




## Waste Forms Technology and Performance: Interim Report

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# 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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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.<sup>1</sup>
- 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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<sup>1</sup> 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



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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<sup>2</sup> 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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<sup>2</sup> 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).

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**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<sup>3</sup> 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,<sup>4</sup> 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<sup>5</sup> 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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<sup>3</sup> 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.

<sup>4</sup> See, for example, the basic research needs reports that are listed in Attachment D.

<sup>5</sup> 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.

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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<sup>6</sup> 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 19<sup>th</sup> 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<sup>®</sup>), 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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<sup>6</sup> 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.

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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,<sup>7</sup> 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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<sup>7</sup> 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.

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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](http://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

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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.<sup>8</sup> 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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<sup>8</sup> 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.

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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.

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For production of SYNROC,<sup>9</sup> 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<sup>10</sup> 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:<sup>11</sup>

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<sup>9</sup> SYNROC (Synthetic Rock) is a monolithic crystalline ceramic containing hollandite, zirconolite, perovskite, and other minor constituents.

<sup>10</sup>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.

<sup>11</sup> 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.



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- *Experimental studies*<sup>12</sup> 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 (Steeffel 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.<sup>13</sup> 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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<sup>12</sup> In contrast to laboratory tests, *experimental studies* are designed to test hypotheses or answer questions about particular waste form properties.

<sup>13</sup> 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.

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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<sup>14</sup> 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<sub>2</sub>, and pH) in the disposal facilities that will host the waste forms.<sup>15</sup> 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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<sup>14</sup> A frothy glass material produced by bulk vitrification tests at the Hanford Site.

<sup>15</sup> 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.

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variety of near-field conditions could provide future flexibility to apply them more widely throughout the clean-up program.

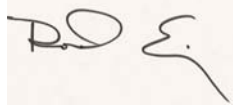
### PLANS FOR THE FINAL REPORT

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, Chair



Rod Ewing, Vice Chair

Attachments

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### Attachment A: References

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**Attachment B: Committee on Waste Forms Technology and Performance**

MILTON LEVENSON, *Chair*, Bechtel International (retired), Menlo Park, California  
RODNEY C. EWING, *Vice Chair*, University of Michigan, Ann Arbor  
JOONHONG AHN, University of California, Berkeley  
MICHAEL J. APTED, INTERRA, Inc., Denver, Colorado  
PETER C. BURNS, University of Notre Dame, Notre Dame, Indiana  
MANUK COLAKYAN, Dow Chemical Company (retired), South Charleston, West Virginia  
JUNE FABRYKA-MARTIN, Los Alamos National Laboratory, Los Alamos, New Mexico  
CAROL M. JANTZEN, Savannah River National Laboratory, Aiken, South Carolina  
DAVID W. JOHNSON, JR, Bells Labs (retired), Bedminster, New Jersey  
KENNETH L. NASH, Washington State University, Pullman  
TINA M. NENOFF, Sandia National Laboratories, Albuquerque, New Mexico

*Staff*

KEVIN D. CROWLEY, Study Director  
DANIELA STRICKLIN, Study Director (Through February 12, 2010)  
SARAH CASE, Staff Officer  
TONI GREENLEAF, Administrative and Financial Associate  
SHAUNTEÉ WHETSTONE, Senior Program Assistant  
JAMES YATES, JR., Office Assistant

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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     **Cementitious waste forms and barriers**  
Fred Glasser, University of Aberdeen, UK
- 9:30-10:00 am     **Combined inert matrix fuels and related waste forms**  
Claude Degueudre, 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

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- 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**



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**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](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](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](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](http://www.er.doe.gov/bes/reports/files/GC_rpt.pdf).

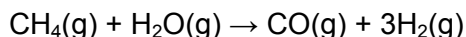
Advice on the Department of Energy's Cleanup Technology Roadmap: Gaps and Bridges. 2009. National Academies Press. Available at [http://www.nap.edu/openbook.php?record\\_id=12603&page=1](http://www.nap.edu/openbook.php?record_id=12603&page=1).

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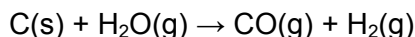
### Attachment E: Fluidized Bed Steam Reforming

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:



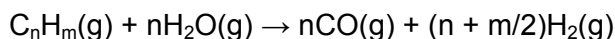
If coal is used as a carbon source, it first undergoes pyrolysis or devolatilization then the char (C) reacts with steam according to the following reaction:



The  $\text{H}_2$  is combined with  $\text{O}_2$  so that no excess  $\text{H}_2$  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  $\text{H}_2$  and  $\text{CO}$ . For organic compounds in the waste stream which undergo pyrolysis to form various hydrocarbons, the reducing environment is generated by the following reaction:

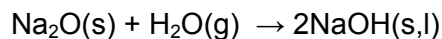


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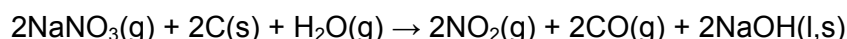
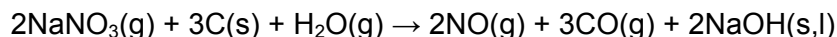
Similarly, the nitrates contained in the liquid waste are reduced to



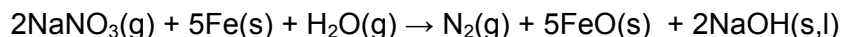
In the steam environment, the sodium oxide is transferred to sodium hydroxide:



yielding the overall reaction



The NO and NO<sub>2</sub> are further reduced to nitrogen gas by the reaction of CO, C, or H<sub>2</sub> 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:



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<sub>2</sub> to CO<sub>2</sub> 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<sub>8</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](Cl<sub>2</sub>). 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<sub>2</sub>SO<sub>4</sub>, the mineral phase is known as nosean, (Na<sub>6</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](Na<sub>2</sub>SO<sub>4</sub>)). Since the Cl, SO<sub>4</sub>, and/or S<sub>2</sub>, 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<sub>4</sub><sup>2-</sup>) or (S<sup>2-</sup>) depending on the REDOX of the sulfur during the steam reforming process. Sodalite minerals are known

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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 supercalcline 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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### **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.

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### **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.