the calculated releases from a disposal system meet safety criteria because of radioelement solubility limits, then the motivation for developing advanced waste forms would be based more on factors such as waste loading, favorable chemical environment during and after waste form dissolution/alteration that assures such a low solubility, and ease of fabrication, rather than durability.

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8

Legal and Regulatory Factors for Waste Form Performance

The second charge of the statement of task for this study (see Box 2.1 in Chapter 2) calls for the identification and description of "Scientific, technical, regulatory, and legal factors that underpin requirements for waste form performance." This chapter describes some key legal and regulatory requirements and agreements that apply to the DOE-EM cleanup program and their implications for waste form performance requirements.

In the context of this report, the term *waste form performance* has a very specific meaning: It is the ability of a waste form to sequester and retain its radioactive and chemically hazardous constituents. As discussed in Chapters 6 and 7, the performance of a waste form depends crucially on the physical and chemical conditions in the near-field environment of the disposal facility into which it will be emplaced. The committee interprets the phrase *requirements for waste form performance* to mean the legal and regulatory requirements that govern how a waste form must perform in a particular disposal environment.

The Department of Energy's (DOE's) cleanup and waste disposal programs operate under a large number of legal and regulatory requirements. These requirements are formalized in contracts, DOE orders, federal agency regulations, and in some cases state agreements and regulations. They include laws and regulations that apply to radioactive, hazardous, and mixed (radioactive and hazardous) wastes as well as agreements and orders that govern specific cleanup and disposal actions. These laws, regulations, and agreements have common objectives—to protect the worker, public health, and the environment.

Two DOE offices are responsible for waste management and disposal. The DOE-Office of Environmental Management (EM) is responsible for cleanup of radioactive and hazardous waste at DOE sites that are part of the cleanup program (see Figure 2.1). DOE-EM is also responsible for disposal of waste at its sites (i.e., low-level waste and the low-activity fraction of high-level waste) as well as for defense transuranic waste at the Waste Isolation Pilot Plant in New Mexico. The DOE-Office of Civilian Radioactive Waste Management[1] (OCRWM) is responsible for disposal of spent nuclear fuel (SNF) and high-level radioactive waste (HLW) from the DOE-EM cleanup program (as well as for disposal of commercial spent nuclear fuel). As noted previously, these activities are carried out under a number of different laws, orders, regulations, and agreements.

8.1 LAWS AND DOE DIRECTIVES

There are several sets of laws and other governmental directives that apply to the DOE-EM cleanup program and have actual or potential implications for waste form performance. These include:

- Atomic Energy Act of 1954
- Nuclear Waste Policy Act of 1982
- Energy Policy Act of 1992
- DOE Order 5400.1
- DOE Order G 435.1
- National Defense Authorization Act Section 3116

These laws and directives are described briefly in the following sections.

8.1.1 Atomic Energy Act of 1954

The Atomic Energy Act of 1954, as amended, designates DOE as responsible for the safe management and final disposal of all radioactive wastes arising from its operations. DOE Order G 435.1, which is described in Section 8.1.5, establishes the technical basis for decisions on the classification, management, and disposal of DOE wastes except SNF and HLW. In some cases Order G 435.1 references other laws and regulations that govern DOE activities.

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[1] OCRWM was established by the Nuclear Waste Policy Act and has responsibility for managing and disposing of spent nuclear fuel and high-level radioactive waste. However, the Obama Administration's budget request for Fiscal Year 2011 eliminates funding for this office. Its responsibilities for spent fuel management are currently being handled by DOE's Office of Nuclear Energy.

8.1.2 Nuclear Waste Policy Act of 1982

The Nuclear Waste Policy Act of 1982 (NWPA), as amended, establishes the current structure for the final disposal of SNF and HLW in a deep geological repository. The NWPA defines the roles and responsibilities for DOE as the implementing organization, the U.S. Environmental Protection Agency (EPA) to develop the safety standards for disposal, and the U.S. Nuclear Regulatory Commission (USNRC) to establish licensing procedures and regulations for a geological repository.

Following the Atomic Energy Act definitions, the NWPA states

> The term ‘high-level radioactive waste’ means:
>
> (A) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and
>
> (B) other highly radioactive material that the [Nuclear Regulatory] Commission, consistent with existing law, determines by rule requires permanent isolation.

The definition of defense HLW in the NWPA is source based (as opposed to radioactivity based) and is rather vague (e.g., “. . . sufficient concentrations”). A broad interpretation of this term could have required the disposal in a geologic repository of approximately 140,000 defense HLW canisters from the Savannah River Site alone. To provide additional clarity to this source-based and vague definition, DOE promulgated Order G 435.1 in 1999 that uses risk criteria to determine what defense wastes actually need to be disposed of in a geologic repository. Using Order G 435.1, DOE was able to reduce the number of Savannah River Site defense HLW canisters requiring geologic disposal to between 6,000 and 8,000.

The NWPA established a statutory capacity limit of 70,000 metric tons of heavy metal for the nation’s first repository, until a second repository is in operation. That limit is not based on technical considerations. The 1987 Amendments to the NWPA directed the Secretary of Energy to focus site characterization activities only at Yucca Mountain, Nevada.

DOE’s OCRWM, also referred to as DOE-RW, was established to research, site, license, and construct a deep geological repository for disposal of commercial and defense spent fuel and defense HLW.[2] As part of

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[2] In an April 30, 1985, memorandum, President Ronald Reagan determined that there was no basis for establishing a separate repository for defense HLW. He directed then-Secretary of DOE John Harrington to arrange for the disposal of these wastes in repositories developed for disposal of civilian SNF and HLW.

its responsibilities, DOE-RW developed Waste Acceptance Criteria (WAC), which are described in Section 8.4, for accepting SNF and HLW for disposal at a U.S. repository.[3]

8.1.3 Energy Policy Act of 1992

The Energy Policy Act of 1992, Section 801, required EPA to develop a site-specific health and safety standard for a geologic repository at Yucca Mountain, Nevada. Section 801 also required EPA to contract with the National Academy of Sciences (NAS) to provide findings and recommendations on reasonable standards for protection of the public health and safety. The Energy Policy Act required EPA to promulgate a regulation that would be "based upon and consistent with" the NAS recommendations. The NAS recommendations, which were published in 1995 (NRC, 1995), were considered and implemented by EPA in Title 40, Part 197 of the Code of Federal Regulations (40 CFR 197). That regulation is described in Section 8.3.2 (see also http://www.epa.gov/radiation/yucca/regs.html).

8.1.4 DOE Order 5400.1

DOE Order 5400.1 establishes requirements, authorities, and responsibilities for DOE operations to ensure compliance with environmental protection laws, regulations, executive orders, and internal DOE policies. The most important part of this order for the purposes of this report is the order's policy statement (emphasis added):

> It is DOE policy to conduct its operations in an environmentally safe and sound manner. . . . DOE is firmly committed to ensuring incorporation of national environmental protection goals in the formulation and implementation of DOE programs. . . . Accordingly, **it is DOE policy to conduct the Department's operations in compliance with the letter and spirit of applicable environmental statutes, regulations, and standards.** . . . [I]t is DOE's policy that efforts to meet environmental obligations be carried out consistently across all operations and among all field organizations and programs. (emphasis added)

Through this order, DOE's waste management and disposal activities are subject to federal, state, and local laws and regulations.

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[3] OCRWM was being disbanded when this report was being finalized. The Obama Administration is withdrawing the license application to construct a repository at Yucca Mountain, Nevada, and has established a Blue Ribbon Commission on America's Nuclear Future to evaluate alternative approaches for managing SNF and HLW.

8.1.5 DOE Order G 435.1

Defense HLW is defined in DOE Order G 435.1 similar to the definition in the NWPA, but it also defines a new classification of *Waste Incidental to Reprocessing*[4] (WIR), which is:

> Waste resulting from reprocessing spent nuclear fuel that is determined to be incidental to reprocessing is not high-level waste, and shall be managed under DOE's regulatory authority in accordance with the requirements for transuranic waste or low-level waste, as appropriate.

WIR that will be managed as low-level radioactive waste (LLW) must meet three criteria (USNRC, 1999):

- Criterion 1: The waste must receive processing to remove key radionuclides to the maximum extent that is technically and economically practical.
- Criterion 2: The waste must be shown to be managed to meet the performance objectives in 10 CFR Part 61, Subpart C.[5]
- Criterion 3. The waste must be incorporated in a solid physical form at concentrations that do not exceed the concentration limits for Class C commercially generated LLW.

DOE Order G 435.1 recommends that the USNRC should be consulted for all determinations of whether a waste is LLW using these criteria.

DOE Order G 435.1 also provides guidance for the near-surface disposal of DOE-EM LLW at DOE sites. This guidance includes the following performance objectives, which are not stated as requirements:

- For off-site members of the public, a limit of an annual effective dose equivalent from all releases and exposure pathways of 0.25 millisieverts per year (mSv/year), excluding dose from radon and its progeny in air.
- For off-site members of the public, a limit on annual effective dose equivalent from releases to the atmosphere of 0.1 mSv/year, excluding the dose from radon and its progeny.
- A limit on release rate of radon at the surface of a disposal facility of 0.7 becquerels per square meter per second (Bq m^{-2} s^{-1}) or, alternatively, a limit on the concentration of radon in air at the boundary of the disposal facility of 20 Bq m^{-3}.

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[4] The definition, evaluation, and impact of WIR from DOE Order G 435.1 are reviewed in Appendix C of NRC (2006).

[5] Title 10, Part 61 of the Code of Federal Regulations provides regulations for the management and disposal of LLW. See Section 8.3.1.

Note that these objectives apply to the performance of the disposal system, not to waste form performance in the disposal system. These performance objectives are similar to those established previously in DOE Order 5820.2A, which was superseded by Order G 435.1. However, if DOE-EM LLW were to be sent to a facility licensed by the USNRC or an Agreement State,[6] performance objectives and other criteria established by those authorities would apply (see Section 8.3.1).

DOE Order G 435.1 specifically states that performance objectives for disposal of DOE LLW apply for 1,000 years after disposal. Calculations of dose beyond 1,000 years should only be considered as qualitative for DOE sites, and only for comparison of disposal alternatives that are otherwise not distinguishable in their dose impacts.

There are additional requirements in DOE Order G 435.1 regarding the conduct of performance assessments, but these are not explicitly stated as performance objectives. For example, performance assessments must include a demonstration that releases from a disposal facility will be maintained as low as reasonably achievable (ALARA). Also, site-specific assessments of potential doses to inadvertent intruders are required for the purpose of establishing limits on concentrations of radionuclides to be disposed of at each site. These performance measures for inadvertent intruders are the same as those established in the superseded DOE Order 5820.2A. Furthermore, an analysis of potential impacts on water resources is required for the purpose of establishing limits on quantities of radionuclides that are acceptable for disposal at each site, based on site-specific criteria. Also, DOE Order G 435.1 specifies that disposal must comply with all other DOE environmental protection requirements.

8.1.6 National Defense Authorization Act Section 3116

Section 3116 (a) of the National Defense Authorization Act (NDAA) states that the Secretary of Energy can determine that radioactive waste resulting from the reprocessing of nuclear fuel is not HLW if it meets specific criteria. The Secretary must consult with the USNRC in making this determination by preparing a Waste Determination Basis Document. The USNRC will review this document and provide a Technical Evaluation Report to inform the Secretary's decision.

The criteria for consideration in waste determinations include:

- Waste does not require permanent isolation in a deep geologic repository

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[6] That is, a state that has signed an agreement with the Nuclear Regulatory Commission authorizing it to regulate certain uses of radioactive materials.

- Waste has had highly radioactive radionuclides removed to the maximum extent practical
- Waste does not exceed concentration limits for USNRC's Class C LLW and will be disposed of:
  - — in compliance with the performance objectives set out in Subpart C of 10 CFR 61
  - — pursuant to a state-approved closure plan or a state-approved permit
- If waste exceeds concentration limits for Class C LLW it will be disposed of:
  - — in compliance with the performance objectives set out in Subpart C of 10 CFR 61
  - — pursuant to a state-approved closure plan or a state-approved permit
  - — pursuant to plans developed by the Secretary in consultation with the USNRC

8.2 STATE AND AFFECTED PARTIES AGREEMENTS

DOE has entered into agreements and consent orders, hereafter referred to simply as *Agreements*, with EPA, states, and in some cases with other affected local parties regarding the disposition of radioactive wastes on sites within these states, mostly notably South Carolina, Idaho, and Washington. The purpose of these Agreements is to ensure that the environmental impacts associated with releases or potential releases of hazardous substances at various DOE sites are thoroughly investigated and that appropriate response actions are undertaken and completed as necessary to protect the public health, welfare, and the environment. Each Agreement establishes a framework and schedule for developing, prioritizing, implementing, and monitoring appropriate response actions at these DOE sites in accordance with CERCLA, RCRA, and state HWMA[7] requirements. Implementation of the Agreements is intended to facilitate cooperation, exchange of information, and participation of the parties in such actions. Where appropriate, interim action alternatives are to be identified at specific sites to promote cooperation among parties prior to the implementation of final actions.

DOE-EM has negotiated with the other parties to these agreements to establish specific characteristics for the waste forms that will be produced as a result of cleanup at its sites. For example, DOE and the state of South

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[7] CERCLA is the Comprehensive Environmental Response, Compensation, and Liability Act; RCRA is the Resource Conservation and Recovery Act; HWMA is the Hazardous Waste Management Act. RCRA is described in Section 8.3.4.

BOX 8.1
Good as Glass

The *Draft Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington* (DOE, 2009) contains a forward written by the Washington State Department of Ecology, which states that "Ecology's measuring stick for a successful supplemental treatment technology has always been whether it is 'as good as glass' (from the WTP [Waste Treatment Plant])." To the Committee's knowledge, quantitative metrics for "as good as glass" have not been explicitly defined in any formally approved document.

A review of the literature reveals that the statement "as good as glass" has been interpreted in several ways. For example, the Draft Dangerous and/or Mixed Waste Research, Development, and Demonstration Permit (RD&D): Demonstration Bulk Vitrification System (DBVS Facility) notes that DOE intends to "evaluate the ability of bulk vitrification to produce immobilized low-activity waste (ILAW) that is comparable to that proposed for the Hanford Site Waste Treatment and Immobilization Plant (WTP) immobilized low-activity waste form" (ECY, 2004). In a notice requesting public comments on the draft permit,[a] the Washington State Department of Ecology noted, "The permittee [the U.S. Department of Energy] intends to demonstrate that the bulk vitrification technology is viable and as protective of the environment as the vitrified (glasslike) waste that will be produced by the Waste Treatment Plant (as good as glass)." In a 2005 letter to EPA (DOE, 2005), DOE suggests a set of performance criteria to support a determination of comparable treatment for bulk vitrification of the Hanford tank waste by showing that bulk vitrification is equivalent to High-level Waste Vitrification (HLVIT), which is considered by EPA to be Best Demonstrated Available Technology (BDAT). A September 2009 Government Accountability Office report makes the following statement (GAO, 2009, p. 43): "[T]he state [of Washington] has maintained that any supplemental treatment technology [for LAW at Hanford] must be shown to

Carolina have agreed that low-activity waste disposed of at the Savannah River Site will be in a grouted waste form (Saltstone). DOE-EM and the State of Washington have agreed that the waste form selected for immobilizing low-activity waste at the Hanford Site will be glass or "as good as glass" (see Box 8.1).

8.3 REGULATIONS

EPA and the USNRC have issued regulations for the management and disposal of HLW, TRU waste, and LLW. These are described briefly in the following sections.

be 'as good as glass,' which means that it must meet or exceed all the same performance standards and disposal criteria to protect human and ecological health that apply to the approved glass form."

How would one demonstrate that an alternative waste form is as good as glass? One approach would be to demonstrate that the alternative waste form meets the same chemical durability performance measure (e.g., long-term fractional dissolution rate, see Chapter 5) as the current baseline Low-Activity Waste Reference Material (LRM) glass (see McGrail et al., 2003). Another approach would be to demonstrate that the disposal system, including the alternative waste form, meets the facility's applicable performance requirements. Such a systems approach, which considers waste form performance in the context of a shallow subsurface disposal facility, appears to have been the basis for the processing, product acceptance, and chemical durability performance measures imposed by DOE for immobilized low-activity waste glass (Mann et al., 2001). This approach allows DOE to take credit for the other engineered and natural barriers in the near-field environment of the disposal facility, which could provide more flexibility in the selection of alternative waste forms. For example, based on a performance assessment, DOE could ensure that the system performance is "as good as glass" in a specific disposal facility either by establishing restrictions on waste loading for specific waste form products that are not limited to glass, or by minimizing the requirements on the durability of the waste form by modifying the facility design to incorporate engineered barriers such as hydraulic barriers that divert water from the waste and getters to trap important radionuclides (Mann et al., 2001, sections ES4 and 7.6.4).

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[a] See http://listserv.wa.gov/cgi-bin/wa?A3=ind0407&L=HANFORD-INFO&E=quoted-printable&P=12240&B=------_%3D_NextPart_001_01C46F91.659F3450&T=text%2Fhtml&XSS=3.

8.3.1 USNRC: 10 CFR Part 61 and Related Guidance for LLW Disposal

Title 10, Part 61 of the Code of Federal Regulations (10 CFR 61) was promulgated by the USNRC to regulate the disposal of low-level waste (LLW) generated at USNRC-licensed facilities except for Greater-Than-Class-C Waste.[8] These regulations would also apply to DOE wastes that are

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[8] Under the Low-Level Radioactive Waste Policy Act, the federal government has responsibility for the disposal of Greater-Than-Class-C (GTCC) Waste from Nuclear Regulatory Commission and Agreement State-licensed activities as well as GTCC-like waste from its own activities. DOE recently issued a draft environmental impact statement (DOE, 2011) that examines four alternative methods for disposing of this waste: (1) geologic disposal in the Waste Isolation Pilot Plant, and/or land disposal in (2) intermediate-depth boreholes; (3) enhanced near-surface trenches, and (4) above-grade vault facilities.

disposed of in commercial facilities. They would not apply to wastes that are disposed of at DOE sites.

Part 61.56 (Waste Characteristics) establishes requirements for the structural stability of waste forms. It states that a waste form

> . . . will generally maintain its physical dimensions and its form, under expected disposal conditions such as weight of overburden and compaction equipment, the presence of moisture, and microbial activity, and internal factors such as radiation effects and chemical changes.

Furthermore, Part 61.7 (Concepts) requires that for Class B and C LLW, the waste form must maintain its gross physical properties and identity for 300 years, and that a concrete cover must be provided as an intruder barrier with an effective life of 500 years. These time scales, although long compared to human life spans and regulatory time scales applied to the disposal of chemically hazardous wastes, are much shorter than the 10^4- to 10^6-year regulatory time scales that apply to the disposal of HLW (see Section 8.3.2). It is also notable that Part 61.51 (Disposal Site Design for Land Disposal) stresses that the disposal system must be designed to complement the natural system, reinforcing the need to consider waste form performance in the context of a system of barriers (see Chapter 7) rather than in isolation.

The USNRC has produced several technical position and contractor reports on LLW waste form test methods and results acceptable to the USNRC staff for implementing 10 CFR 61. Appendix A of USNRC (1991) addresses cement waste form characterization and qualification, including test-sample preparation, sampling, and analysis. More recently, the USNRC has published technical guidance for the disposal of decommissioning LLW within engineered disposal systems (USNRC, 2006) and waste incidental to reprocessing (USNRC, 2007). The latter report provides guidance to DOE for conducting WIR determinations (see Section 8.1.6) at the Savannah River Site (SRS) in South Carolina and the Idaho National Laboratory (INL) in Idaho pursuant to the NDAA, as well as at the Hanford Site in Washington and the West Valley Site in New York. The document discusses the background and history of waste determinations; applicable criteria and how they are applied and evaluated; review of associated performance assessments for disposal systems and inadvertent intruder analyses; removal of highly radioactive radionuclides; and USNRC monitoring activities that will be performed at SRS and INL in accordance with the NDAA.

The Center for Nuclear Waste Regulatory Analyses (CNWRA, 2009) recently issued the report titled *Review of Literature and Assessment of Factors Relevant to Performance of Grouted Systems for Radioactive Waste Disposal*. This report focuses on potential time-dependent changes in chemical, hydraulic, and structural properties of LLW cements and how they might affect the overall release performance of LLW disposal systems.

8.3.2 EPA: 40 CFR Parts 191 and 197 for HLW Disposal

EPA promulgated Title 40, Part 191 of the Code of Federal Regulations (40 CFR 191), as required under the NWPA, as the environmental protection standard for the geological disposal of SNF, HLW, and TRU waste. SNF and HLW are specifically defined in the Atomic Energy Act, whereas TRU waste is defined in 40 CFR 191 as waste containing more than 100 nanocuries per gram (nCi/g) of alpha-emitting transuranic isotopes having half lives greater than 20 years, except for (1) HLW; (2) wastes that DOE has determined, with the concurrence of the USNRC, do not need the same degree of isolation required for HLW (e.g., WIR); or (3) wastes that the USNRC has approved for disposal on a case-by-case basis in accordance with 10 CFR 61. EPA developed 40 CFR 191 in the early 1980s, when the understanding of geological disposal of long-lived nuclear wastes was in its infancy. Accordingly, EPA developed rather stringent safety standards to assure the safety of the overall repository system.

The standards in 40 CFR 191 establish three specific types of performance objectives to be met by a repository: (1) an individual protection requirement, (2) a containment requirement, and (3) a groundwater protection requirement.

- The individual protection requirement states that there must be reasonable expectation that "any member of the public" in the accessible environment will not receive a dose in excess of 15 millirems per year during a compliance period of 10,000 years.
- The containment requirements are defined probabilistically such that there must be less than a 0.1 probability that the release limits are exceeded and less than a 10^{-3} probability that they are exceeded by a factor of 10. The release limits were established for individual radionuclides based on cumulative activity released per 1,000 metric tons of heavy metal.
- The groundwater standard provides a tabulated allowable concentration for various radionuclides at the compliance boundary.

All of these performance objectives apply to the disposal system as a whole and impose no performance requirements on waste forms. It should be noted that these three separate safety requirements (individual protection, cumulative release, and groundwater concentration limits) within 40 CFR 191 are not necessarily self-consistent with each other.

The final 40 CFR 197, which was promulgated by EPA as required under the Energy Policy Act of 1992, establishes a dose limit of 15 millirems per year for a reasonably maximally exposed individual for an initial period of 10,000 years after repository closure, and 100 millirems per year allowable dose rate for the period between 10,000 and 1 million years, in response to the NAS recommendations (NRC, 1995). The EPA drinking water standard is also to be applied. As with 40 CFR 191, the Yucca Mountain-specific safety standard sets performance requirements on the total repository system but places no performance requirements on waste forms.

8.3.3 USNRC: 10 CFR Parts 60 and 63 for HLW Disposal

The NWPA directed the USNRC to develop licensing procedures for geological repositories for SNF and HLW that are consistent with the environmental standards developed by EPA. Much of the USNRC's regulation applies to licensing procedures and acceptable levels of evidence, rather than establishing additional requirements. The USNRC's licensing procedures for a generic repository, which are contained in Title 10, Part 60 of the Code of Federal Regulations (10 CFR 60), do not differ significantly from the USNRC's Yucca Mountain-specific licensing procedures, which are contained in Title 10, Part 63 of the Code of Federal Regulations (10 CFR 63). However, as discussed below, there are differences in the applicable safety standards.

Like 40 CFR 191, however, 10 CFR 60 was developed in the early 1980s when there was less complete knowledge of the properties and processes that are most important for long-term isolation of nuclear waste in geological disposal systems. Accordingly, one element of 10 CFR 60 that was not included in 10 CFR 63 was the set of provisions from 10 CFR 60, Subpart E (Technical Criteria). Part 60.113 (Waste Package Performance Objective) established so-called "subsystem" performance objectives for individual barrier components of the repository system in addition to the overall performance requirements established in the draft 40 CFR 191. Part 60.113 stated that "assuming anticipated processes and events," containment within the waste packages would be "substantially complete" for a period between 300 and 1,000 years after permanent closure. Further, Part 60.113 set forth an engineered barrier system release objective, requiring that after the containment period, the release of each radionuclide from the engineered barrier system (EBS) cannot exceed 10^{-5} parts per year of the inventory calculated to be present 1,000 years after permanent closure.

The context for this 10^{-5} parts per year release rate from the EBS is important, in part because of subsequent efforts in the United States to link waste form performance to this EBS performance value. In the early 1980s, preliminary studies (e.g., Crandall, 1983) on the dissolution behavior of borosilicate glass as a matrix for defense HLW showed a range of fractional dissolution rates between 10^{-4} to 10^{-6} parts per year (at these rates the glass waste form would totally dissolve in 10,000 to 1 million years). In the early 1980s there were no specific disposal concepts, no system-level performance analyses, and only draft disposal safety standards. In the absence of a specific disposal system context, the USNRC decided to set a sub-system performance target for the EBS (but not the waste form *per se*) based on a waste form fractional dissolution rate that was both known to be achievable and likely to aid in long-term performance of any disposal concept.

At that time, DOE was seeking to make decisions on the selection and qualification of a waste form for its defense HLW. Borosilicate glass was selected on the basis of industrial simplicity of the process, extensive nuclear experience in Europe with vitrifying HLW, adequate waste loading, reasonable processing rates, reasonable processing costs, reasonable durability, and a number of other factors. DOE wanted to develop a testing basis to show that borosilicate glass would be acceptable in any of the several geologically diverse repository host rocks (salt, basalt, granite, tuff, and argillite) then being considered. The difficulty was that EBS designs were still under development and there was considerable divergence among such designs for different host rocks. Moreover, the understanding that repository performance was dominated by radioelement solubilities was also just being developed (NRC, 1983; see Chapter 7).

Therefore, a conservative approach was taken to construe Part 60.113 as a benchmark for borosilicate glass waste forms; if it could be shown that the long-term fractional dissolution rate was equal to or less than 10^{-5} parts per year for the most soluble and long-lived radionuclides such as selenium-79, technetium-99, cesium-135, and iodine-129, then borosilicate glass should provide acceptable performance for any repository site or concept. This conservative approach was extended to include consideration of phenomena such as glass cracking and crystallization, which could increase the leach rates above 10^{-5} parts per year. Without accounting for these effects, it was judged that a homogeneous glass with a leach rate of 10^{-5} parts per year should perform adequately in a systems analysis.

Subsequent analyses by the USNRC showed that the assumption that a 10^{-5} parts per year sub-system performance target would meet safety regulations for disposal systems was not justified (USNRC, 1999): “[US]NRC was not able to demonstrate, however, that compliance with the subsystem criteria alone was sufficient to meet the assumed EPA standards, nor that compliance with the assumed EPA standards would suffice to assure compliance with the subsystem criteria.”

Furthermore, there was widespread criticism of the sub-system approach in 10 CFR 60 both in the United States and internationally;

application of such sub-system requirements was seen as unduly restricting the options and isolation strategies available for achieving a safe yet optimized disposal system. Sub-system performance objectives were criticized as overly prescriptive, lacking a strong technical basis, lacking a clear link to overall performance measure, and unclear in wording and implementation. No other nation has safety regulations that impose such sub-system performance objectives; it is left to the institution implementing the repository to develop and qualify a set of multiple barriers that, in concert with specific waste forms and site characteristics, will comply with system-level safety requirements.

In addition, the NAS specifically concluded that "because it is the performance of the total system in light of the risk-based standard that is crucial, imposing subsystem performance requirements might result in suboptimal design" (NRC, 1995). This conclusion was directed specifically to the USNRC, in the context of revisions that the USNRC needed to make to its new 10 CFR 63 regulations to be consistent with a new EPA standard for Yucca Mountain. Following these observations from the NAS, the USNRC made the following comment in promulgating its revised 10 CFR 63 (USNRC, 1999):

> Identification of such subsystem performance measures was expected to be helpful input to DOE's design process, without being overly restrictive. It is now recognized that [US]NRC attempted to define such criteria on the basis of limited, existing knowledge, without benefit of research and site-specific information that only later was acquired during characterization of a specific site at Yucca Mountain. (p. 8643)

and

> More specifically, [the 1992 Energy Policy Act, EnPA-Public Law 102-486] and NAS [NRC, 1995] have specified an approach that would require the performance of a Yucca Mountain repository to comply with a health based standard established in consideration of risk to a hypothetical critical group, and further, that this would be the only quantitative standard for the post-closure performance of the repository. This approach is incompatible with the approach taken in the existing generic criteria that relies on quantitative, subsystem performance standards. The Commission proposed to leave the existing generic requirements intact and in place, if needed, for sites other than Yucca Mountain. Although their application could be expected to be difficult, the Commission assumes that it would be afforded adequate time and resources in future years to amend its generic regulations for any additional repository site that might be authorized. (p. 8648)

Based on the technical reasoning provided by both the NAS report (NRC, 1995) and the USNRC's own analysis, the USNRC abandoned sub-system performance objectives in 10 CFR 63—thus eliminating specific requirements for waste form performance. It can be reasonably expected that this same decision to omit sub-system performance objectives would be adopted by the USNRC for any revisions to 10 CFR 60 as applied to other repository sites.

Part 60.135 establishes requirements for HLW packages and components. It requires that wastes be in solid, consolidated form and shall not contain explosive, pyrophoric, or chemically reactive materials in an amount that could compromise the ability of the geologic repository to satisfy performance objectives. It also requires that the waste package shall not contain free liquids in an amount that could compromise performance objectives or result in spillage and spread of contamination in the event of waste package perforation during the period through permanent closure. None of these requirements specifically relate to waste form performance in disposal systems.

8.3.4 Resource Conservation and Recovery Act

RCRA[9] gives EPA cradle-to-grave authority to regulate the generation, transportation, treatment, storage, and disposal of hazardous waste[10] to protect human health and the environment. RCRA was established in 1976 and has been amended several times since enactment.

RCRA gives EPA the authority to establish land disposal requirements (LDRs) for hazardous wastes. The requirements (promulgated in Title 40, Part 268 of the Code of Federal Regulations) require that hazardous wastes be treated to meet specific treatment standards prior to land disposal. The treatment standards are expressed in terms of specific contaminant levels, or specific treatment technologies that must be applied to reduce the toxicity or mobility of hazardous constituents. If a waste is listed or characteristically hazardous it must be treated to meet specific contaminant levels which

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[9] 42 U.S.C. §6901 et seq, promulgated in 40 CFR 260 et seq.

[10] EPA defines hazardous waste as waste with properties that make it dangerous or potentially harmful to human health or the environment. There are three classes of hazardous wastes that are relevant to this discussion: wastes that are listed as hazardous (i.e., *listed wastes*) because of their process history; wastes that are characteristically hazardous (i.e., *characteristic wastes*) because they exhibit one or more of the following four characteristics: ignitability, corrosivity, reactivity, or toxicity; and wastes that contain both radioactive and hazardous constituents (*i.e., mixed wastes*). There are four types of hazardous wastes: (1) mixed listed waste; (2) characteristically hazardous mixed waste; (3) listed hazardous waste; or (4) characteristically hazardous waste. HLW at Savannah River and West Valley fall into the second category, whereas HLW at Idaho and Hanford fall into the first category.

are referred to as *universal treatment standards* (UTS). EPA can also define treatment standards for specific wastes; the specific treatment technologies are referred to as *best demonstrated available technology* (BDAT). Wastes that do not meet one of these treatment standards are prohibited from land disposal unless EPA has granted a variance or exclusion or the waste is managed under an EPA-approved no-migration petition.

SNF or HLW generated during the reprocessing of SNF are hazardous for one (or more) of the RCRA metals. EPA has established a BDAT for treatment of HLW generated during the reprocessing of fuel rods: HLW vitrification, referred to as *HLVIT*. DOE-EM has established that HLW vitrification at the Savannah River Site and West Valley is BDAT and therefore meets EPA's LDRs. Consequently, vitrified HLW at these sites currently qualify for disposal.

HLW at Idaho and HLW/LAW at Hanford do not currently qualify for disposal because they contain listed wastes. Moreover, even if the Federal EPA approves HLVIT of these wastes as BDAT, a state EPA can still require that the waste meet more stringent standards—for example, that it be delisted prior to disposal. DOE-EM will likely need to consult with its regulators (EPA and states hosting the disposal facilities for these waste streams) to clarify this issue.

8.4 WASTE ACCEPTANCE CRITERIA

Waste acceptance criteria (WAC) are established by the owners/operators of waste disposal facilities. They provide specific requirements that waste must meet to be acceptable for disposal. WAC include such specifications as the types of waste accepted, including its physical and chemical forms; the container to be used for disposal, including its packaging and labeling; and allowable contamination levels on the outside of the container.

Within the DOE system WAC have been established for disposal of SNF and HLW in a geologic repository; TRU waste at the Waste Isolation Pilot Plant in New Mexico; and LLW and mixed waste in land-disposal facilities at DOE sites. The WAC for the Waste Isolation Pilot Plant is discussed in some detail in NRC (2001, 2002a, and 2004) and is not repeated here. The remainder of this section will focus on WACs for SNF and HLW.

OCRWM published a Waste Acceptance System Requirements Document (WASRD) to establish waste acceptance criteria imposed by the Civilian Radioactive Waste Management System (CRWMS) on SNF and defense HLW delivered into the CRWMS (DOE, 2008). The purpose of the WASRD is to ensure that the characteristics and properties of waste forms received into the CRWMS would not hinder or prevent safe handling, emplacement, and final disposal into a repository.

With respect to acceptance of SNF for disposal, uranium oxide fuels present few issues, unless there has been significant deterioration or alteration of the fuel, as was the case for some of the spent fuel in wet storage at the Hanford Site.[11] Metallic uranium SNF, however, presents key WAC issues with respect to both pyrophoric behavior and reactivity to groundwater under repository disposal conditions. To address WAC concerns for DOE's damaged oxide SNF and metallic SNF, DOE has been studying various treatment options to generate acceptable reprocessed waste forms, most notably electrometallurgical methods leading to a Fe/Zr (cladding) metal waste form and a glass-bonded zeolitic waste form (NRC, 2000b).

Section 4.8 of the WASRD specifically addresses acceptance criteria and specific requirements for HLW, which at that time was taken to be borosilicate glass sealed inside an austenitic stainless steel canister. There are various requirements regarding the dimensions, weight, labeling, thermal output, criticality potential, radionuclide content, and handling characteristics of the HLW. With respect to dangerous properties, the WASRD states

> The HLW canister materials shall preclude chemical, electrochemical, or other reactions (such as internal corrosion) of the canister or waste package such that there will be no adverse effect on normal handling, transportation, storage, emplacement, containment, isolation, or on performance under abnormal occurrences such as a canister drop accident and premature failure in the repository.

Section 4.8.1 (B) on Product Consistency states

> 1. The Producer shall demonstrate control of waste form production by comparing production samples or process control information, separately or in combination to the Environmental Assessment benchmark glass (Jantzen, 1993) using the Product Consistency Test (ASTM C1285-97 or equivalent.
>
> 2. For acceptance, the mean concentrations of lithium, sodium, and boron in the leachate, after normalization for the concentrations in the glass, shall be less than those of the benchmark glass.

Product Consistency Test A (PCT-A) is specifically used to evaluate whether the chemical durability and elemental release characteristics of nuclear, hazardous, and mixed waste glass waste forms have been consis-

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[11] About 2,300 tonnes of spent fuel in wet storage in the K-Basins at the Hanford Site have been retrieved, dried, and packaged in steel canisters. This spent fuel is now in interim storage at the site.

tently controlled during production.[12] It is a seven-day leach test performed at 90°C to simulate the heat of radioactive decay and involves the measurement of release rates of lithium, sodium, and boron from borosilicate glass waste forms. These soluble elements were chosen because they are released at the same rate (i.e., congruently; see Chapter 5, Box 5.2) as the most soluble, long-lived radionuclides (e.g., technetium-99, iodine-129, and cesium-135).

The applicability of PCT for quality control was determined by extensive testing of both simulated and radioactive glass waste forms. These tests may or may not be applicable to alternative HLW waste forms, such as ceramics or metals, when these elements are not present or their release mechanisms are different, as stated in the procedure's documentation. Mechanistic testing is required to determine the adequacy of this test to other waste forms, and often this mechanistic testing is not performed before the PCT-A test is applied to different waste forms. PCT-A is not a performance requirement in the sense that it provides any information about the long-term (10^4-10^6 year) radionuclide-release performance of such a waste form in a multiple-barrier geological disposal system.

The PCT response can be useful, however, in the following manner: If a glass is made in a consistent manner and within a consistent range of composition by process control, then the imposed process control leads to composition control that, in turn, leads to consistent dissolution rate (hence, performance) control, within certain bounds (see Chapter 5). In this way, waste form producers have demonstrated that composition control can be used to bound acceptable performance. Also the PCT-B test can provide information about the longer-term radionuclide-release performance in a multiple-barrier geological disposal system when used in conjunction with the durability response of other kinetically based tests, such as the Single-Pass Flow-Through Test (SPFT) and the Pressure Unsaturated Flow (PUF) Test. The use of testing for these purposes is discussed in more detail in Chapter 5.

There are no requirements in the WASRD on waste form performance with respect to meeting long-term, post-closure regulatory safety standards for radionuclide release rates. This purposeful absence of waste form performance requirements by the repository implementer reflects (1) the understanding that the safety of a multiple barrier repository system does not rely on the performance of any one sub-system barrier, including

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[12] PCT methods A and B evaluate the chemical durability of homogeneous glasses, phase-separated glasses, devitrified glasses, glass ceramics, and/or multiphase glass-ceramic waste forms, collectively referred to as "glass waste forms," by measuring the amounts of the chemical species released to a specified volume of test solution over a specified time interval. These tests are described in more detail in Chapter 5.

the waste form, and (2) the desirability for the repository implementer to retain flexibility in the design, safety, and optimization of the overall disposal system.

8.5 DISCUSSION

The DOE-EM program operates under an extensive set of legal and regulatory requirements, key features of which were described in this chapter. Some of these requirements have been imposed by outside entities, including the U.S. Congress, state legislatures, and Federal and state regulatory authorities. Other requirements have been self imposed by DOE and appear in DOE orders and in Agreements with states and other agencies.

As noted in this chapter, some laws, regulations, orders, and Agreements establish requirements for the production and use of waste forms in the cleanup program. For example, RCRA waste intended for land disposal must be processed to meet specific treatment standards. The treatment standards are expressed in terms of specific contaminant levels (UTS) or specific treatment technologies (BDAT) (see Section 8.3.4). Additionally, DOE has Agreements with states that specify the characteristics of waste forms that are suitable for disposal (e.g., see Box 8.1), and DOE has in some cases established its own criteria for accepting waste forms for disposal (e.g., see Section 8.4 on Waste Acceptance Criteria).

However, the committee was unable to identify any specific requirements for waste form performance in *disposal systems*. Performance requirements have been established for disposal systems as a whole, but the committee could not identify any sub-system performance requirements that apply specifically to waste forms.

The RCRA requirements for disposal of hazardous waste, which DOE has agreed to follow under Order 5400.1, could reduce DOE-EM's flexibility to pursue optimization of its overall waste management system, especially for disposal of Hanford HLW/LAW at Idaho HLW. Vitrified HLW from Savannah River and West Valley currently qualify for geological disposal because they meet EPA's BDAT requirements. However, is not clear whether immobilized Hanford HLW/LAW and Idaho HLW would also satisfy RCRA requirements under a BDAT rationale. DOE-EM will need to consult with its regulators (EPA and states hosting the disposal facilities for these waste streams) to clarify this issue.

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9

Possible Opportunities in Waste Form Science and Technology

The previous chapters of this report have focused on the current state of development of waste form science and technology. The focus of this chapter is on the future: It describes some exciting trends and recent developments in materials science, processing technologies, and computational simulation and their potential applications to DOE programs, especially the Department of Energy-Office of Environmental Management's (DOE-EM's) cleanup program. This chapter is intended to address the last two charges of the committee's statement of task (see Box 2.1. in Chapter 2) by providing examples of how scientific and technological advances may improve the DOE-EM cleanup program.

Advances in waste form science and technology could have important applications in other DOE programs as well. For example, the development of advanced nuclear fuel cycles by DOE's Office of Nuclear Energy (DOE-NE) and others will require the design of new materials for recycling or immobilizing radionuclide streams that are unlike DOE's legacy wastes, and also the development of new approaches for modeling nuclear fuels (e.g., Devanathan et al., 2010). Inert matrix fuels or new target materials, which are contemplated for use in reactors designed to "burn" transuranium elements, could be designed not only for their performance in those reactors, but also for ease of recycling and disposal (Peters and Ewing, 2007). Some of the examples provided in this chapter are potentially useful for these applications, especially for managing actinides.

Several recent workshops and studies have identified exciting new research opportunities in materials science, including the development of improved waste forms, processing technologies, and computational capabilities. The reports include the following:

- Summary Report of the Nuclear Energy Research Initiative Workshop, April 23-25, 1998 (see the report of working group #4). Available at http://www.ne.doe.gov/pdfFiles/nerachWorkshop.pdf.
- Basic Research Needs for Advanced Nuclear Energy Systems, July 31-August 3, 2006 (see the panel #5 report on advanced waste forms). Available at http://www.er.doe.gov/bes/reports/files/ANES_rpt.pdf.
- Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems, February 21-23, 2007 (see sections related to subsurface geologic storage and modeling/simulation of geologic systems). Available at http://www.er.doe.gov/bes/reports/files/GEO_rpt.pdf.
- Basic Research Needs for Materials under Extreme Environments, June 11-13, 2007 (see section on nuclear energy). Available at http://www.er.doe.gov/bes/reports/files/MUEE_rpt.pdf.
- Global Nuclear Energy Partnership Integrated Waste Management Strategy Waste Treatment Baseline Study. GNEP-WAST-AI-RT-2007-00034. 2007 (see vol. 1 sections on processing and stabilization with different types of waste forms). Available at http://www.engconfintl.org/9arIWMS.pdf.
- Directing Matter and Energy: Five Challenges for Science and the Imagination, A Report from the Basic Energy Sciences Advisory Committee, 2007 (see chapter 7 on designing new materials). Available at http://www.er.doe.gov/bes/reports/files/GC_rpt.pdf.
- Alternative Waste Forms: Aqueous Processing (Ryan et al., 2009).
- Alternative Waste Forms for Electro-Chemical Salt Waste (Crum and Vienna, 2009).

Additionally, the recent National Research Council report *Frontiers in Crystalline Matter from Discovery to Technology* (NRC, 2009), which was sponsored in part by DOE, outlines an exciting agenda for the development of new materials for special applications. Although most of the examples in this report are for high-technology applications (e.g., microelectronics, superconductivity, and heterostructures), opportunities also exist for the development of new waste form materials.

The committee sees possible innovations developing from at least three directions:

- New waste form materials designed for specific performance functions (e.g., high durability in specific disposal environments; compatibility with specific waste streams) or designed to remain stable over different ranges of time, depending on the half-life of the radionuclide.

- New processing technologies that can handle complex, highly radioactive waste streams and produce more consistent waste form products.
- Advanced techniques for understanding and modeling waste form–near-field interactions.

In the sections that follow, the committee provides some examples of potential innovations in each of the three categories (i.e., materials, processing technologies, and models) mentioned above. *These examples are presented to illustrate the wide variety of possibilities; they should not be viewed as inclusive or as recommendations for specific investigations.* The examples are provided primarily to illustrate what might be developed by DOE-EM even with modest investments. Some of these examples are incremental in that they build on research programs that have obvious relations to the ongoing DOE-EM cleanup mission. Others are simply "outside-the-box" ideas that may warrant attention by DOE-EM.

9.1 NEW DEVELOPMENTS IN MATERIALS SCIENCE

The following examples illustrate how advances in materials science can be used to develop new and improved waste form materials for specific applications, for example, for immobilizing specific waste streams or for disposal in specific geological environments. These materials may benefit from further development or application; some have not been fully explored by the waste management community. These examples are intended to be illustrative, not comprehensive. The committee has made no effort to determine whether these materials are suitable for particular DOE-EM waste streams.

9.1.1 Amorphous Materials Designed with Short-Range and Intermediate-Range Order

There continues to be substantial progress in the characterization and understanding of the structure of glass and the interplay between glass composition, structure, and properties. This progress is the direct result of advances in materials characterization techniques, mainly spectroscopic techniques (Hawthorne, 1992; Pierce et al., 2010), including the use of synchrotron sources for X-ray scattering and X-ray absorption spectroscopy (Brown et al., 1995). A recent workshop has reviewed the possible applications of synchrotron radiation techniques to materials that contain radionuclides (ANL, 2010).

The application of advanced spectroscopy techniques has provided a greatly improved understanding of the structural properties of glasses, particularly short-range (nearest-neighbor atomic spacing) and intermediate-range (the connectivity extending across several metal-metal distances) order (Calas et al., 2010) (Figure 9.1). As a result, it now appears feasible to use *amorphous network engineering* to tailor glass compositions with specific atomic sites for incorporating radionuclides (e.g., Martin et al., 2002). Great progress has also been made in simulating glass structures and calculating the energetics that control glass durability (Garofalini, 2001; Poole et al., 1995). The improved knowledge of glass structure and durability should provide increased confidence in understanding glass behavior in disposal environments.

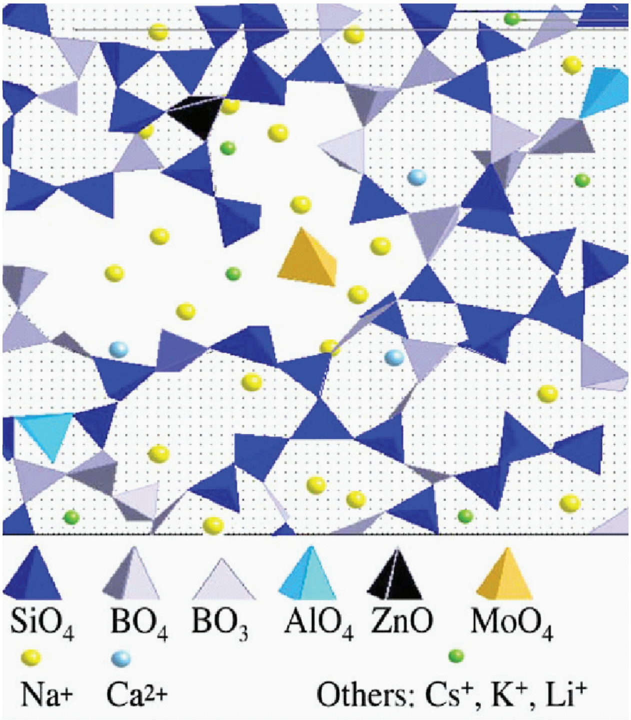

FIGURE 9.1 Schematic diagram showing the complexity of the structure of glass with both short-range (the individual coordination polyhedra) and intermediate range (extending across the different rings of polyhedra). With the increased understanding of the structure of glass, one can use the intermediate-range order for the atomic-scale incorporation of specific radionuclides.
SOURCE: Calas et al. (2010), Figure 2.

9.1.2 Glass-Ceramic Materials

Although glass may accommodate waste loadings of up to 38 weight percent, there are certain constituents (e.g., chromium, sulfate [$SO_4^=$], titanium, zirconium, phosphorus, and actinides) that have limited solubilities in certain glass compositions. Similarly, crystalline ceramics often have thin selvages of amorphous material along their grain boundaries. As noted in Chapter 3, there is a continuum of glass and crystalline phases within many materials. In fact, such glass-ceramic materials (GCMs) are probably more common than is generally appreciated because processing technologies are generally limited in their ability to provide phase-pure materials.

The multi-phase nature of GCMs makes them useful for immobilizing radioactive waste. As noted in Chapter 3, GCMs could be designed to incorporate long-lived radionuclides (e.g., actinides) into crystalline phases of greater durability and shorter-lived radionuclides (e.g., some fission products) into less durable glass phases. This approach was proposed more than 20 years ago (e.g., Hayward, 1988). However, recent advances in materials processing technologies may make it feasible to actually produce these materials at reasonable scales and costs.

There still remain a number of challenges for designing GCMs for radionuclide immobilization. The physical properties and leaching behavior of GCMs may differ from either pure glass or an assemblage of fully crystalline phases because of the coupling of processes between the phases. For example, crystalline phases that contain actinides may expand as radiation damage accumulates; this expansion may cause microcracking in the surrounding glass (Figure 9.2). The interface between the glass and crystal may be the point of maximum leach rate and radionuclide release on initial contact with water, resulting in a high instantaneous release followed by slower matrix dissolution.

Nevertheless, GCMs have already demonstrated utility as waste forms for iodine (Garino et al., in press). They can accommodate a greater range of radionuclides and achieve higher waste loadings (see Figure 3.1 in Chapter 3) than many materials now in use. They can also be produced at lower temperatures.

9.1.3 AO_x Isometric Structures

Incremental changes in the composition and structure of a material can result in substantial improvements in its performance as a waste form. For example, uranium dioxide (UO_2), which comprises the matrix of commercial nuclear fuels, has a simple, isometric fluorite (CaF_2) structure, the same structure as many actinide oxides. During the past decade, derivative structures such as $A_2B_2O_7$ pyrochlore, which contains two cation sites

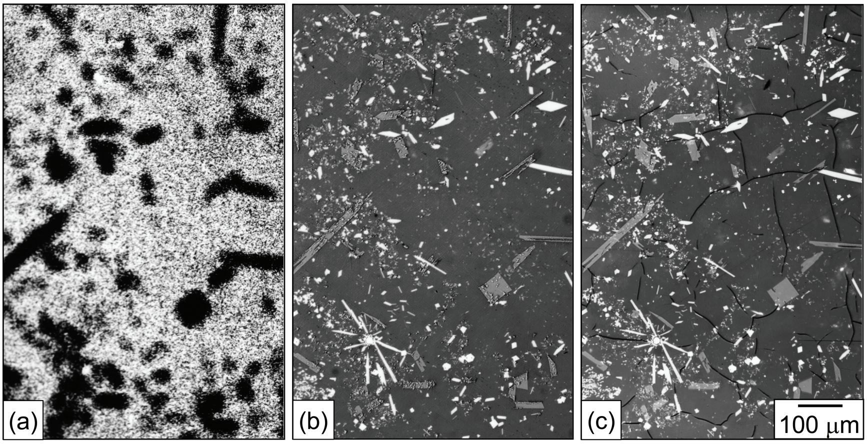

FIGURE 9.2 Effect of alpha-decay in crystalline phases on microstructure in a partially devitrified glass: (a) alpha-autoradiograph showing curium-244 concentrated in crystalline phases; (b) optical micrograph of region in (a) indicating no microcracks after 6 × 10^{15} alpha-decays/g; and (c) microcracking in same region from amorphization of crystalline phases after 2.4 × 10^{17} alpha decays/g.
SOURCE: (a) Courtesy of William J. Weber, University of Tennessee; (b) and (c) Weber et al. (1998), Figure 6.

(A, B) and one missing oxygen, have been examined for possible use for incorporating actinides, either as part of an inert matrix fuel or for direct disposal in a repository. A typical composition that has been investigated for this purpose is titanate pyrochlore $(Gd,Pu)_2(Ti,Hf)_2O_7$. This material is very susceptible to radiation damage because of alpha-decay from the incorporated actinides (in this case plutonium), which causes the material to be transformed to an amorphous state. However, if the composition is changed by substituting zirconium for titanium to produce $(Gd,Pu)_2(Zr,Hf)_2O_7$, the material has an entirely different response to radiation damage and does not become amorphous even at very high radiation doses.

This difference in behavior is illustrated schematically in Figure 9.3. The curves in the figure show the doses required to amorphize three pyrochlore materials as a function of temperature. The temperature at which thermal annealing dominates over damage accumulation—that is, the point at which the curves become vertical and a material can no longer be amorphized—is different for these three materials. By selecting a composition for which the thermal annealing occurs at low temperatures (e.g., Gd_2ZrTiO_7 in Figure 9.3), one can ensure that the waste form never becomes amorphous because of radiation damage.

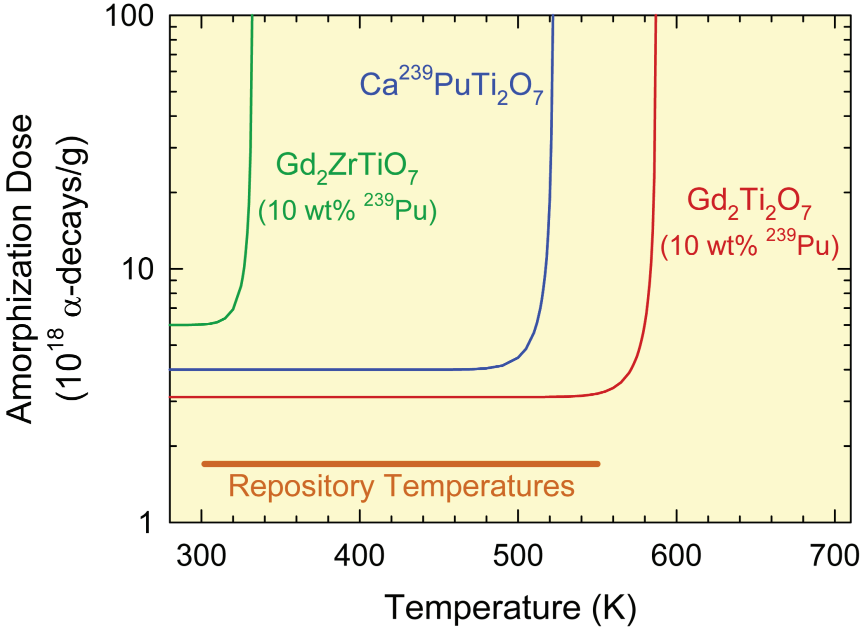

FIGURE 9.3 Predicted temperature dependence of amorphization in pyrochlore phases containing plutonium-239. The curves bend upward at elevated temperatures because of thermal annealing. Where the curves become vertical the material remains crystalline at high alpha-decay doses. The range of potential repository temperatures is indicated by the horizontal line. SOURCE: Ewing et al. (2004).

This annealing behavior could be used to advantage for disposing of minor actinides immobilized in pyrochlore waste forms. Such waste forms could be disposed of in boreholes drilled several kilometers into Earth's crust, where temperatures are sufficiently elevated (because of the geothermal gradient) to prevent waste form amorphization (Figure 9.3).

Pyrochlore materials are potentially useful for immobilizing other radionuclides besides actinides. For example, Weck et al. (2010) recently synthesized a series of rare-earth technetate pyrochlores that can potentially be used to immobilize long-lived fission products such as technetium-99. Russian researchers are investigating new approaches for technetium immobilization (e.g., Laverov et al., 2010).

9.1.4 Complex Structure-Types

There are a number of more structurally complicated materials—for example, complex oxides, silicates, phosphates, and vanadates—that have not been fully considered or developed as waste forms. Some of these materials were described in Chapter 3.

For example, murataite and garnet have recently received attention as potential host phases for actinides (Laverov et al., 2006, 2009a,b, 2010). Murataite-based ceramics ($A_6B_{12}C_4TX_{40-x}$)[1] have atomic periodicities that are multiples of the basic AX_2 structure of fluorite (CaF_2); however, they have more complicated compositions and multiple cation sites. These sites can be used to immobilize waste streams that have complex compositions, thus eliminating the need for further chemical separation (Laverov et al., 2006, 2010; Lukinykh et al., 2008). These materials accommodate high actinide waste loadings and can be designed to remain crystalline over long periods of disposal, as was shown previously for pyrochlore (Yudintsev et al., 2007). However, phase-pure murataite is difficult to make. Usually, it is one phase in a polyphase assemblage containing (mostly) other titanates, which can help to encapsulate the actinide-bearing murataite.

Garnet ($A_3B_2[TO_4]_3$), which has an isometric structure with three cation sites that can accommodate actinides and lanthanides, may also be a useful waste form material. Recent work (Laverov et al., 2010) has shown that garnet leach rates and radiation response can be changed substantially by changing its composition. Crystalline phosphates of the $NaZr_2(PO_4)_3$ (NZP[2]) family continue to be of interest mainly in the context of high-level radioactive waste (HLW) immobilization because the unique NZP structure can incorporate a variety of cations, including plutonium (Hawkins et al., 1997; Zyryanov and Vance, 1997). The NZP structure is a three-dimensional network of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra in which plutonium can substitute for Zr, as in $Na(Zr,Pu)_2(PO_4)_3$ (Orlova et al., 1994).

Apatite has a complicated, low-symmetry crystal structure: $A_{10}(BO_4)_6(OH, F, Cl)_2$, where A = calcium (Ca), sodium (Na), rare earths, fission products, and actinides; and B = silicon (S), phosphorus (P), vanadium (V), or chromium (Cr). It has been studied extensively as a host for toxic metals, and it also has great potential as an advanced waste form for complex radioactive waste streams because of its complex crystal chemistry, structural flexibility, and good chemical durability. A wide range of waste components (e.g., tri- and tetra-valent actinides, strontium, cesium) can be incorporated into the apatite structure by coupled substitutions at the cation and anion sites (Carpéna et al., 1998, 2001; Langmuir and Apted, 1992; Maddrell and Abratitis, 2004). Iodine, for example, can be incorporated in the structural channel in a lead vanadate apatite structure

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[1] Note: A = cations in 8-fold coordination; B = cations in 6-fold coordination; C = cations in a trigonal bipyramid (6-fold); T = cations in 4-fold coordination.

[2] NZP denotes the sodium zirconium phosphate structural family.

($Pb_{10}(VO_4)_{6-x}(PO_4)_xI_2$). The interest in this material has also resulted in the examination of new technologies, such as spark plasma sintering, for its synthesis (Campayo et al., 2009).

9.1.5 Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are a relatively new class of porous materials that consist of metal atoms (ions) linked together by multifunctional organic ligands (Figure 9.4). An incredibly diverse group of MOFs have been synthesized because of the wide variations in possible linkages between the organic and inorganic components of each framework. With the diversity in framework topology and surface moities, MOFs can be constructed with extremely large surface areas and with surface adsorption molecules.

The field of "reticular" chemistry (Batten et al., 1995; Hoskins and Robson, 1990; Yaghi and Li, 1995; Yaghi et al., 2003) and the development of MOFs are less than a decade old (O'Keeffe et al., 2000). Nevertheless, MOFs have already been considered for many applications in the energy field, for example, hydrogen storage, carbon dioxide sequestration, and methane sequestration. The most recent development (Furukawa et al., 2010) has been the synthesis of three-dimensional crystal structures that have exceedingly high internal surface areas. These high surface areas could be useful for radionuclide separations. Further, pore spaces in MOFs can be engineered to specific sizes, which could also be useful for separations.

It is easy to imagine the design and use of MOFs for immobilizing iodine and technetium. In fact, there is ongoing research funded by DOE-NE on the use of MOFs as separation materials for radio-iodine (Sava et al., 2011). At Sandia National Laboratories, research is focused on existing and novel MOFs for high loadings of I_2 separated from both liquid and gas streams. Published results have shown that various MOF/I_2 phases (including ZIF-8 and HKUST-1 MOFs) can be successfully incorporated into low-temperature glasses to form GCMs.

9.1.6 Self-Assembled Mesoporous Materials

Mesoporous[3] materials have attracted considerable attention since their discovery in the early 1990s (Beck et al., 1992; Kresgie et al., 1992). An important innovation has been to functionalize the surfaces of these materials (Anthony et al., 1993; Sayari, 1996) with self-assembled organic

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[3] Mesoporous materials have regularly arranged pores ranging from 2-50 nanometers in diameter. They have high surface areas (up to 1,500 square meters per gram) and uniform pore sizes and shapes.

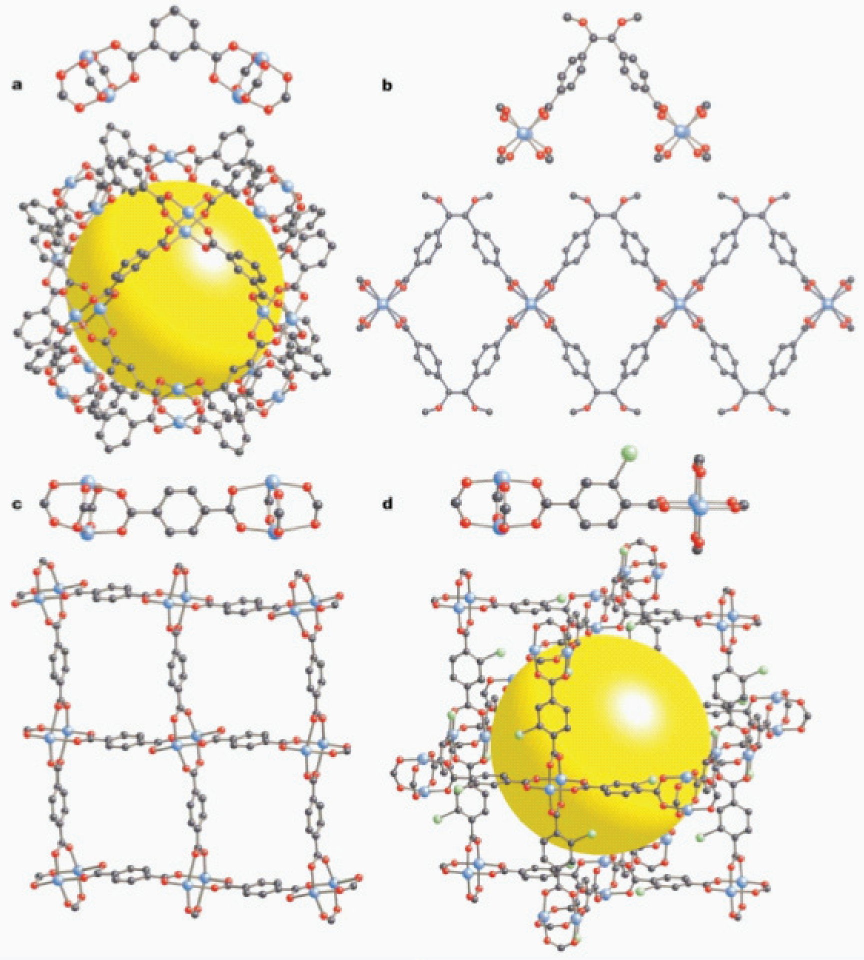

FIGURE 9.4 Framework structures are built of a linked framework of "paddle-wheel" units. The units can assume many different geometries and can accommodate a wide variety of elemental and molecular species. The small spheres are carbon, oxygen, bromine, and metal atoms. The large spheres illustrate the size of the cavities in some of the geometric arrangements.
SOURCE: Yaghi et al. (2003).

monolayers that provide a substrate with high chemical selectivity, allowing these materials to be used as chemical sensors (Kumar et al., 1994) and in chemical separation processes (Wirth et al., 1997).

Investigators at Pacific Northwest National Laboratory have extended this technology with the development of self-assembled mercaptan on mesoporous silica (SAMMS) (Feng et al., 1997a,b) for the removal of mercury from waste water and organic wastes. A further extension of this technology would be the development of mesoporous materials that are functionalized for the separation of specific radionuclides and suitable for the synthesis of waste forms. Advantages include high radionuclide loadings, high selectivity, and the possibility of a chemically durable final product (Feng et al., 1997b).

There are many related structures that share the features of MOFs and mesoporous materials. Recently, a sulfide structure has been synthesized that is selective for cesium by incorporation into its open framework (Ding and Kanatzidis, 2010). Thus, even framework chalcogenide[4] structures hold the potential for the sequestration of radionuclides.

9.1.7 Actinide Clusters and Frameworks

Nanoscale control of actinide materials is a new research field with potential applications in nuclear waste form development. Cage molecules containing from 20 to 60 uranium atoms as well as peroxide, hydroxyl, and oxygen have been reported over the past five years (Burns et al., 2005; Forbes et al., 2008; Sigmon et al., 2009a,b,c; Unruh et al., 2010). These clusters have diameters up to 3 nanometers. They are built of uranyl peroxide hydroxide hexagonal bipyramids that are linked through shared equatorial edges. This linkage results in topological squares, pentagons, hexagons, and a wide variety of cluster types. Several of these have fullerene topologies, including a cluster with 60 uranium atoms that is topologically identical to C_{60} buckminsterfullerene (Figure 9.5). It may be possible to tune the compositions and topologies of these structures for use as precursors in the creation of novel waste forms or nuclear fuels. Such clusters present the possibility of nanoscale control of chemical composition and properties of materials.

A new complex supertetrahedral framework has been recently discovered which consists of borate and thorium polyhedral (NDTB-1) (Wang et al., 2010). This compound has a cationic framework that contains anions within channels and cages that balance the framework charge. Borate polyhedra occur both in ordered positions within the framework and as disordered constituents of the channels. This compound has been shown to rapidly ion exchange these disordered borate groups with a variety of anionic groups, including TcO_4^-. This or other custom-designed materials with similar properties may be used to separate and/or sequester technetium to reduce its concentration in waste streams.

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[4] Materials containing sulfur, selenium, and tellurium, usually as sulfides, selenides, and tellurides.

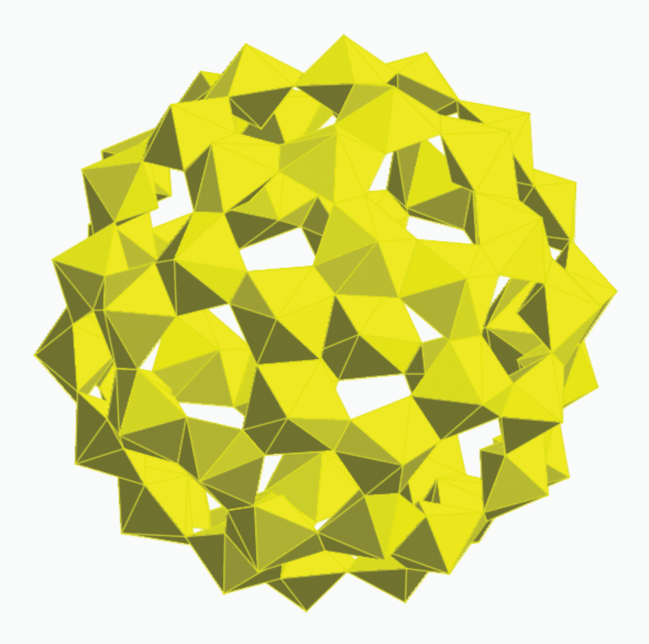

FIGURE 9.5 A cluster consisting of 60 uranium polyhedra (yellow) joined across shared edges of the polyhedra. This U_{60} cluster has the same topology as a C_{60} cluster, known as a "buckey ball."
SOURCE: Courtesy of Peter Burns, University of Notre Dame.

9.1.8 Multi-Scale Computational Simulation of the Properties of Materials

One of the most rapidly developing research areas in materials science is the use of computational simulation to determine fundamental physical and chemical properties of materials. In the 1980s, the use of pseudopotentials to capture the behavior of chemically active electrons combined with density functional theory[5] allowed the study of systems consisting of hundreds to thousands of atoms. At the same time, the rapid development of computer technology (faster processors and more efficient algorithms) led to the development of new tools for modeling the structure and properties of materials—and indeed, the new field of computational chemistry (Cygan, 2001).

There are now a wide variety of standard computational packages that are routinely used in studies of solid-state materials, including studies of

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[5] This theory is used in chemistry and physics to investigate the electronic structures of materials.

nuclear materials (Stan, 2009; Stan et al., 2007) and even potential waste form materials (Ferriss et al., 2010) at a number of scales (Figure 9.6). These techniques are particularly useful for the study of highly radioactive materials for which actual experiments are time consuming and expensive. Computational simulations can be used to investigate a wide range of compositions or structure types and to focus experimental efforts on the most critical, bench-marking data requirements. Computational simulations can be extended to study surface reactions and corrosion mechanisms (Rosso, 2001) and radiation effects in materials (Ewing and Weber, 2010).

9.1.9 Design of Materials for Specific Performance Requirements

With the dramatic advances being made in computational chemistry it is now becoming feasible to use computational techniques for materials discovery and design (NRC, 2009; see Figure 9.7). This innovation has

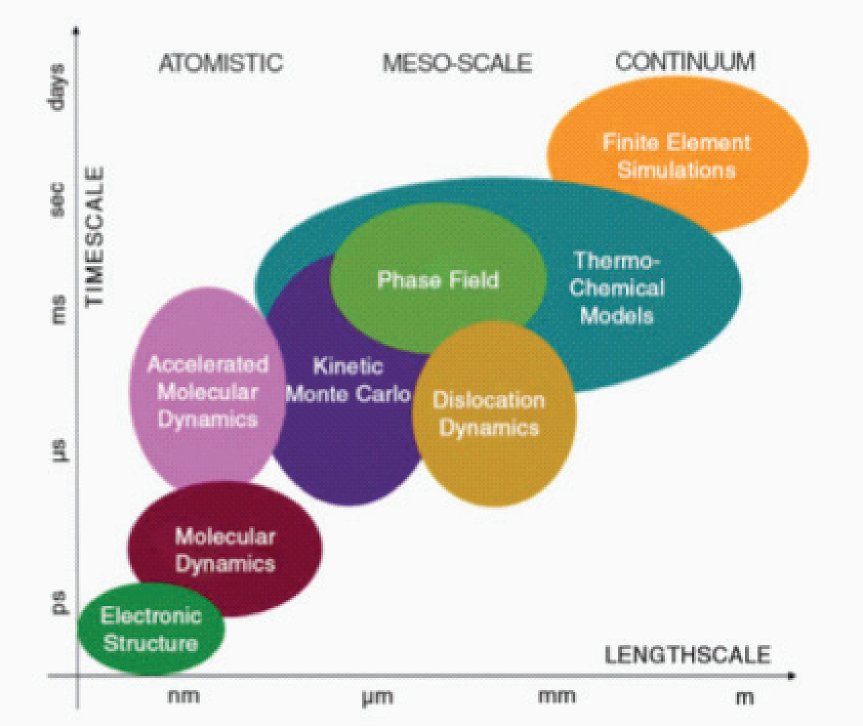

FIGURE 9.6 Multi-scale theoretical and computational methods used for materials model development and computer simulations.
SOURCE: Stan (2009).

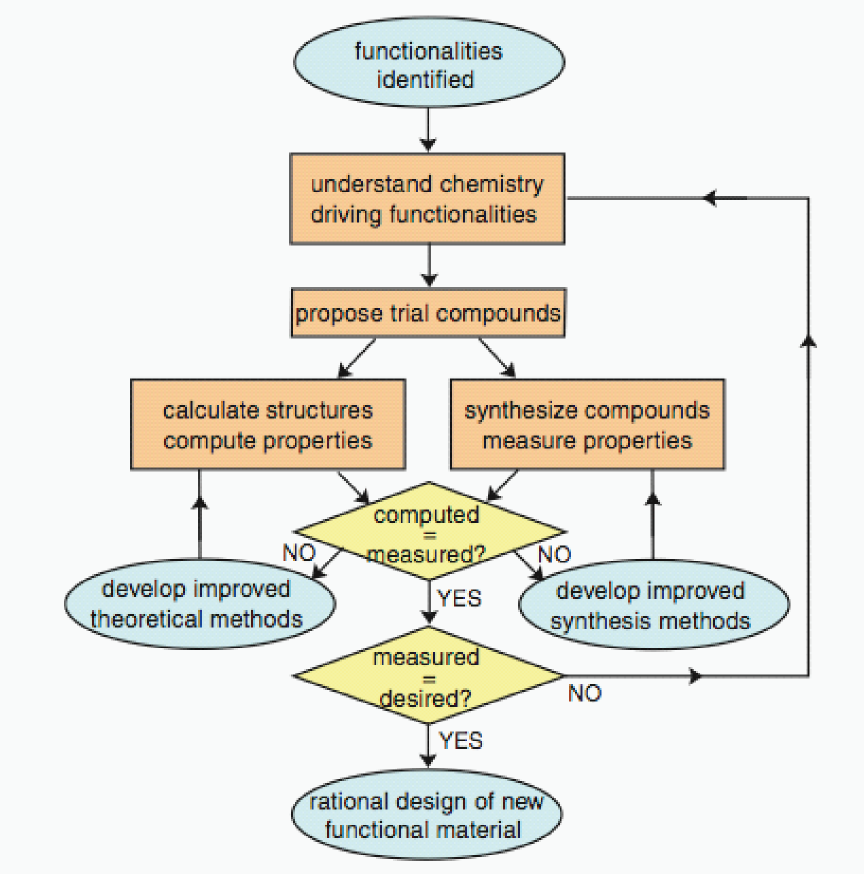

FIGURE 9.7 Schematic illustration of a methodology for the discovery and design of new materials.
SOURCE: NRC (2009).

potentially important applications to radioactive waste form development: Once a waste form's performance requirements are established for a particular disposal environment, one can design materials to meet those requirements. As examples, glass waste form compositions might be changed to enhance chemical durability or crystalline waste form composition might be adjusted to enhance thermal annealing of radiation damage (as discussed in Section 9.1.2). Such applications are, in fact, in their infancy, but their potential is great.

Computational simulations can also be combined with experimental techniques now in routine use in chemistry and pharmacology. For example, combinatorial chemistry methods reduce the time required to invent new catalysts and drugs. Xiang et al. (1995) has applied combinatorial chemistry techniques to the discovery of new superconducting materials. These techniques can be used in nuclear waste processing to invent new waste form formulations, increase theoretical understanding of material properties, evaluate the waste form performance, and shorten the time it takes to develop new waste processing technologies. Undoubtedly, adapting these techniques to waste form development will require additional development work.

9.2 NEW DEVELOPMENTS IN WASTE FORM PROCESSING TECHNOLOGIES

New waste form materials will be of use in the DOE-EM cleanup program only if they can be synthesized and produced at industrial scales. Fortunately, there have been many incremental improvements as well as important innovations in processing technologies that are potentially applicable to production of waste forms. Some examples are described in this section.

9.2.1 Computational Simulation of Material Processing

Recent advances in chemical engineering, materials science, and metallurgy provide the basis for development of new technologies for nuclear waste processing. Advances in computational science and recently emerging tools in Computational Fluid Dynamics (CFD) (e.g., the Ansys® suite of tools, MFIX by National Energy Technology Laboratory, and Barracuda® by CPFD Software) have led to significant incremental improvements in processing equipment and enhanced processing capabilities.

For example, such tools are currently in use to study flow patterns in Joule-heated melters equipped with gas bubblers (Matlack et al., 2008) and also for hot gas filter cleanup design (VanOsdol et al., 1996). Barracuda® and MFIX are being used to model hydrodynamic phenomena and chemical reactions in fluidized beds. This software enables engineers to develop trouble-free efficient process designs from the start; reduce the risk of scale-up from pilot to commercial plants; and avoid operational problems and downtime. These simulation tools are being used to scale-up fluidized bed gasifiers, polymerization reactors, and combustors.

These state-of-the-art computational capabilities can pave the way for the development of novel waste form processing techniques. For example, fluidized bed steam reforming is being developed for the processing of sodium-bearing waste at the Idaho National Laboratory (see Chapter 4). The operational challenges for this technology include generation of fines, product agglomeration, and particle size control. CFD simulation tools can help to address such operational challenges, specifically to:

- Reduce attrition of bed material through the proper design and placement of internal components (e.g., reduce jets by the proper design of grids; design the internal cyclones and diplegs) and minimize carry-over.
- Optimize operating conditions through the proper choice of the bed support, which enables smoother fluidization.
- Reduce scale-up risks through the appropriate inclusion of the kinetics of particle growth combined with the bed hydrodynamics.

Once a simulation tool is built for these purposes it can also be used for troubleshooting during actual operations.

In recent years there have also been developments in tools to simulate the steady state and dynamic behavior of chemical processes. For example, the Aspen® suite of products (which were developed by Aspentech) is used widely in the chemical industry for such purposes. CFD models, when combined with such simulation software, can be a powerful way to monitor and control waste processing equipment such as fluidized beds and melters together with the entire plant associated with these processes.

9.2.2 Innovative Uses of Existing Technologies

Some existing processing technologies in use in other industries are also finding new applications for waste form production. These technologies are described in Chapter 4 and in the committee's interim report (Appendix C). Fluidization technology, namely steam reforming, is being considered as a potential technology for the immobilization of a wide variety of high-sodium, low-activity wastes such as those existing at the Hanford Site, Idaho National Laboratory, and Savannah River Site. Cold crucible induction melting (CCIM), which is a well-established process in other industries, is being considered for immobilization of HLW and possible low activity waste in glass. As noted in Chapter 4, this technology can be used to immobilize waste streams containing chromium, aluminum, zirconium, sulfate, or phosphate, which can cause problems in Joule-heated melters. CCIM is also being integrated with an oxygen plasma to destroy organics and reduce post gas processing loads. Hot isostatic pressing (HIP), another well-established technology in other industries, is currently being considered for the production of waste forms containing calcine HLW at the Idaho National Laboratory.

9.3 NEW DEVELOPMENTS IN MODELING WASTE FORM–NEAR-FIELD INTERACTIONS

The ultimate objective of the DOE-EM cleanup program is the safe disposal of legacy waste. The evaluation of safety requires the ability to computationally simulate the behavior of radionuclides in the waste form and other engineered and geologic barriers in the near-field environment of a disposal facility. Recent advances in computational capacity and new conceptual approaches to reactive transport modeling (Steefel et al., 2005) offer new opportunities for understanding and simulating the release and mobility of radionuclides in disposal environments.

As discussed in some detail in Chapter 7, the development of high-fidelity models (Steefel et al., 2005) that realistically simulate radionuclide transport both at local and repository scales represents a conceptual advancement in simulation capabilities. Such models can be used to evaluate performance of a disposal facility not only with respect to radiological risk, but also for other performance metrics such as repository size.

9.4 DISCUSSION

As was noted in Chapter 2, the DOE-EM cleanup program is not expected to be completed for at least another four decades. Consequently, DOE-EM will have ample opportunities in the coming decades to incorporate advances in science and technology on waste forms, waste form processing technologies, and waste form–near-field modeling into its baseline approaches to increase program efficiencies, reduce lifecycle costs and risks, and advance scientific understanding and stakeholder confidence. The past 30 years have seen a steady increase in scientific and technological advances, perhaps best exemplified by the successful application of vitrification technologies to immobilize HLW. Still, these past successes do not preclude the exciting possibilities of new and innovative strategies for improving waste management systems.

The committee realizes that DOE-EM is already successfully immobilizing radioactive waste and making huge financial investments in the construction of facilities, such as the Waste Treatment Plant at the Hanford Site, which will be used to vitrify HLW. However, not every waste stream is a good match for vitrification, nor can all waste streams be accommodated in presently planned facilities. Consequently, prudence dictates that some fraction of the DOE-EM program should be devoted to capturing and using innovative science and technology. In fact, the "strategic initiatives" of the EM Engineering & Technology Roadmap (DOE, 2008) are entirely consistent with the development and use of new waste form materials, new processing technologies, and improved modeling and computational capabilities.

- Advances in the science of materials design provide new methods for efficiently exploring innovative waste form materials. Computational simulation may provide an efficient and rapid means of surveying the properties of materials for immobilizing highly radioactive wastes without having to complete the full range of costly and time-consuming experiments. Once these computational surveys are completed, key experiments can be performed to confirm (or not) the results.
- Advances in materials processing can lead to improvements in waste form production rates and product quality at reduced production costs.
- Advances in computational capabilities, combined with new conceptual models for materials performance in disposal environments, can provide new insights into long-term materials performance in specific disposal environments.

In the development of new materials, technologies, and computational capabilities, the next 50 years is an eternity, and the prospects for innovative improvements are huge. The incorporation of new science and technology into the DOE-EM cleanup program need not interrupt the significant progress that is being made at present but can, if done well, enhance its prospects for future successes.

It can take decades to develop and introduce new technologies for processing radioactive waste. For example, it took about two decades from the decision to use borosilicate glass for HLW immobilization at Savannah River to the first "hot" (radioactive) operations at the Defense Waste Processing Facility. Some waste forms materials (e.g., ceramics) have been studied for almost 30 years but have not yet found widespread implementation for radioactive waste immobilization. It is imperative for DOE-EM to get this development of new processing technologies started in earnest to reap its benefits for the cleanup program in a timely fashion.

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Appendixes

Appendix A

Biographical Sketches of Committee Members

Levenson, Milton (Chair)

Milton Levenson is an independent consultant. He is a chemical engineer with more than 60 years of experience in nuclear energy and related fields. His technical experience includes work related to nuclear safety, fuel cycle, water reactors, advanced reactors, and remote control technologies. His professional experience includes research and operations positions at the Oak Ridge National Laboratory, the Argonne National Laboratory, the Electric Power Research Institute, and Bechtel. He was elected to National Academy of Engineering in 1976. Mr. Levenson is a fellow and past president of the American Nuclear Society, a fellow of the American Institute of Chemical Engineers, and recipient of the American Institute of Chemical Engineers' Robert E. Wilson Award in Nuclear Chemical Engineering. He is the author of more than 150 publications and presentations and holds three U.S. patents. Mr. Levenson has served as chairman or committee member for several National Academies studies. He received his B.Ch.E degree from the University of Minnesota.

Ewing, Rodney C. (Vice-Chair)

Rodney C. Ewing is the Edward H. Kraus Distinguished University Professor in Geological Sciences with joint appointments in the Departments of Nuclear Engineering and Radiological Sciences and Materials Science and Engineering at the University of Michigan. Prior to arriving at Michigan, he was Regents' Professor in the Department of Earth and Planetary Sciences at the University of New Mexico. During 2010-2011 he was a Visiting Professor at the Center for International Security and Cooperation at Stanford University. His professional interests are in mineralogy and materials science, and his research has focused on radiation effects in complex ceramic materials and the long-term durability of radioactive waste forms. He is a fellow of the American Association for the Advancement of Science, the Geological Society of America, and the Mineralogical Society of America, and a member of Sigma Xi. He is a past president of the International Union of Materials Research Societies and the Mineralogical Society of America. Dr. Ewing is currently a Fellow of the American Geophysical Union, the Materials Research Society, the American Ceramic Society, and the Geochemical Society. In 2006, he was awarded the Lomonosov Great Gold Medal of the Russian Academy of Sciences, and in 2007, he was awarded an Honorary Doctor of Université Pierre et Marie Curie. He received M.S. and Ph.D. degrees in geology from Stanford University.

Members

Ahn, Joonhong

Dr. Joonhong Ahn is a professor of radioactive waste management and nuclear fuel cycle at the University of California, Berkeley. His research interests include the performance assessment of deep geological disposal systems for high-level radioactive wastes (HLW), especially analyses of mass transport through engineered barriers and the natural geological barrier. He is also interested in the future of nuclear energy in the Asia/Pacific region. He has published papers on (1) the transport of radionuclides through a fractured geological medium; (2) the mass transport of radionuclides in a shallow-land repository for low-level wastes; (3) the sensitivity analysis of radionuclide transport through a fractured medium; (4) radionuclide diffusion in a fracture network by applying percolation theory and fractal geometry; (5) the mass transfer and transport analyses for engineered barriers; (6) bentonite expansion into fractures in a host rock surrounding the engineered barriers and mass transport in the same region; (7) analysis of the autocatalytic criticality of buried fissile materials; (8) mass-flow analysis for the nuclear fuel cycle; and (9) waste-form modeling by applying linear-programming approach. Professor Ahn currently serves as a member of the Nuclear and Radiation Studies Board of the National Academies, and the chair of the Book-Publishing Committee of the American Nuclear Society. In the past he has served as a member of the planning committee for the Atomic Energy Society of Japan (1992-1995). He was at the review committee (1992) for the first official report to the Atomic Energy Commission on Nuclear Fuel Development Corporation of Japan. He served as the editor for Radioactive Waste Research (1994-1996), a journal of the Division of Radioactive Waste Management, Atomic Energy Society of Japan. He received his Ph.D. degree in nuclear engineering from the University of California, Berkeley, and Doctor of Engineering degree from the University of Tokyo.

Apted, Michael J.

Dr. Michael J. Apted is a scientific consultant, currently associated with Monitor Scientific, LLC, with more than 25 years of experience in nuclear-waste disposal research and development, primarily in the design and testing of engineered barrier systems (EBS), hydrogeochemical modeling, and safety assessment. For the Electric Power Research Institute, he is the research and development manager for post-closure risk assessment studies regarding disposal of spent nuclear fuel and high-level waste at the Yucca Mountain Site in Nevada. He is a member of the International Technical Advisory Committee (ITAC) to the Nuclear Waste Management Organization of Japan (NUMO) and serves as a coordinator for NUMO's International Tectonics Committee. Dr. Apted is Chairman of the EBS and Technology Support Group for STUK, the safety authority in Finland. He also has consulted for nuclear waste repository implementation and regulatory agencies in Sweden, Switzerland, South Africa, Canada, Taiwan, and South Korea. Dr. Apted is a past chairman for the Materials Research Society's Symposium on the Scientific Basis for Nuclear Waste Management. He has organized, conducted, and authored reports for the International Atomic Energy Agency (IAEA) and the Nuclear Energy Agency (NEA). He has served on various National Academies committees related to nuclear waste disposal. Dr. Apted has presented and/or published over 150 papers in the above technical subjects. He has a B.S. degree in chemistry from the Massachusetts Institute of Technology and a Ph.D. degree in geochemistry from the University of California, at Los Angeles.

Burns, Peter C.

Dr. Peter C. Burns is The Henry Massman Professor of Civil Engineering, Director of the Energy Frontier Research Center, concurrent Professor of Chemistry and Biochemistry, and chair of the Department of Civil Engineering and Geological Sciences at the University of Notre Dame. His research focuses on the solid state and environmental chemistry of heavy metals, especially actinides including uranium, neptunium, and plutonium. Current emphasis includes studies of the structures and stabilities of uranium, thorium, and plutonium clusters containing as many as 60 metal atoms.

Much of this research is applied to nuclear waste disposal and understanding the mobility of actinides and heavy metals in the environment. In 2001, Burns was awarded the Mineralogical Society of America Award and became a life fellow. He was awarded the Donath Medal of the Geological Society of America in 1999, as well as several other society awards. He has published more than 200 archival journal papers dealing with various aspects of actinides. He is currently the president of the Mineralogical Association of Canada and a member of the council of the Mineralogical Society of America. He received his Ph.D. degree in geology from the University of Manitoba.

Colakyan, Manuk

Dr. Manuk Colakyan is currently a senior technical leader at the Dow Chemical Company. Dr. Colakyan received a bachelor's degree in chemical engineering from Istanbul Technical University. After completing his doctorate at Oregon State University, he joined Union Carbide Corporation (UCC) where he has held positions both in R&D and Engineering Departments and then the Dow Chemical Company when Dow acquired UCC in 2001. He has led the Solids Processing and Reaction Engineering Groups and worked with many of Union Carbide's and Dow's processes. He is an expert in fluidization technology and continues to apply his technical knowledge to improve production and safety of commercial processes. His work includes measurement and modeling of reaction kinetics for heterogeneously and homogeneously catalyzed reactions; identification and evaluation of catalysts for gas-liquid-solid, gas-solid reactions; commercial scale implementation of catalyst/reactors; and solids processing and handling. Dr. Colakyan is active in the American Institute of Chemical Engineers, having served as a group chair and, programming chair for the Particle Technology Forum.

Fabryka-Martin, June

Dr. June Fabryka-Martin is a staff scientist in the Environmental and Earth Sciences Division at Los Alamos National Laboratory (LANL) in Los Alamos, NM. Dr. Fabryka-Martin's work experiences span a broad range of topics related to radiological issues and disposal of wastes in the deep subsurface. Her work in these areas has addressed such topics as modeling radiation fluxes and nuclear reaction rates in geologic media for studies pertaining to the geochemistry of fission products and plutonium, interpreting geochemical and isotopic compositions as indicators of water-rock reactions and groundwater flow paths, characterizing legacy transuranic waste streams produced by past Los Alamos National Laboratory activities, and evaluating the sustainability of deep subsurface injection of brine concentrates from desalinization facilities. Her studies of spatial distributions of chloride and chlorine-36 in the subsurface at Yucca Mountain played significant roles in the development and testing of hydrologic process models for assessing the viability of this site as a geologic repository for radioactive waste, in particular by highlighting the potential role of fast transport paths in this geologic setting. Dr. Fabryka-Martin has served as a member of the U.S. Environmental Protection Agency's Science Advisory Board's (SAB) Radiation Advisory Committee and has contributed to over 10 SAB reports and advisories over the past decade. She holds Ph.D. and M.S. degrees in hydrology and water resources from the University of Arizona.

Jantzen, Carol M.

Dr. Carol M. Jantzen is a senior advisory scientist with the Savannah River National Laboratory. For the past 33 years she has performed research and development in glass, ceramic, cement, geopolymer, and mineral waste forms. She has worked on waste form interactions with various geologic media related to problems of nuclear and hazardous waste management and waste disposal. She has developed waste form durability tests and standards for the stabilization of high level, hazardous, and mixed (radioactive and hazardous) wastes. Her research spans vitreous, crystalline ceramic, mineral, and cementitious waste form development, processing, and characterization in both the U.S. and Europe. She helped develop techniques for stabilizing nuclear and hazardous wastes, including mining wastes. In 2008 she won the Wendell Weart Lifetime Achievement Award in nuclear waste management for more than three decades of outstanding contributions to nuclear waste management. She is a fellow, past president, and distinguished life member of the American Ceramic Society. Dr. Jantzen was also a member of the National Research Council's Commission on Physical Sciences, Mathematics, and Astronomy from 1997 to 2000. Jantzen received a Ph.D. degree in materials science and engineering from the State University of New York at Stony Brook with a specialization in glass chemistry, glass decomposition mechanisms, and glass durability. Her postdoctoral research was in cement stabilization of U.S. and U.K. wastes in the Department of Inorganic Chemistry at the University of Aberdeen in Scotland.

Johnson, David W.

Dr. David W. Johnson is the retired director of metallurgy and ceramics research at Bell Laboratories, Lucent Technologies, and adjunct professor of materials science at Stevens Institute of Technology. His research activities included fabrication and processing of glass and ceramics with emphasis on materials for electronic and photonic applications. He is a Fellow, Distinguished Life Member, and Past President of the American Ceramic Society (ACerS), and is a member of several other professional societies. Dr. Johnson won the Taylor Lecture Award and the Distinguished Alumni Award from Pennsylvania State University; the Ross Coffin Purdy Award for the best paper in ceramic literature, the Fulrath Award, the John Jeppson Award, and the Orton Lecture Award from the American Ceramic Society; and received the Industrial Ceramics 2000 prize from the Academy of Ceramics. He was elected to the National Academy of Engineering in 1993 for his discovery of new compositions and processing techniques and their transfer to manufacturing and he is a member of the Academy of Ceramics. He holds 46 U.S. patents and has published numerous papers on materials sciences. He graduated from Pennsylvania State University, earning a B.S. degree in ceramic technology in 1964 and a Ph.D. degree in ceramic science in 1968.

Nash, Kenneth L.

Dr. Kenneth L. Nash has been a professor of chemistry at Washington State University for the past 6 years. During the past 30+ years, his research has focused principally on chemical separations science, environmental chemistry and the basic coordination chemistry of actinides and important fission products (mainly lanthanides). He has published extensively on the fundamental solution chemistry of actinides, solvent extraction and ion exchange, environmental chemistry/radioactive waste management, and applications of basic science to solving real-world problems associated with the use of radioactive materials. Previous to his current position, Dr. Nash conducted and directed basic and applied research on actinide and fission product chemistry and chemical separations at Argonne National Laboratory for 20 years and in environmental science at the U.S. Geological Survey for 5 years. He is active in the Nuclear Chemistry and Technology Division and in the Industrial and Engineering Chemistry Division of the American Chemical Society. He is also co-editor in chief of the journal Solvent Extraction and Ion Exchange, associate editor of the journal Radiochimica Acta, on the editorial board of the journal Separation Science and Technology, and co-editor of three symposium series books. Dr. Nash was a visiting scholar at the Japan Atomic Energy Research Institute at Tokai-mura in 2000, and is the 2003 recipient of the Glenn T. Seaborg Award for Actinide Separations. He completed his Ph.D. degree in inorganic chemistry at Florida State University in 1978.

Nenoff, Tina

Dr. Tina Nenoff is currently a Distinguished Member of the Technical Staff at Sandia National Laboratories, in the Surface and Interface Sciences Organization. She has been on the technical staff at Sandia for over 15 years. Her research interests include how the nanoscale properties of materials can be tuned to affect bulk scale properties. Her current research is directed toward the synthesis and then application of novel zeolitic and molecular sieve phases for catalysis and separations. Areas of focus include (1) the synthesis and characterization of novel inorganic molecular sieve materials and waste forms for the selection and storage of radiological isotopes; (2) the predictive modeling and synthesis of inorganic aluminosilicate and nonaluminosilicate crystalline zeolitic bulk phases and membranes for Separations and Catalysis of light gases or organic molecules; and (3) energy and cost efficient catalytic reactive separations of industrial feedstock chemicals. Her programs span from basic to applied research of novel inorganic materials for separations and waste forms, catalysis and membrane applications. She has over 125 peer reviewed publications, 4 book chapters, and 7 U.S. Patents. Dr. Nenoff is a member of both the American Chemical Society and the Materials Research Society and is a reviewer for a number of journals. She received her Ph.D. degree in inorganic/solid state chemistry from the University of California, Santa Barbara.

Appendix B

Workshop on Waste Form Technology and Performance

The Lecture Room

The National Academy of Sciences (NAS) Building
2101 Constitution Avenue, NW, Washington, DC 20418

Wednesday, November 4, 2009

8:15-8:30 am	**Welcome and Introduction** Milt Levenson and Rod Ewing
Session I:	*International Perspectives*
8:30-9:00 am	**Glass and spent fuel corrosion, coupling of waste forms to the near field, and long-term models of performance** Berndt Grambow, Laboratoire de Physique Subatomique et des Technologies Associees (SUBATECH), France
9:00–9:30 am	**Cementatious waste forms and barriers** Fred Glasser, University of Aberdeen, U.K.
9:30-10:00 am	**Combined inert matrix fuels and related waste forms** Claude Degueldre, Paul Sheerer Institute, Switzerland

10:00-10:30 am	**Break**
10:30-11:00 am	**Ceramic and phosphate glass waste forms and cold crucible technology** Sergey Stefanovsky, SIA Radon, Russia
11:00-11:30 am	**Overview of CEA's and French initiatives related to waste forms** Etienne Vernaz, Commissariat à l'Énergie Atomique, France
11:30 am-12:00 pm	**Overview of Australia/ANSTO initiatives related to waste forms** Kath Smith and Bruce Begg, Australian Nuclear Science and Technology Organisation (ANSTO), Australia
12:00-1:00 pm	**Lunch**
Session II:	*Select Domestic Issues*
1:00-1:30 pm	**Computational methods applied to the design and evaluation of waste forms** Bill Weber, Pacific Northwest National Laboratory
1:30-2:00 pm	**Overview of waste forms and near-field interactions in a performance assessment perspective** Carl Steefel, Lawrence Berkeley National Laboratory
2:00-2:30 pm	**Matching waste forms to waste processing strategies** Mark Peters, Argonne National Laboratory
2:30-3:00 pm	**Impact of waste forms on overall repository performance assessment** Peter Swift, Sandia National Laboratories
3:00-3:15 pm	**Break**
3:15-3:45 pm	**Overview of the Vitreous State Laboratory and geopolymer development** Ian Pegg and Werner Lutze, Catholic University of America

3:45-4:15 pm	**Cementitious Barriers Partnership** David Kosson, Vanderbilt University
4:15-4:45 pm	**Industry perspectives on potential waste forms from recycling** Rod McCullum, Nuclear Energy Institute
4:45-5:15 pm	**Panel discussion** All participants
5:15 pm	**Adjourn**

Appendix C

Interim Report

Waste Forms Technology and Performance

INTERIM REPORT

Committee on Waste Forms Technology and Performance

Nuclear and Radiation Studies Board
Division on Earth and Life Studies

NATIONAL RESEARCH COUNCIL
OF THE NATIONAL ACADEMIES

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NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

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June 15, 2010

Yvette Collazo
Deputy Assistant Secretary for Technology
Innovation and Development
Office of Environmental Management
U.S. Department of Energy
Washington, DC 20585

Subject: Interim Report on Waste Form Technology and Performance

Dear Ms. Collazo:

The Committee on Waste Forms Technology and Performance (Attachment B) was appointed by the National Research Council in May 2009 to examine requirements for waste form (Box 1) technology and performance in the context of the disposal system in which the waste will be emplaced. The complete statement of task for this study is given in Box 2.

The Department of Energy, Office of Environmental Management (DOE-EM) requested this interim report to provide timely information for fiscal year 2011 technology development planning. **The committee has focused this interim report on opportunities associated with selected aspects of the last three bullets of its statement of task (Box 2).** These tasks are:

- The state-of-the-art tests and models of waste forms used to predict their performance for time periods appropriate to their disposal system.[1]
- Potential modifications of waste form production methods that may lead to more efficient production of waste forms that meet their performance requirements.
- Potential new waste forms that may offer enhanced performance or lead to more efficient production.

The committee judges that the opportunities identified in this report are sufficiently mature to justify consideration by DOE-EM as it plans its fiscal year 2011 technology development program.

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[1] The focus of this interim report is primarily on tests and models for assessing waste form durability (see Footnote 6). The final report will provide a more detailed discussion of waste form performance over time periods of concern for disposal.

Box 1: Waste Forms

The International Atomic Energy Agency defines waste immobilization as the conversion of a waste into a waste form by solidification, embedding, or encapsulation. The waste form can be produced by chemical incorporation of the waste species into the structure of a suitable matrix (typically a glass or ceramic) so that the radioactive species are atomistically bound in the structure. Chemical incorporation is typical for high-level radioactive waste. Encapsulation of waste, on the other hand, is achieved by physically surrounding it in materials (typically bitumen, grout, or cement) so it is isolated and radionuclides are retained. Encapsulation is typically used for low-level or intermediate-level waste and may include some chemical incorporation.

The primary role of a waste form is to immobilize radioactive and/or hazardous constituents in a stable, solid matrix for storage and eventual disposal. In a well-designed disposal system, the waste forms and disposal facility into which they are emplaced work together to sequester radioactive and hazardous constituents. The near-field environment of the disposal site and other engineered barriers, if present, establish the physical and chemical bounds within which the waste form performs its sequestering function. This promotes the maintenance of waste form integrity over extended periods, which helps to slow the release of radioactive and other hazardous constituents from the waste form and the transport of these constituents out of the disposal facility.

In addressing these charges, the committee has focused primarily, but not exclusively, on high-level radioactive waste (HLW) cleanup, which is the longest schedule, highest cost, highest risk, and arguably DOE-EM's most difficult technical cleanup challenge (see, for example, DOE, 1998, 2010a; NRC, 2001, 2006). At present, tank waste retrieval and closure are limited by schedules for treating and immobilizing HLW in the Defense Waste Processing Facility, which is currently operating at the Savannah River Site; the Waste Treatment Plant, which is under construction at the Hanford Site; and a facility to be designed and constructed at the Idaho Site. Accelerating schedules for treating and immobilizing HLW by introducing new and/or improved waste forms and processing technologies could also accelerate tank waste retrieval and closure schedules.

The committee used its expert judgment to identify the opportunities described in this report. This judgment was informed through a series of briefings, site visits, and a scientific workshop. The committee received briefings on DOE's current programs and future plans for waste processing, storage, and disposal from DOE-EM, national laboratory, and contractor staff, including information on comparable international programs. The committee visited the Hanford Site (Washington), Idaho Site, Savannah River Site (South Carolina), and their associated national laboratories (Pacific Northwest National Laboratory, Idaho National Laboratory, and Savannah River National Laboratory, respectively) to observe DOE's waste processing and waste form production programs and to hold technical discussions with site and laboratory staff. The committee also organized a workshop to discuss scientific advances in waste form development and processing. This workshop, which was held in Washington, D.C., on November 4, 2009, featured presentations from researchers in the United States, Russia, Europe, and Australia. The workshop agenda is provided in Attachment C.

Box 2: Statement of Task

The National Academies will examine the requirements for waste form technology and performance in the context of the disposal system in which the waste form will be emplaced. Findings and recommendations will be developed to assist DOE in making decisions for improving current methods for processing radioactive wastes and for selecting and fabricating waste forms for disposal. The study will identify and describe:

- Essential characteristics of waste forms that will govern their performance within relevant disposal systems. This study will focus on disposal systems associated with high-cost waste streams such as high-level tank waste and calcine but include some consideration of low-level and transuranic waste disposal.

- Scientific, technical, regulatory, and legal factors that underpin requirements for waste form performance.

- The state-of-the-art tests and models of waste forms used to predict their performance for time periods appropriate to their disposal system.

- Potential modifications of waste form production methods that may lead to more efficient production of waste forms that meet their performance requirements.

- Potential new waste forms that may offer enhanced performance or lead to more efficient production.

The committee will not make recommendations on applications of particular production methods or waste forms to specific EM waste streams.

A major focus of the DOE-EM cleanup program is on retrieving legacy wastes resulting from nuclear weapons production and testing and processing them into waste forms suitable for disposal in onsite or offsite facilities. Some waste requires minimal processing to make it suitable for disposal; for example, lightly contaminated solid waste generated during facility decommissioning may be suitable for disposal in near-surface engineered facilities with little or no processing. Other waste will require more extensive processing to make it suitable for disposal; for example, HLW, liquid wastes from facility decontamination, contaminated resins from groundwater cleanup, and radioactive sources and other nuclear materials used in civilian and defense applications may require processing to destroy organic components; to remove components that are incompatible with the processing method or final waste form or that are not acceptable for disposal; and to immobilize radioactive and other hazardous components. DOE-EM is using a variety of waste forms to immobilize these components.

The committee observes that the DOE-EM cleanup program is successfully processing waste and producing waste forms at several sites. For example, DOE has completed HLW vitrification at the West Valley, New York, site. DOE is also retrieving HLW from tanks at the Savannah River Site, separating it into high-activity and low-activity waste streams, and processing these waste streams into high-activity waste glass for disposal in a future geologic repository and low-activity waste saltstone for near-surface onsite disposal. However, DOE-EM's cleanup program is not expected to be completed for at least another four decades. Consequently, as this program continues, DOE-EM will have opportunities to incorporate emerging developments in science and technology on waste forms and waste form production technologies into its baseline approaches to increase program efficiencies, reduce lifecycle costs and risks, and advance scientific understanding of and stakeholder confidence in waste form behavior in different disposal environments. In short, scientific advances, both now and in the future, will offer the potential for better solutions to DOE-EM's waste management challenges. It may be important for DOE-EM to maintain sufficient flexibility in its cleanup program to take advantage of these advances.

Based on an analysis of the information it has gathered, the committee observes that waste form science and technology have advanced significantly over the past three decades. The committee judges that there are opportunities to apply these advances in the DOE-EM cleanup program, both now and in the future, to reduce schedules, costs, and risks. The committee offers several observations about potential opportunities in this interim report. Detailed findings and recommendations will be provided in the committee's final report.

Waste form-relevant science and technology are advancing rapidly along several fronts—for example, chemical and materials processing in industry, waste management in advanced nuclear fuel cycle programs, and management of special nuclear materials in national security applications. There have been numerous recent reports on the development of waste forms and processing technologies for advanced nuclear fuel cycles; some examples are given in Attachment D. Examples of these technologies include:

- Waste form materials designed for significantly higher waste loadings or for improved performance in specific disposal environments.
- Waste processing technologies that can handle large volumes of highly radioactive wastes or that produce highly uniform waste form products.
- Advanced analytical and computational techniques that can be used to understand and quantitatively model interactions between waste forms and near-field[2] environments of disposal facilities.

Many of these technologies are potentially applicable to DOE-EM waste streams. However, not all are ready for full-scale implementation.

This interim report and the committee's final report provide only snapshots of these advances. **To take full advantage of future scientific and technological**

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[2] The *near-field environment* is generally taken to include the engineered barriers in a disposal system (e.g., waste canisters) as well as the host geologic media in contact with or near these barriers whose properties have been affected by the presence of the repository. The *far-field environment* is generally taken to include areas beyond the near field, including the biosphere (e.g., OECD-NEA, 2003).

advances, DOE-EM will need to identify, develop where needed, and incorporate where appropriate state-of-the-art science and technology on waste forms and waste form production processes, especially for high-cost, high-risk, and/or orphan[3] waste streams. DOE-EM can become cognizant of scientific and technological advances by collaborating with appropriate governmental, scientific, and technical organizations to identify waste forms and waste form production technologies that are potentially applicable to DOE-EM waste streams. For example, collaborations can be established with other DOE offices,[4] especially the Office of Science and Office of Nuclear Energy; other government agencies (e.g., Department of Defense); scientific, academic, and industrial organizations; and especially other nations' radioactive waste management programs.

DOE-EM is operating its cleanup program under various regulatory requirements and legal agreements with states and the U.S. Environmental Protection Agency. Modifications of existing requirements or agreements might be necessary before DOE-EM could implement the technologies identified in this report. However, it is outside of the committee's scope to consider how the use of the technologies identified in this report might impact those requirements and agreements.

WASTE FORM AND PROCESSING OPPORTUNITIES

The committee has identified four opportunities consistent with its statement of task (Box 2):

- Production of crystalline ceramic[5] waste forms using fluidized bed steam reforming
- Production of glass, glass composite, and crystalline ceramic waste forms using cold crucible induction melters
- Production of glass, glass composite, and crystalline ceramic waste forms using hot isostatic pressing
- Evaluation of the long-term durability of new waste form materials using experimental studies, laboratory tests, and model development

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[3] A waste stream is referred to as *orphan* when it has no clear-cut disposition pathway. The DOE-EM cleanup program has identified several orphan waste streams including, for example, actinide targets, beryllium reflectors, certain radioactive wastes produced outside of the nuclear fuel cycle, and sealed radiation sources. Many of these orphan waste streams are volumetrically small compared to the inventories of high-level waste, transuranic waste, and low-level waste that exist at DOE sites.

[4] See, for example, the basic research needs reports that are listed in Attachment D.

[5] A crystalline material has a well-defined, periodic-ordering of its atomic structure. Crystalline ceramic materials can consist of one or more crystalline phases. In contrast, a glass is aperiodic and lacks long-range atomic-scale ordering. Glass composite materials consist of a mixture of both glass and crystalline phases.

The first three opportunities involve new applications of existing technologies to DOE-EM waste streams. These waste form production technologies are being used commercially and appear to be applicable for processing and immobilizing a range of DOE-EM waste streams, especially HLW streams. DOE-EM is already planning to apply these technologies to some of its waste streams, as discussed in the following sections. The committee concurs with DOE-EM about the applicability of these technologies and offers observations in this interim report on the wider application of these technologies in the cleanup program.

The fourth opportunity involves extending the application of experiments, tests, and model development for evaluating the durability[6] of new waste form materials over time periods for concern for disposal (typically 10^3-10^6 years). This would provide DOE-EM with future flexibility to use new waste forms in its cleanup program and enhance the long-term safety of disposal.

Fluidized Bed Steam Reforming Technology

Fluidized Bed Steam Reforming (FBSR; see Attachment E for a brief technology description) is a robust technology for processing wastes. Its primary advantages are high throughput and ability to accommodate a wide range of feeds and additives, including feeds containing anionic sulfur and nitrogen species, halides, and organics that are incompatible with some other types of waste forms and waste form production processes.

FBSR is based on fluidized bed technology, which was invented in the 19th century and found widespread use in the refining and chemical industries starting around World War II. Applications of fluidized bed technology in nuclear fuel production, fuel recovery, and waste processing date back to late 1950s and early 1960s. For example, fluidization was used for the reduction and hydrofluorination of uranium concentrates and calcination of high-level radioactive waste. Two calcination facilities were successfully operated at the Idaho National Engineering Laboratory (now Idaho National Laboratory) from 1963 to 1981 and from 1981 to 2000 to immobilize HLW.

The FBSR process is already being used commercially for processing nuclear waste. A commercial facility to continuously process organic radioactive wastes at moderate temperatures in a hydrothermal steam environment was built by Studsvik in Erwin, Tennessee, in 1999. The Erwin facility uses a steam reforming technology, referred to as THermal Organic Reduction (THOR®), to pyrolyze organic resins loaded with Cs-137 and Co-60 from commercial nuclear facilities. The Erwin facility has the current capability to process a wide variety of solid and liquid streams including ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions at radiation levels of up to 400R/hr (Mason et al., 1999).

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[6] Durability is a measure of the resistance of a waste form to physical and chemical alteration and the associated release of contained radioactive or hazardous constituents.

FBSR is not a combustion process and is Clean Air Act (CAA) compliant. It has also been shown to be Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) compliant for mercury, chlorine, carbon monoxide, total hydrocarbons, and heavy metals. A significant benefit of the FBSR process is that liquid secondary wastes are not produced (Mason et al., 1999). Many years of operating and design experience with fluidized beds in the chemical industry and the availability of computational fluid dynamics tools significantly reduce development and operating risks for potential EM applications.

Depending on the starting material feeds, FBSR produces a range of waste form compositions. If kaolinite is added to an alkali-rich waste (e.g., the low-activity waste fraction of neutralized HLW) during processing,[7] a crystalline ceramic waste form is produced that is composed of Na-Al-Si feldspathoid mineral analogs (e.g., sodalite) that serve as potential hosts for a number of radionuclides (Attachment E). Bench scale, pilot scale, and engineering-scale tests have all produced this mineral assemblage using a variety of DOE waste simulants as feed materials. Additionally, an illite-type clay additive has been tested at the bench scale and shown to form dehydroxylated mica, which is a good host for lanthanides, cesium, strontium, barium, rubidium, and thallium (Jantzen and Williams, 2008). It is reasonable to expect that these mineral assemblages would also serve as hosts for the radioactive forms of these elements that are present in DOE-EM waste streams.

DOE-EM plans to apply FBSR to some of its waste streams. An FBSR facility is being designed and constructed at the Idaho Site for treatment of decontamination solutions (referred to as *sodium-bearing waste*) for potential disposal in the Waste Isolation Pilot Plant (Marshall et al., 2003). Another facility is being designed for use at the Savannah River Site to process HLW in Tank 48, which contains nitrates, nitrites, and organic sodium tetraphenyl borate (NaTPB). This process will produce carbonate or silicate phases which can be fed to the Defense Waste Processing Facility for vitrification (Jantzen, 2004). DOE-EM has also carried out pilot-scale testing on a variety of simulated wastes to produce aluminosilicate ceramic waste forms.

The committee observes that there are at least two potential types of applications of FBSR in the DOE-EM cleanup program:

1. As a front-end process for conditioning waste feed streams:

    - For accelerating liquid evaporation at the front end of the HLW vitrification process, which could enable increased waste throughputs to the Joule-heated melters (see Attachment F) and increased production rates of high-activity and low-activity waste forms.

    - For processing waste streams, including resins, containing large quantities of organic materials and nitrates. The planned application of FBSR to process Savannah River tank waste containing high concentrations of NaTPB is an example of such an application. FBSR also has potential applications for processing waste streams containing

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[7] The addition of kaolinite in the FBSR process is somewhat analogous to the addition of glass-forming materials (i.e., glass frit) in the vitrification process.

organic solvents and radionuclide-loaded organic resins, for example, the technetium-99-loaded resins generated by groundwater cleanup efforts at the Hanford Site.

2. As a process for production of crystalline ceramic waste forms:

   - For processing alkaline HLW with bulk aluminosilicate additives (e.g., kaolinite), which could produce waste forms with good radionuclide retention properties and waste loadings comparable to or greater than borosilicate glass (Jantzen, 2006). This process could also reduce or eliminate the need for effluent recycling. This process is potentially applicable to both high-activity and low-activity waste streams and in fact has been demonstrated at the pilot scale on Hanford waste simulants (see www.thortt.com for technical papers).

   - For processing recycle liquids from HLW waste processing operations. This application has already been demonstrated at pilot scale for low-activity secondary waste simulants at Hanford.

FBSR is a mature technology. Its deployment in DOE-EM applications may require some up-front development work to tailor it to specific waste streams, but relatively little basic research is likely to be required. For example, development work might be required to better understand and ameliorate the attrition of granular bed material present in FBSR. Such attrition can be reduced through development work that is focused on the proper design of internal components, dust collection equipment, operating conditions, and selection of additive materials. All of these have well known solutions in the chemical or petroleum industry applications of fluidized beds.

Any waste forms produced using FBSR must, like all other waste forms, undergo characterization work to understand key structural characteristics, for example, how radionuclides are incorporated into atomic structures. See the section entitled “Waste Form Durability: Experiments, Tests, and Model Development” for additional discussion of this issue.

Cold Crucible Induction Melter Technology

The Cold Crucible Induction Melter (CCIM) is a promising technology for producing glass, glass composite, and crystalline ceramic waste forms. CCIMs are potential replacements for Joule-heated melters (JHMs; see Attachment F), which are part of the current DOE baseline for production of high-activity and low-activity waste glass.

A CCIM consists of water-cooled metal tubes that are arranged to form a crucible. An inductor surrounding the crucible produces a high-frequency alternating current that induces eddy currents (and resultant Joule heating) of materials contained in the crucible. The melting process is usually initiated by inserting a resistive heating element into the crucible to obtain sufficient melt to couple with the electromagnetic field. At that point, the resistive element can be removed so that no foreign materials are in contact with the melt. A solid “skull” of quenched waste material, typically a few millimeters in thickness, forms along the crucible wall, protecting it from degradation and corrosion.

CCIMs have several advantages over both current-generation and advanced JHMs. They allow for higher throughputs and waste loadings. They are operationally simpler and allow for faster recoveries from system upsets.[8] The absence of internal electrodes and refractories allows for increased melter longevity and permits higher-temperature operation compared with current-generation JHMs. As a consequence, CCIMs can be used to process a wider range of waste compositions, including corrosive wastes that are incompatible with current-generation JHMs. Additionally, they can more easily accommodate differing glass compositions, including iron phosphate glasses, that are incompatible with some JHM internal components. CCIMs can be cycled frequently with varying feed compositions without thermal damage or loss of compositional control. And they are capable of producing crystalline ceramics through controlled crystallization.

CCIM is a flexible processing method that can be used in conjunction with other technologies. For example, an integrated process that combines an oxygen plasma and induction-heated cold crucible is reported by Vernaz and Poinssot (2008). This process, which is still under development, is referred to as the Advanced Hybrid System for Incineration and Vitrification (SHIVA). It consists of a single reaction vessel which has three functions: (1) incineration (2) vitrification, and (3) gas post-combustion. This is a promising technology for processing wastes containing radioactive, organic, and other hazardous chemical constituents that are difficult to separate by other processes. The plasma decomposes organic material, significantly reducing its volume, and produces a high-quality containment material (glass in this instance).

CCIM development began in France and Russia in the 1970s (Elliott, 1996). The Russians are using CCIMs to process radioactive waste at the Mayak Plant, and the French are using a CCIM to vitrify HLW at an industrial scale at the La Hague plant. DOE-EM is currently investigating CCIM technology for possible use in its HLW immobilization programs.

CCIM is a mature technology for the vitrification of fission product solutions and decontamination waste streams. It also has potential applications for processing metallic waste streams (Vernaz, 2009). The underlying technology is proven, but operational experience in large-scale waste stream processing environments is limited in comparison to JHMs. Its deployment in DOE-EM applications may require some up-front development work to ensure its compatibility with specific process flowsheets, but no basic research is likely to be required.

Because CCIMs are smaller per unit of throughput and operationally more robust than JHMs, they could potentially be back-fitted to the Defense Waste Processing Facility at Savannah River and the Waste Treatment Plant at Hanford. For example, IPET (2003) examined the feasibility of replacing the JHMs in the Waste Treatment Plant at Hanford with CCIMs. It concluded that two CCIMs could be retrofitted into each of the

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[8] Simpler and more robust processing technologies are generally preferable because system upsets can pose critical bottlenecks for operations that must be conducted in hot-cell environments to protect workers from high radiation fields.

two melter cells in the plant. If the melters were installed before the plant was hot commissioned, about 4 months would be required to modify the melter cells and install the new equipment (IPET, 2003, p. 4.70). Additional time would be required to install the melters after hot commissioning—either to decontaminate the melter cells prior to installation of the new equipment or to construct a new melter facility.

Hot Isostatic Pressing Technology

Hot isostatic pressing (HIP) produces waste forms through the application of heat and pressure. The waste and other materials to be processed are loaded into a can, which is welded shut and placed in a pressure vessel inside an electrically heated furnace. The loaded can is heated and a high isostatic pressure is applied, which compresses the waste into a solid, monolithic waste form.

The HIP process, originally referred to as gas-pressure bonding, was first developed by Battelle Memorial Institute in the mid 1950's (ASME, 1985). Its initial use was for manufacturing nuclear fuels, but it is now a well-established technology used by a wide range of industries for castings, tool making, and manufacturing of ceramic components. The Australian Nuclear Science and Technology Organisation (ANSTO) has developed and demonstrated HIP for immobilizing radioactive wastes from medical isotope production; it plans to commence the commissioning of a HIP facility for this purpose at the end of 2011 (Kath Smith and Bruce Begg, ANSTO, written communication). HIP has never been used to immobilize nuclear waste in the United States. In January 2010, DOE announced its formal decision to use HIP to convert the HLW calcine at the Idaho Site into ceramic-like waste forms (DOE, 2010b). However, the technology readiness assessment is still in progress and a safety assessment has not yet been completed.

HIP is a mature and safe technology as demonstrated by its wide use outside the nuclear industry. The pressure vessels are designed with stringent codes such as those developed by the TÜV (Technischer Überwachungs-Verein [Technical Inspection Association], a German product safety and quality assurance testing firm) and the American Society of Mechanical Engineers (ASME). The conservative ASME code and inspection regime are designed to ensure that vessel integrity is maintained over its service life. Other safety features include active and passive over-pressure control systems and safety shields.

HIP also has many potential advantages for processing nuclear waste. Notably, it produces monolithic waste forms with substantially reduced volumes compared to untreated waste streams. Because the waste is processed in a sealed can, there are no volatile emissions. Also, there is no direct contact between the waste and the HIP apparatus, so secondary waste generation is minimized. HIP is compatible with a wide range of waste compositions, although it has a limited tolerance for gases and volatiles. It can produce glass, glass composite, and crystalline ceramic waste forms.

Unlike many other consolidation technologies, HIP does not require stringent control of physical properties such as viscosity, melt temperature, or melt conductivity, therefore permitting significantly higher waste loadings. However, it does require that the waste form additives be tailored to sequester radionuclides in specified host phases.

For production of SYNROC,[9] for example, REDuction/OXidation (REDOX) conditions must be controlled to form the desired phase assemblages. In addition, processing conditions (pressure and temperature) must be closely controlled.

Although HIP is a flexible technology it does have some limitations. Crystalline ceramic waste forms produced by HIP (as well as conventional press and sinter technology) may contain intergranular glassy phases, especially when incorporating waste containing alkali or alkaline earth species in the presence of glass formers such as silicon or boron. This intergranular glass may limit product durability (e.g., Clarke, 1981; Cooper et al., 1986; Zhang et al., 2010). Also, HIP has been demonstrated only at small scales to date. The small size of the waste cans and long times required for heating currently limits the application of this technology to volumetrically small waste streams.

Given its flexibility, HIP is potentially applicable to a range of DOE-EM waste streams, including orphan waste streams (see Footnote 3) whose diversity requires versatile methods for treatment and immobilization, as well as waste streams that are difficult or inefficient to process by other technologies because of physical or chemical heterogeneity. However, additional studies are needed to demonstrate the safety and compatibility of this technology with specific waste streams and to address its scalability to high-volume waste streams.

Waste Form Durability: Experiments, Tests, and Model Development

As discussed in Box 1, the primary function of a waste form is to sequester radioactive or hazardous constituents in stable, solid matrices either by chemical incorporation or encapsulation. Demonstrating that a given waste form has sufficient durability (see Footnote 6 for a definition) to perform this function over the long time periods of concern for disposal (typically 10^3-10^6 years as noted previously) is a scientific and technical challenge and arguably presents a major obstacle to stakeholder acceptance of waste form disposal strategies. The primary challenge involves extrapolating the durability behavior observed in short-term laboratory tests to these longer time scales—that is, evaluating long-term durability of waste forms.

Short-term (typically days to months) laboratory tests[10] cannot be used directly to evaluate long-term durability. Such evaluation requires the establishment of parallel but connected programs of experimental studies, laboratory tests, and model development tailored to specific combinations of waste forms and disposal environments:[11]

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[9] SYNROC (Synthetic Rock) is a monolithic crystalline ceramic containing hollandite, zirconolite, perovskite, and other minor constituents.

[10] A *laboratory test* is a standard procedure for obtaining measurements of a particular waste form property such as leaching rate. Tests generally follow standardized protocols to ensure measurement consistency and repeatability.

[11] See, for example, ASTM C 1174-07 (Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste), which describes methods for predicting the long-term behavior of materials used in the geologic disposal of spent nuclear fuel and high-level radioactive waste.

- *Experimental studies*[12] are used to identify the mechanism(s) of waste form alteration and release of contained radioactive and other hazardous constituents of concern. This information is used to develop *mechanistic models* that account for the important physical and chemical processes that govern waste form alteration and radionuclide release. Studies of natural analogs—e.g., glasses and ceramics that have survived in natural environments for thousands of years—can also provide useful information on release mechanisms that operate over long time periods and might not be observed in the laboratory.
- *Laboratory testing* is used to measure short-term release rates of radioactive and hazardous constituents from the waste form and the formation of reaction products. The American Society of Testing and Materials (ASTM) has developed a suite of tests that can be used to measure release rates for some types of waste form materials, including certain glass, glass composite, glass ceramic, and metallic materials. However, these tests are not suitable for application to all waste form materials.
- *Coupled models* are used to evaluate long-term waste form durability for a given set of near-field conditions in a disposal environment. These models couple the mechanistic release models described above with *transport models* that account for the movement of radioactive and hazardous constituents (which can be in dissolved, colloidal, or gaseous form) from the altered waste form into the near-field environment of the disposal facility (Steefel et al., 2005). The parameters used in these coupled models are frequently derived from laboratory tests.

Key features of the coupled models can also be abstracted to develop *performance models* of the disposal system. These models are used to assess the long-term performance of the disposal system, which is usually expressed in terms of an annual dose to maximally exposed individuals who live near the facility at some specified future time.[13] The waste form and other engineered and natural barriers in the disposal system are intended to function together to reduce these doses by retarding the release of radionuclides and other hazardous constituents from the facility.

As the foregoing discussion suggests, experimental studies, laboratory testing, and modeling work proceed hand-in-hand: the experimental results are used to identify appropriate tests; the experiments and tests inform the modeling work; and the modeling work uncovers additional needs for information that inform further experimental and testing work. This development work usually requires considerable investment of time, especially if testing protocols need to be developed, modified, or qualified for new materials.

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[12] In contrast to laboratory tests, *experimental studies* are designed to test hypotheses or answer questions about particular waste form properties.

[13] Because the current U.S. regulatory system for radioactive waste disposal is dose based, the transport of radionuclides from a disposal facility into the biosphere is considered as part of the performance assessment that is used to estimate annual doses. Understanding the long-term durability of waste forms can provide valuable information for higher-level safety analyses of disposal systems.

The long-term durability of borosilicate glass, the waste form material being used by DOE-EM to immobilize HLW, has been established using the approaches described above. DOE-EM has also used borosilicate glass as a reference standard for benchmarking the durability of other waste form materials. For example, at the Hanford Site, DOE-EM and the state of Washington have agreed that the waste form selected for immobilizing low-activity waste for near-surface disposal must be "as good as glass," meaning that it must have at least the same durability as the Low Activity Waste Reference Material (LRM), a borosilicate glass developed for Hanford's low-activity waste.

On the other hand, DOE-EM has identified orphan waste streams that have no identified disposition pathways (see Footnote 3). Once waste forms for such waste streams are identified, their long-term durability would need to be established using the methods that are described in this section.

Demonstrating the durability equivalence of different waste form materials is not a simple matter. The tests used to evaluate the durability of one waste form material cannot be applied to another waste form material unless it can be demonstrated that both materials undergo alteration and radionuclide release by the same mechanism(s). For example, tests used for evaluating the long-term durability of borosilicate glass are applicable, either directly or with some modification, to some other types of glass, glass composite, and glass-ceramic waste forms. However, by themselves, they are probably not applicable—or are inadequate—to establish the durability equivalence of other waste form materials such as cements, hydroceramics, or geopolymers. Moreover, some test measurements that are critical for estimating release rates, for example surface area measurements, have not been standardized for waste form materials such as foam glass[14] and crystalline ceramics. The final judgment of the suitability of a waste form for any specific geologic environment will inevitably be the result of a combination of the results of standard tests, experiments, models, as well as confirmatory field and analog studies, as outlined, for example, in the ASTM Standard C 1174-07 (see Footnote 11).

The durability comparison also requires the specification of the near-field conditions (e.g., water flow rate, porewater composition, partial pressure of CO_2, and pH) in the disposal facilities that will host the waste forms.[15] The same waste form might exhibit widely different durability behaviors if they are disposed of in facilities having different near-field conditions. For example, durability of a waste form in wet environments can be tested as a function of pH using buffer solutions as leachants.

The assessment of long-term durability will be required for any new waste forms that DOE-EM intends to use in its cleanup program. In the committee's judgment, assessment of the long-term durability of crystalline ceramic waste forms represents a key near-term opportunity for DOE-EM. Crystalline ceramic materials produced, for example, by FBSR and HIP have been identified elsewhere in this interim report as flexible waste forms with many potential applications, including high-activity and low-activity waste immobilization. Evaluating the long-term durability of these materials for a

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[14] A frothy glass material produced by bulk vitrification tests at the Hanford Site.

[15] Site-specific durability tests are of particular concern for near-surface disposal where the waste form may be the primary engineered barrier to the release of radionuclides.

variety of near-field conditions could provide future flexibility to apply them more widely throughout the clean-up program.

PLANS FOR THE FINAL REPORT

As noted previously, this interim report has focused on near-term opportunities that the committee judges will be useful to DOE-EM for planning its fiscal year 2011 technology development programs. The committee's final report will address the statement of task in its entirety. It will provide a more detailed assessment of waste forms, processing technologies, and state-of-the-art tests and models. It will also identify longer-term research, development, and deployment opportunities for DOE-EM's cleanup program. The final report is scheduled for completion in September 2010.

Sincerely yours,

Milt Levenson

Milt Levenson, Chair

Rod E

Rod Ewing, Vice Chair

Attachments

Attachment A: References

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Attachment B: Committee on Waste Forms Technology and Performance

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Attachment C: Workshop Agenda

Workshop on Waste Form Technology and Performance

The Lecture Room

The National Academy of Sciences (NAS) Building
2101 Constitution Avenue, NW, Washington, DC 20418

Wednesday, November 4, 2009

8:15-8:30 am	**Welcome and Introduction** Milt Levenson and Rod Ewing
Session I:	***International Perspectives***
8:30–9:00 am	**Glass and spent fuel corrosion, coupling of waste forms to the near field, and long-term models of performance** Berndt Grambow, Laboratoire De Physique Subatomique Et Des Technologies Associees (SUBATECH), France
9:00–9:30 am	**Cementatious waste forms and barriers** Fred Glasser, University of Aberdeen, UK
9:30-10:00 am	**Combined inert matrix fuels and related waste forms** Claude Degueldre, Paul Sheerer Institute, Switzerland
10:00-10:30 am	**Break**
10:30-11:00 pm	**Ceramic and phosphate glass waste forms and cold crucible technology** Sergey Stefanovsky, SIA Radon, Russia
11:00-11:30 pm	**Overview of CEA's and French initiatives related to waste forms** Etienne Vernaz, Commissariat à l'Énergie Atomique, France
11:30-12:00 pm	**Overview of Australia/ANSTO initiatives related to waste forms** Kath Smith and Bruce Begg, Australian Nuclear Science and Technology Organisation (ANSTO), Australia
12:00-1:00 pm	**Lunch**
Session II:	***Select Domestic Issues***
1:00–1:30 am	**Computational methods applied to the design and evaluation of waste forms** Bill Weber, Pacific Northwest National Laboratory

1:30-2:00 pm	**Overview of waste forms and near-field interactions in a performance assessment perspective** Carl Steefel, Lawrence Berkeley National Laboratory
2:00-2:30 pm	**Matching waste forms to waste processing strategies** Mark Peters, Argonne National Laboratory
2:30-3:00 pm	**Impact of waste forms on overall repository performance assessment** Peter Swift, Sandia National Laboratories
3:00-3:15 pm	**Break**
3:15-3:45 pm	**Overview of the Vitreous State Laboratory and geopolymer development** Ian Pegg and Werner Lutze, Catholic University of America
3:45-4:15 pm	**Cementitious Barriers Partnership** David Kosson, Vanderbilt University
4:15-4:45 pm	**Industry perspectives on potential waste forms from recycling** Rod McCullum, Nuclear Energy Institute
4:45-5:15 pm	**Panel discussion** All participants
5:15 pm	**Adjourn**

Attachment D: Selected Recent Reports on Science and Technology for Waste Immobilization

Summary Report of the Nuclear Energy Research Initiative Workshop, April 23-25, 1998 (see the report of working group #4). Available at http://www.ne.doe.gov/pdfFiles/nerachWorkshop.pdf.

Basic Research Needs for Advanced Nuclear Energy Systems, July 31- August 3, 2006 (see the panel #5 report on advanced waste forms). Available at http://www.er.doe.gov/bes/reports/files/ANES_rpt.pdf.

Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems, February 21-23, 2007 (see sections related to subsurface geologic storage and modeling/simulation of geologic systems). Available at http://www.er.doe.gov/bes/reports/files/GEO_rpt.pdf.

Basic Research Needs for Materials under Extreme Environments, June 11-13, 2007 (see section on nuclear energy). Available at http://www.er.doe.gov/bes/reports/files/MUEE_rpt.pdf.

Global Nuclear Energy Partnership Integrated Waste Management Strategy Waste Treatment Baseline Study. GNEP-WAST-AI-RT-2007-00034. 2007 (see vol. 1 sections on processing and stabilization with different types of waste forms).

Directing Matter and Energy: Five Challenges for Science and the Imagination, A Report from the Basic Energy Sciences Advisory Committee, 2007 (see chapter 7 on designing new materials). Available at http://www.er.doe.gov/bes/reports/files/GC_rpt.pdf.

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Attachment E: Fluidized Bed Steam Reforming

A bed of granular material can be made to exhibit fluid-like properties by passing a liquid or gas through it. This process is referred to as *fluidization*, and the apparatus that supports this process is referred to as a *fluidized bed*. Fluidization came to age during World War II, when the urgent demand for aviation gasoline led to the development and construction of the first fluid bed catalytic cracker. In addition to gasoline production, fluidization technology is broadly used in coal gasification and combustion, mineral processing, food processing, pharmaceuticals, soil washing, manufacturing of polymers, waste treatment, and environmental remediation. Its applications include several unit operations such as drying, heating/cooling, particle coating, and chemical reactions.

The Fluidized Bed Steam Reforming (FBSR) of nuclear waste is a relatively new technology, though the fluidization phenomenon and steam reforming are well established in the chemical engineering field. Steam reforming is a method for generating hydrogen by reacting fossil fuels with water. For example, for natural gas:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

If coal is used as a carbon source, it first undergoes pyrolysis or devolatilization then the char (C) reacts with steam according to the following reaction:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

The H_2 is combined with O_2 so that no excess H_2 exists in the system at any one time. This combination is exothermic and provides energy in the form of heat for the autocatalytic operation of the FBSR.

The FBSR consists of two fluidized beds. The first one operates in a reducing environment and its function is to evaporate the liquid nuclear waste stream; destroy organics; reduce nitrates, nitrites, and nitric acid to nitrogen gas; and form a stable solid waste product. The first stage fluidized bed of the FBSR process is referred to as the Denitration and Mineralization Reformer, or DMR. The DMR uses superheated steam as the fluidizing media. The bed material consists of granular solid additives and co-reactant(s), such as carbon, clay, silica, and/or catalysts. Liquid waste is directly fed to the fluidized bed after minor pre-treatment (e.g., to concentrate or dilute solubles) except the addition of clay.

By analogy to the above steam reforming chemistry, the carbon fed to FBSR (coal in this instance) produces H_2 and CO. For organic compounds in the waste stream which undergo pyrolysis to form various hydrocarbons, the reducing environment is generated by the following reaction:

$$C_nH_m(g) + nH_2O(g) \rightarrow nCO(g) + (n + m/2)H_2(g)$$

Similarly, the nitrates contained in the liquid waste are reduced to

$$2NaNO_3(g) + 3C(s) \rightarrow 2NO(g) + 3CO(g) + Na_2O(s)$$

In the steam environment, the sodium oxide is transferred to sodium hydroxide:

$$Na_2O(s) + H_2O(g) \rightarrow 2NaOH(s,l)$$

yielding the overall reaction

$$2NaNO_3(g) + 3C(s) + H_2O(g) \rightarrow 2NO(g) + 3CO(g) + 2NaOH(s,l)$$

$$2NaNO_3(g) + 2C(s) + H_2O(g) \rightarrow 2NO_2(g) + 2CO(g) + 2NaOH(l,s)$$

The NO and NO_2 are further reduced to nitrogen gas by the reaction of CO, C, or H_2 generated from the reaction of the organic material with steam as shown above. The nitrates can also be reduced by the addition of a catalyst or a metal. For example:

$$2NaNO_3(g) + 5Fe(s) + H_2O(g) \rightarrow N_2(g) + 5FeO(s) + 2NaOH(s,l)$$

The second fluidized bed of the FBSR process operates in an oxidizing environment and is referred to as the Carbon Reduction Reformer, or CRR. The fluidizing gases are the off-gas from the first stage and added oxygen. Its function is to gasify carbon fines carried over in the process gases from the DMR, oxidize CO and H_2 to CO_2 and water, and convert trace acid gases to stable alkali compounds by reacting these acids with the bed media consisting of calcium carbonate and/or calcium silicate particles.

The addition of bulk aluminosilicates to the fluidized bed results in the production of anhydrous feldspathoid phases such as sodalite. The sodalite family of minerals (including nosean) are unique because they have cage-like structures formed of aluminosilicate tetrahedra. The remaining feldspathoid minerals, such as nepheline, have a silica “stuffed derivative” ring type structure. The cage structures are typical of sodalite and/or nosean phases where leach testing has indicated that the cavities in the cage structure retain anions and/or radionuclides which are ionically bonded to the aluminosilicate tetrahedra and to sodium cation.

Sodalite has the formula $Na_8[Al_6Si_6O_{24}](Cl_2)$. In sodalites and analogues with sodalite topologies, the cage is occupied by two sodium and two chlorine ions. When the 2NaCl are replaced by Na_2SO_4, the mineral phase is known as nosean, ($Na_6[Al_6Si_6O_{24}](Na_2SO_4)$)). Since the Cl, SO_4, and/or S_2, are chemically bonded and physically restricted inside the sodalite cage structure, these species do not readily leach out of the respective FBSR waste form mineral phases. Thus, FBSR waste forms can be useful for immobilizing these species to prevent their leaching into groundwater.

Other minerals in the sodalite family, namely hauyne and lazurite which are also cage structured minerals, can accommodate either ($SO_4^{=}$) or ($S^{=}$) depending on the REDOX of the sulfur during the steam reforming process. Sodalite minerals are known to accommodate Be in place of Al and S_2 in the cage structure along with Fe, Mn, and Zn, e.g., helvite ($Mn_4[Be_3Si_3O_{12}]S$), danalite ($Fe_4[Be_3Si_3O_{12}]S$), and genthelvite ($Zn_4[Be_3Si_3O_{12}]S$). These cage-structured sodalites were minor phases in HLW supercalcine waste forms and were found to retain Cs, Sr, and Mo into the cage-like structure, e.g., Mo as $Na_6[Al_6Si_6O_{24}](NaMoO_4)_2$. In addition, sodalite structures are known to retain B, Ge, I, and Br in the cage-like structures. Indeed, waste stabilization at Idaho National Laboratory currently uses a glass-bonded sodalite ceramic waste form (CWF) for disposal of electrorefiner wastes for sodium-bonded metallic spent nuclear fuel from the EBR II fast breeder reactor.

Attachment F: Joule Heated Melters

The DOE-EM program for immobilizing high-level waste currently utilizes Joule-heated melters (JHMs) to produce high-level waste waste glass. In Joule heating an electric current is passed through a material, in this case glass. The internal resistance of the material causes the electric currents to be dissipated as heat. A JHM is usually lined with refractory, and the glass is Joule heated by electricity transferred through the melt between nickel-chromium alloy electrodes, usually Inconel. The nominal melt temperature in JHMs is 1150°C, which is only 200°C lower than the melting point of the Inconel electrodes. These melters can be calcine fed or slurry fed and vitrification is a continuous or semi-continuous process.

JHM's have been used for waste glass production in the United States, France, and Japan because of the high production rate and high glass quality. The size of these systems is limited only by the replacement crane capacity since all the structural support is provided by a stainless steel shell which contains the refractory. The Defense Waste Process Facility at Savannah River Site is the largest production melter of this type ever built. A larger one is under construction for use at the Waste Treatment Plant at the Hanford Site and replacement of this system (due to its size) is by rail instead of by crane.

Attachment G: Reviewer Acknowledgments

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making the published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The content of the review comments and draft manuscript remains confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their participation in the review of this report:

Patricia Culligan, Columbia University
George Keller (NAE), Mid-Atlantic Technology, Research and Innovation Center
Alexandra Navrotsky (NAS), University of California, Davis
Alfred Sattelberger, Argonne National Laboratory
Carl Steefel, Lawrence Berkeley National Laboratory
Etienne Vernaz, CEA, Nuclear Energy Division, Marcoule
Raymond Wymer, Oak Ridge National Laboratory (retired)

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by Ed Przybylowicz, appointed by the National Research Council, who was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the National Research Council.

Appendix D

Glossary

Advanced Joule-Heated Melter. A Joule-Heated Melter that incorporates design improvements to increase throughputs and waste loadings.

Bitumen. A viscous hydrocarbon and a major component of asphalt.

Cement. An inorganic material that sets and hardens as a result of hydration reactions.

Ceramicretes. Phosphate-bonded ceramics, also known as chemically bonded phosphate ceramics.

Chemical incorporation. The process by which radioactive and hazardous constituents are bound into a material at atomic scale.

Cold Crucible Induction Melter. Water-cooled tubes that are arranged to form a crucible that can be heated by induction.

Cold Pressing and Sintering. A process for forming crystalline ceramics at room temperature involving the application of compressive stress.

Colloid. A sub-micron particle suspended in a liquid.

Congruent dissolution. Release of species in stoichiometric proportion to their presence in a waste form material.

Crystalline ceramics. Inorganic, non-metallic solids that contain one or more crystalline phases.

Diffusion-controlled release. Release of constituents by diffusion through the waste form material, including through an encapsulant and/or surface layers containing reaction products, if present.

Disposal environment. The time-dependent physical and chemical conditions in a facility designed for the disposal of radioactive waste.

Disposal facility. Physical infrastructure of the facility, including tunnels or surface excavations, the surrounding host rock, and engineered barriers, including the waste form if present.

Disposal system performance. The ability of a disposal system to sequester radioactive and hazardous constituents in the near field.

Disposal system. Refers to both physical infrastructure and how the natural and engineered barriers in that infrastructure function to sequester radioactive and hazardous constituents.

Dissolution. A process (or processes) by which mass transport from a solid waste form to a liquid takes place as the result of mechanistic reactions in which chemical bonds are broken and constituents are released from a material and become solvated in a test solution.

Dissolution rate. The rate of mass removal per unit time normalized to surface area of the material.

Durability. The resistance of a waste form material to chemical and physical alteration and the associated release of contained radioactive and hazardous constituents.

Encapsulation. The process by which radioactive and hazardous constituents are physically surrounded and isolated by the material.

Experiment. The application of tests to a waste form material to gain a better understanding of its degradation behavior and the release of radioactive constituents.

Far-field environment. The region beyond the near field, including the biosphere.

Fluidized bed. A bed of granular material that exhibits fluid-like properties by passing a liquid or gas through it.

Fluidized Bed Steam Reforming. A process for thermally treating and immobilizing waste through the use of fluidized bed technologies.

Geologic repositories. Facilities constructed in geologic formations located hundreds of meters below Earth's surface that are designed for the disposal of higher-hazard wastes such as spent nuclear fuel, high-level radioactive waste, and transuranic waste.

Geopolymers. Ceramic-like, inorganic polymers made from aluminosilicates cross-linked with alkali metal ions.

Glass. An amorphous solid material produced by cooling a material from a molten to a solid state without crystallization.

Glass-ceramic materials. Materials that contain both crystalline and glass phases.

Hazardous waste. Waste that is toxic or otherwise hazardous because of its chemical properties. Waste can be designated as hazardous in any of three ways: (1) It contains one or more of more than 700 materials listed as hazardous; (2) it exhibits one or more hazardous characteristics, which include ignitability, corrosivity, chemical reactivity, or toxicity; or (3) it arises from treating waste already designated as hazardous.

High-level radioactive waste. Waste material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and other highly radioactive material that the Nuclear Regulatory Commission, consistent with existing law, determines by rule to require permanent isolation.

Hot Isostatic Pressing. A process for producing waste forms through the simultaneous application of heat and isostatic pressure.

Hot Uniaxial Pressing. A process for forming crystalline ceramics at elevated temperature that involves the application of uniaxial compressive stress.

Hydroceramics. Concrete-type materials that are made by curing a mixture of inorganic waste, calcined clay, vermiculite, sodium sulfide (Na_2S), and sodium hydroxide (NaOH) with water under hydrothermal conditions.

Immobilization. The solidification, embedding, or encapsulation of radioactive and chemically hazardous waste to create a waste form.

Incongruent dissolution. Preferential release of some species from a waste form material relative to other species.

In-Container Vitrification. A batch process by which contaminated soil, liquid waste mixed with soil, and glass formers are vitrified *in situ* in a refractory-lined steel vessel.

Joule-Heated Melter. A refractory-lined container with nickel-chromium alloy electrodes that is used for vitrifying waste.

Joule heating. Heating obtained by passing an electrical current through a resistively conducting material.

Leaching. The loss of radioactive or chemical constituents from a waste form by diffusion or dissolution.

Low-level radioactive waste. Radioactive material that is not high-level radioactive waste, spent nuclear fuel, transuranic waste, or 11(e)(2) byproduct material (mill tailings) that the Nuclear Regulatory Commission, consistent with existing law, classifies as low-level radioactive waste.

Mesoporous materials. Materials that have regularly arranged pores ranging from 2-50 nanometers in diameter.

Metal-organic frameworks. A relatively new class of porous materials that consist of metal atoms (ions) linked together by multifunctional organic ligands.

Mixed low-level waste. Waste that contains both low-level waste and hazardous waste components.

Mixed transuranic. Waste that meets the definitions of both transuranic and hazardous wastes.

Near-field environment. The engineered barriers in a disposal system (e.g., waste canisters) as well as the host geologic media in contact with or near these barriers whose properties have been affected by the presence of the repository.

Orphan waste stream. A waste stream that has no clear-cut disposition pathway.

Performance. The ability of a waste form (waste form performance) or a disposal system containing the waste form (disposal system performance) to sequester radioactive and chemical constituents.

Performance assessment. Methodology for estimating the future behavior of a disposal system involving the modeling of processes and events that might lead to releases and exposures.

Plasma heating. An electrical heating process in which plasma is created by passing a gas through an electrical arc.

Portland cement. A common cement type that consists of calcium silicates, other aluminum and iron containing phases, and additives such as gypsum to control set time.

Qualification. See *Waste Form Qualification*.

Reaction affinity-controlled release. Release of constituents from a material that is controlled by the difference in Gibbs free energy between the thermodynamically stable state and the metastable reactants.

Release mechanisms. The process that controls the rate of mass transport out of a waste form material during dissolution.

Shallow-land disposal facilities. Facilities excavated into sediments located within 10 meters or so of Earth's surface that are designed for the disposal of lower-hazard wastes such as low-level radioactive waste.

Solubility. The thermodynamically limited saturation state or equilibrium concentration limit of species in solution.

Solubility-controlled release. Release of constituents from a material that is bounded by the use of the maximum saturation of a constituent species from the waste form in the given leachant (solution) environment.

Spent nuclear fuel. Fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing.

Standard test protocols. A standardized procedure for testing a specific type of material to generate a clearly defined test response.

Transuranic (TRU) waste. Waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, with half-lives greater than 20 years, per gram of waste, except for: (1) high-level radioactive wastes; (2) wastes that the Department [of Energy] has determined, with the concurrence of the [EPA] Administrator, do not need the degree of isolation required by this part; or (3) wastes that the [Nuclear Regulatory] Commission has approved for disposal on a case-by-case basis in accordance with Title 10, Part 61 of the Code of Federal Regulations.

Waste acceptance criteria. Specific requirements that waste must meet to be acceptable for disposal in a given facility.

Waste form. Radioactive waste material and any encapsulating or stabilizing matrix in which it is incorporated.

Waste form performance. The ability of a waste form to sequester and retain its radioactive and chemically hazardous constituents.

Waste form qualification. Demonstration that a waste form material will have acceptable performance in a specific disposal facility and can be fabricated with acceptable performance control.

Waste form test protocols. Standard tests developed by organizations such as the American Nuclear Society, American Society of Testing and Materials, International Atomic Energy Agency, and the International Organization for Standardization.

Waste incidental to reprocessing. Waste resulting from reprocessing spent nuclear fuel that is determined to be incidental to reprocessing and is not high-level waste.

Waste loading. The quantity of waste, usually expressed as a weight percent, that can be incorporated into a waste form.

Appendix E

Acronyms

AJHM	Advanced Joule-Heated Melter
ALT	accelerated leach test
ANSI	American Nuclear Standards Industry
ANSTO	Australian Nuclear Science and Technology Organisation
ASME	American Society of Mechanical Engineers
BDAT	best demonstrated available technology
CAA	Clean Air Act
CCIM	Cold Crucible Induction Melter
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFD	computational fluid dynamics
CFR	Code of Federal Regulations
CID	Central Internet Database
CNWRA	Center for Nuclear Waste Regulatory Analyses
CP&S	Cold Pressing and Sintering
CRR	Carbon Reduction Reformer
CRWMS	Civilian Radioactive Waste Management System
CWF	ceramic waste form
DBVS	Demonstration Bulk Vitrification System
DMR	Denitration and Mineralization Reformer

DOE-EM	U.S. Department of Energy, Office of Environmental Management
DOE-NE	U.S. Department of Energy, Office of Nuclear Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EBS	engineered barrier system
EPA	U.S. Environmental Protection Agency
FBSR	Fluidized Bed Steam Reforming
FCC	Fluid Catalytic Cracker
FUETHP	formed under elevated temperature and pressure
FY	fiscal year
GCMs	glass-ceramic materials
GTCC	Greater-Than-Class-C
HAW	high-activity waste
HLW	high-level radioactive waste
HLVIT	HLW vitrification
HWC	Hazardous Waste Combustor
HWMA	Hazardous Waste Management Act
ICU	In-Container Vitrification
ILAW	immobilized low-activity waste
INL	Idaho National Laboratory
JHM	Joule-Heated Melter
LAW	low-activity waste
LDR	land disposal restrictions
LLW	low-level radioactive waste
LRM	LAW Reference Material
LRO	long-range order
MACT	Maximum Achievable Control Technology
MCC	Materials Characterization Center
MOFS	metal-organic frameworks
MRN	modified random network
MRO	medium-range order
MT	metric tons (tonnes)
MTHM	metric tons heavy metal
MTRU	mixed transuranic

NAS	National Academy of Sciences
NBO	non-bridging oxygen atoms
NDAA	National Defense Authorization Act
NRC	National Research Council
NWPA	Nuclear Waste Policy Act
NWTRB	Nuclear Waste Technical Review Board
NWTS	Nuclear Waste Terminal Storage
NZP	sodium zirconium phosphate
OCRWM	Office of Civilian Radioactive Waste Management
ONWI	Office of Nuclear Waste Isolation
PA	performance assessment
PCT	Product Consistency Test
PHP	plasma hearth process
PMF	powder mineral fuels
PNNL	Pacific Northwest National Laboratory
PUF	Pressurized Unsaturated Flow
R&D	research and development
RCRA	Resource Conservation and Recovery Act
Redox	reduction-oxidation
SHIVA	Advanced Hybrid System for Incineration and Vitrification
SNF	spent nuclear fuel
SPFT	Single-Pass Flow-Through
SRO	short-range order
SRS	Savannah River Site
SSV	self-sustaining vitrification
SYNROC	synthetic rock
THOR®	Thermal Organic Reduction
TRU	transuranic
TSPA-LA	Total System Performance Assessment—License Application
TST	transition state theory
USNRC	U.S. Nuclear Regulatory Commission
UTS	universal treatment standards
VHT	Vapor Hydration Test
VSL	Vitreous State Laboratory
WAC	waste acceptance criteria

WASRD	Waste Acceptance System Requirements Document
WIPP	Waste Isolation Pilot Plant
WIR	waste incidental to reprocessing
WISP	Waste Isolation System Panel
WTP	Waste Treatment Plant