ENGINEERED CEMENTITIOUS BARRIERS FOR LOW-ACTIVITY RADIOACTIVE WASTE DISPOSAL

Workshop Summary and Recommendations for DOE Office of Environmental Management

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March 28, 2007

Sponsors

ACKNOWLEGEMENTS AND DISCLAIMERS

This report and the workshop summarized in this report was a joint collaborative effort between the Savannah River National Laboratory and The Consortium for Risk Evaluation with Stakeholder Participation.

This report was prepared for the United States Department of Energy in part under Contract No. DE-AC09-96SR18500 and is an account of work performed in part under that contract. Reference herein to any specific commercial product, process, or service by trademark, name, manufacturer, or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring of same by Washington Savannah River Company or by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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This report is based in part on work supported by the U. S. Department of Energy, under Cooperative Agreement Number DE-FC01-06EW07053 entitled 'The Consortium for Risk Evaluation with Stakeholder Participation III' awarded to Vanderbilt University. The opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily represent the views of the Department of Energy or Vanderbilt University.

Printed in the United States of America

Prepared For
U.S. Department of Energy

EXECUTIVE SUMMARY

This report provides a summary of the current state of knowledge and information gaps identified through a workshop on the use of engineered cementitious barriers for shallow land disposal of low-activity radioactive wastes. The workshop was held in support of DOE Office of Environmental Management (DOE-EM) on December 12-14, 2006 in Aiken, SC. The purpose of the workshop was to facilitate technical exchange among subject matter experts across the DOE complex, additional national and international experts, and representatives from local advisory groups and state and federal agencies with roles at DOE sites. One hundred and ten people attended the workshop in person while another 250 people participated either in full or in part via web cast.

This report also provides recommendations for technical programs to improve design, use, and long-term performance assessments of engineered cementitious barriers for enhanced shallow land disposal of radioactive waste and entombments. The bases for recommendations include: reducing project cost and schedule, improving the technical bases for design, construction, operation, and performance predictions, and facilitating improved stakeholder understanding and acceptance.

Engineered cementitious barriers are being successfully used by the US DOE and commercial low-activity waste (LAW) disposal facilities as part of waste forms and containment systems to enhance the overall performance by:

1) Limiting the flux of water that comes in contact with the waste and subsequent release or leaching of radionuclides from the disposal unit,
2) Modifying the chemistry of the disposal environment to reduce the mobility of the radionuclides in the disposal unit, and
3) Providing physical stability to prevent subsidence and deter intrusion and physical disruption.

Several issues and gaps in current knowledge have been identified and recommendations are made in the areas of:

1) Standards of practice for use of cementitious materials in DOE-EM waste management missions, performance assessments, and test methods,
2) Data bases and knowledge retention,
3) Field monitoring and validation of performance and performance models, including sample archive programs, pilot-scale field tests, and monitoring programs,
4) Defensibility and credibility, including independent review and knowledge exchange, stakeholder involvement, and independent funding, and
5) Leveraging resources with initiatives by other federal agencies, national laboratories, international programs and university research.

The technical exchange, as provided through the workshop, and the recommendations included in this report are beneficial to the DOE-EM mission by facilitating improvements in the design, implementation, and assessment of engineered cementitious barriers used or planned for use in the DOE complex.

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LIST OF ACRONYMS

ALARA	As Low As Reasonably Achievable
ANL	Argonne National Laboratory
ANS	American Nuclear Society
ASTM	American Standard and Testing Material
CEA-Seclay	Commission Energy Atomic, Seclay, France
CRESP	Consortium for Risk Evaluation with Stakeholder Participation
D&D	Decontamination and Decommissioning
DHI	Danish Hydraulic Institute
DIAL	Diagnostic Instrumentation and Analysis Laboratory
DOE	Department of Energy
DOE-EM	Department of Energy Office of Environmental Management
DOE-OS	Department of Energy Office of Science
ECN	Energy Research Centre of the Netherlands
EM	Environmental Management
EPA	Environmental Protection Agency
EPSCoR	Experimental Program to Stimulate Competitive Research
EXAFS	Extended X-Ray Absorption Fine Structure
HLW	High Level Waste
INL	Idaho National Laboratory
ISO	International Standards Organization
LAW	Low-Activity Waste
LBNL	Lawrence Berkeley National Laboratory
MSE	MSE Technology Applications, Inc.
NIST	National Institute of Standard and Technology
NRC	Nuclear Regulatory Commission
ORISE	Oak Ridge Institute for Science and Education
PA	DOE Performance Assessments
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SUMMA	SUMMA Consortium
TCLP	Toxicity Characteristic Leaching Procedure
TEM	Transmission Electron Microscopy
USEPA	United States Environmental Protection Agency
XANES	X-Ray Adsorption Near-Edge Structure Spectroscopy

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INTRODUCTION

Design, construction, and performance assessment of engineered cementitious barriers are critical path items for many DOE EM projects across the complex. These projects include Hanford secondary waste treatment, Savannah River Site tank waste treatment, i,e., saltstone, fill materials for high level waste (HWL) tanks, concrete vault for low activity waste disposal and D&D entombments and debris encapsulation.

Engineered cementitious barriers are used by both the US DOE and commercial low-activity waste (LAW) disposal facilities[1] to enhance the overall performance of the disposal facility by:

1) Limiting the flux of water that comes in contact with the waste and subsequent release or leaching of radionuclides from the disposal unit;
2) Modifying the chemistry of the disposal environment to reduce the mobility of the radionuclides in the disposal unit and environment; and,
3) Providing physical stability to prevent subsidence and deter intrusion and physical disruption.

DOE-EM has accomplished great strides in the use of engineered cementitious barriers as part of its environmental restoration and waste management program. The progress achieved so far, the currently planned uses, and potential environmental and programmatic benefits of expanding the use of engineered cementitious barriers drive the need to identify knowledge gaps, which if adequately addressed, would improve the effectiveness and further facilitate the use of these materials and systems.

The recent workshop on the "Use of Cementitious Materials for Radioactive Waste Treatment, Containment, Environmental Restoration and Decommissioning" provided an international forum for assessing the use of engineered cementitious materials for shallow land (near-surface) disposal of low-activity radioactive waste and for in-situ entombment (closure) of radioactively contaminated structures. The workshop was sponsored by the DOE Office of Environmental Management (DOE-EM) and was held December 12-14, 2006 in Aiken, SC.

The purpose of the workshop was to facilitate technical exchange among subject matter experts across the DOE complex, additional national and international experts, and representatives from local advisory groups and state and federal agencies with roles at DOE sites. The technical exchange, as provided through the workshop, and the recommendations included in this report will benefit the DOE-EM mission by facilitating improvements in the design, implementation, and assessment of engineered cementitious barriers used or planned throughout the DOE complex.

The workshop was attended by local, state and federal stakeholders in addition to national and international experts in the fields of engineered cementitious barriers for radioactive waste disposal, construction materials, transport modeling through porous media and long term

[1] Shallow, near-surface land burial is used for disposal of low-activity radioactive waste. Disposal of low-activity waste generated by the US DOE must comply with DOE Order 435.1. Disposal of low-activity waste generated by commercial activities (nuclear power, medical applications, industrial applications, etc.) is regulated by the US NRC which licenses LAW disposal facilities.

performance assessment. One hundred and ten (110) people attended the workshop. Two hundred and fifty (250) participated via the workshop web cast.

The agenda of the workshop is provided as Attachment 1 and summaries of the presentations are provided in Attachment 2. Electronic proceedings of the workshop were prepared in DVD format and are included as Attachment 3.

Objectives

The objective of this report is to use information obtained from the workshop to:

1) Document the current state of knowledge;
2) Identify information gaps; and,
3) Provide recommendations for technical programs to improve the design, use, and long term performance assessments of engineered cementitious barriers for enhanced shallow land disposal of radioactive waste and entombments. The bases for recommendations include: reducing project cost and schedule, improving the technical bases for design, construction, operation, and performance predictions, and facilitating stakeholder understanding and acceptance. These recommendations are derived from the workshop presentations and discussions, and further consultations with experts in the field of engineered cementitious barriers.

This report is not intended to be a critique of DOE projects or a summary of lessons learned.

CURRENT PROGRAM STATUS

Workshop participant discussions were used to establish the current status regarding the use of engineered cementitious materials and barriers in the DOE complex. The use of cementitious materials for low-activity radioactive waste disposal (waste forms, concrete containments, tank fill materials, environmental restoration and entombments) began in the early 1970s and has progressed significantly over the last 40 years. Numerous examples of successful deployment of engineered cementitious barriers for waste management and environmental restoration exist throughout the DOE complex. Most of this work was based on material science and engineering developed for conventional applications of cementitious materials, literature information, and/or data generated for specific operational needs or projects. Although DOE has numerous successful applications of cementitious barrier technology, the current technical bases for using these materials are often limited to short term laboratory testing, empirical extrapolation of literature data for related materials, and limited or no case-specific field testing.

The materials science and engineering of cementitious materials have been investigated from the micro-scale to the macro-(structure) scale. The majority of the studies have been directed towards conventional concrete, structural engineering, and waste management applications. Peer reviewed technical publications, standard practice documents, standard test methods, empirical relationships, and building codes provide the technical understanding and basis for the successful use of the multitude of different cementitious materials. National and international professional organizations and committees have been generating, reviewing and distributing this information in numerous formats including peer reviewed publications and professional meetings for many decades.

A substantial amount of this information has been incorporated into DOE waste disposal projects[2]. However, disposal of DOE radioactive waste presents several challenges that require unique technical approaches and application-specific data beyond that which has been developed for conventional applications. These special needs reflect the nature of the constituents to be managed (e.g., long-lived radionuclides and radionuclides that are highly mobile in the near surface environments). The consequences of these needs include: selecting disposal sites that provide robust features for controlling migration of radionuclides, and designing, constructing, monitoring and maintaining engineered barriers with very long service lives, on the order of 100s to 1000s of years.

Stakeholders, including state regulators, citizens' groups (represented by the SRS Citizens Advisory Board), and federal regulating organizations (EPA and NRC), are aware of the general limitations in material characterization and predictive methodology (computational analyses to make long term predictions based on limited assemblages of short term data). Consequently, stakeholders are sensitive to the need for monitoring materials and waste in existing landfills and for using this information to test modeled assumptions and predict performance.

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[2] The level of information included in many DOE-EM applications and assessments reflects the long life-cycle of many projects, which may span more than a decade from planning to implementation. As such, this workshop, addresses the need to evaluate the gaps between current practice and recent progress in understanding of materials and systems design and performance.

Long term laboratory testing, field testing, and monitoring of full-scale structures and actual materials used in DOE waste disposal facilities has been very limited. Test methods for long term evaluations and accelerated aging are lacking and guidance on the use of data generated by long-term testing, accelerated testing, analogues, and field testing is limited.

Although numerous standardized laboratory test protocols have been used throughout the DOE complex for short term evaluations of engineered construction materials, many of the test protocols do not account for the current understanding of the mechanisms and processes that control long-term system leaching and structural performance. Short term leach testing, physical property testing, and structural, thermodynamic, and transport calculations/modeling are typically performed to meet specific operational needs and project schedules. In addition, short term test protocols are often modified on an ad-hoc basis to investigate specific phenomena. Current data bases which include such information are difficult to use and defend in uncertainty analyses because they lack internal consistency.[3]

Independent peer review of test methods and data is challenging because of the lack of standardized approaches and protocols. The absence of peer-reviewed input data limits the effectiveness of subsequent reviews of the long-term performance modeling which relies on these data to generate concepts and cases for assessment.

Data and understanding of cementitious engineered barriers are used as input to design of disposal systems, DOE Performance Assessments (PA)[4] and Composite Analyses[5] per DOE Order 435.1. The DOE performance assessment process evaluates waste disposal activities for facilities to provide a reasonable expectation of compliance with performance objectives. The necessary performance objectives are intended to provide protection of human health and the environment based on:

- Dose from a combination of all exposure pathways;
- Dose from air pathway;
- Release of radon; and,
- Water resource protection in compliance with applicable federal, state and local requirements.

Currently, property data for engineered cementitious materials used as performance assessment input are often limited by the following constraints:

- Samples of the actual materials are unavailable because the materials are contaminated with radionuclides and unsuitable for testing in existing facilities with test equipment designated for non-radioactive samples. Laboratories for testing radioactive samples are

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3 The current data bases are compilations from many sources. They contain data that has been generated by a variety of methods which may or may not incorporate current understanding of mechanisms and test protocols.

4 Performance Assessments also include intruder analyses to establish limits on the concentrations of radionuclides that may be exposed of in the near surface environment.

5 Composite Analyses must provide a reasonable expectation that requirements for protection of the public will not be exceeded, accounting for all sources of radioactive material that may be left at the DOE site and may interact with the disposal facility.

limited in number and typically can handle only very small amounts of material in order to maintain acceptable dose levels.

- Current operations do not include programs for collecting and testing samples from ongoing disposal operations with the intent of improving current and future systems performance. Furthermore, system monitoring programs are designed to meet minimum regulatory compliance (typically through groundwater monitoring at a designated point of compliance) rather than to provide information that would allow interventions to pre-empt potential adverse impacts.
- Programs do not exist for pilot-scale field testing of materials or structural components prior to, or in parallel with, operations.
- Many of the experimental designs for material evaluation and selection are overly specific and consequently do not address the full potential for data collection and generation of results that would be useful to describe performance under variable conditions or under the range of conditions encountered throughout the DOE complex.
- Programs do not exist for archiving laboratory or field samples in order to provide specimens for aging studies and to test assumptions.

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STAKEHOLDER PERSPECTIVES

The workshop included presentation and discussion of perspectives from representatives of several stakeholder groups, including a citizens' advisory board (SRS Citizen's Advisory Board), state regulators (South Carolina and Washington), the Nuclear Regulatory Commission (NRC), and the U.S. Environmental Protection Agency (EPA). The views presented provided a window on issues and on the potential to improve credibility and acceptance of using engineered cementitious barriers to enhance the performance of DOE radioactive waste near surface disposal facilities and waste management activities.

The SRS Citizen's Advisory Board member stated the following attributes were needed for an acceptable approach:[6]

- Regulatory-accepted monitoring with appropriate oversight;
- Peer-reviewed technology demonstrated at an adequate scale;
- Peer-reviewed performance prediction model; and,
- Contingency plan if actual performance does not meet requirements in the short term, 1 to10s of years) or long-term predictions (post closure, 100s to 1000s of years).

These attributes imply several programmatic features not currently in place, including:

- Comprehensive, independent peer-review at key stages of projects;
- Technology demonstrations to support performance predictions;
- Performance prediction strategies that include practical implementation of computational methods and reflect current mechanistic understanding including uncertainty assessments; and,
- Recovery plans that include programs for monitoring and strategies for recovery that, if needed, facilitate timely intervention.

The NRC representative pointed out several key sources of uncertainty in predicting the performance of shallow land radioactive waste disposal facilities:[7]

- The time frame for regulatory analysis for waste isolation may extend to thousands of years or beyond, especially if long-lived isotopes are disposed in near surface environments. Such time frames may or may not be able to be addressed with research.
- Physical properties of engineered cementitious materials (and other engineered barriers) are difficult to measure and predict over long time periods (>100s of years).
- Unsaturated hydraulic properties and contaminant transport properties of engineered barriers are difficult to quantify, interpret, and predict under field conditions given the uncertainties involved in long term (100s to 1,000s of years) assessments.
- Limited experience and leaching data for the interaction between engineered barriers and certain radionuclides (e.g., Sn-126, Se-79, Np-237).
- Degradation mechanisms and long-term performance data of unique chemically engineered cement waste forms are limited in both availability and time frame.
- The influence of fractures on degradation mechanisms and degradation rates.

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[6] See presentation by Joe Ortaldo (SRS Citizens' Advisory Board).
[7] See presentation by David Esh (US NRC).

- Oxidation of reducing formulations over time when disposed of in oxidizing near-surface environments.
- Extension of laboratory-scale, short-term tests to large-scale, long-term applications.

The EPA representative acknowledged the limitations of the current leach tests used as pass/fail criteria for shallow land disposal (e.g., TCLP, ANS 16.1).[8] The representative indicated that the Agency has been seeking and developing alternative approaches and test protocols that provide the following improvements:

- Better accuracy over a range of conditions;
- Better foundation in basic science (i.e., less reliance on empirical relationships);
- Enhanced applicability in environmental assessments (i.e., groundwater fate and transport modeling);
- Applicability to a broad range of waste types and a range of conditions that affect leaching and disposal facility management; and,
- Validation of both the laboratory test methods and field comparability.

Ongoing efforts by researchers[9] to develop supplementary test protocols that take into consideration a mechanistic approach and understanding of leaching mechanisms are viewed favorably by the EPA Science Advisory Board. These efforts include collaborative research between Vanderbilt University and Energy Research Centre of the Netherlands and DHI Water & Environment (Denmark); the latter two organizations being involved in a parallel development program for the European Union under the Directorate General for Environment.

[8] See presentation by Susan Thorneloe (EPA, Office of Research and Development) and Greg Helms (EPA, Office of Solid Waste).
[9] This research is supported by in part by EPA.

RELATED INTERNATIONAL EFFORTS

Research efforts in several countries are focused on both practical and predictive aspects of using engineered cementitious barriers for radioactive waste disposal. Several countries (Canada, France and the United Kingdom) have invested in long-term (10 to 20 years) test programs to support materials design and aging studies.

France has a major research program on long-term performance of cementitious waste forms. This program is tied directly to the French Legal Reference Case for management of nuclear wastes[10]. French representatives at the workshop noted significant ongoing collaboration with the U.S. DOE on civilian nuclear power and related spent fuel management. However, collaboration with DOE-EM on waste management issues has not been substantially established. An eagerness to develop such collaboration was expressed.

One Canadian research group has made substantial progress in developing mechanistic models for predicting service life of concrete structures.[11] This effort is supported by an international industrial consortium which includes the U.S. Army Corps of Engineers. Mechanistic degradation analyses and durability prediction approaches that have been applied to and "tested" on conventional concrete applications provide an excellent starting point for evaluating, designing and improving containment structures and entombments for radioactive waste disposal.

A team effort between researchers from the Energy Research Centre of the Netherlands, DHI Water & Environment (Denmark) and Vanderbilt University (US) has made extensive progress in characterizing leaching phenomena and developing associated mechanistic release models for engineered cementitious materials (primarily waste forms) and wastes.[12]

Additional notable international research programs related to engineered cementitious materials used in waste applications are being carried out in the United Kingdom[13] and Switzerland. Areas of advancement include cement-waste interactions and the chemistry of contaminant transport.

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[10] See presentation by Christophe Gallé (CEA-Seclay).
[11] See presentation by Jacques Marchand (Laval University).
[12] See presentation by Susan Thorneloe (USEPA, Office of Research and Development) and Greg Helms (USEPA, Office of Solid Waste).
[13] See presentation by Fred Glasser (University of Aberdeen).

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DATA GAPS AND ISSUES

One outcome of the Workshop on the Use of Cementitious Barriers for Low-Activity Radioactive Waste Treatment, Containments, Environmental Restoration and D&D is a summary of perceived data gaps and issues associated with enhancing the performance of near-surface radioactive waste disposal sites through the use of engineered barriers. These needs are DOE complex-wide and fall into two categories:

1) Providing a technical basis for improving designs; and,
2) Reducing risk in predicting long-term performance.

Current data gaps and issues related to disposal of LAW in shallow land environments are listed below.

Standardized Practice

Performance Criteria

Standardized performance criteria and evaluation methods are needed for each of the primary engineered cementitious barriers used in the DOE complex, including waste forms, stabilization materials for high level waste tanks, environmental remediation, and entombment and encapsulation of decommissioning and demolition wastes. Availability of such standards would serve as a basis for a consistent approach across the DOE complex and provide a basis for comparison of treatment methods[14].

A complex-wide systems approach would also reduce the need for each new project to rediscover or develop new design specifications for test methods and requirements for physical properties, contaminant retention, and waste compatibility.

Issue/Gap: Currently, Although the performance objectives in specified in DOE O 435.1 provide a set of standards for assessing engineered barriers post-closure, DOE currently does not have a complex-wide guidance document(s) for:

- Establishing performance criteria and testing actual performance for individual/specific engineered barriers that are part of larger disposal units/facilities with numerous engineered barriers;
- Selecting appropriate test methods;
- Interpreting the test results; and,
- Using result to develop concepts and cases for deterministic performance models or in probabilistic models.

Performance Assessment Modeling

The need for predicting long-term performance of engineered cementitious barriers used in DOE LAW disposal facilities and HLW tank closure programs is driven by the need for disposal of long-lived mobile radionuclides. Such isotopes are often distributed throughout the DOE waste inventory in considerably higher abundance compared to commercial LAW. At the present time, each DOE performance assessment uses a *unique* strategy, set of assumptions,

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[14] The need for standardized methodology/criteria for comparing treatment approaches and selecting an appropriate technology is exemplified by the current need to manage and dispose of secondary wastes from the Office of River Protection Waste Treatment Plant.

boundary conditions (time frames, starting conditions), material properties from actual materials and various databases, structural analyses, computer codes, and approach to uncertainty analyses. The tendency in the DOE complex is to use computational analyses and numerous simplifying, "conservative"[15] assumptions to predict performance of LAW disposal sites, often with limited data or validation of assumptions.

Issue/Gap: A significant issue related performance assessments is the need for guidance on approaches and options for managing risk over the long time frames required as a consequence of the long-lived radionuclide inventory requiring disposal.

Characterization

Waste Characterization

Radiological, chemical, mineralogical, and physical characterization for each waste type is required to optimize the engineered cementitious barriers employed in the waste disposal system. Waste characterization requires samples of actual waste (e.g. tank residuals) or process flow sheets based on bench-scale and pilot-scale testing (e.g., Hanford secondary waste). Although collecting samples of radioactive waste is time consuming and poses ALARA concerns, accurate representation of the waste is essential for characterizing the solubility of the solid phases and the speciation of the soluble phases and thereby defining the starting conditions. Waste characterization data are also required for designing the engineered barriers, predicting the fate of the contaminants in the waste-engineered barrier composite systems, and preparing non-radioactive simulants for engineering property and constructability evaluations and feasibility demonstrations.

Issue/Gap: Characterization data is required for designing waste treatments and for prediction of engineered cementitious barrier performance under near-surface conditions. Samples of actual waste types are limited. Consequently, characterization data for actual waste is limited, both in the type of information generated and in the number of samples analyzed.

Needs exist for improving tools for:

- Retrieving radioactive waste samples from high-level waste tanks,
- Designing tools for in-tank radiological, chemical and mineralogical characterization of tank residuals,
- Designing in-line sampling and characterization techniques for liquid waste feed streams in processing facilities using cementitious materials, e.g., saltstone.

Methodologies for characterizing large volumes of material based on a small number of samples should also be reviewed. Certain characteristics such as mineralogy may be independent of the number of samples.

Micro-characterization techniques, such as, SEM and TEM, and electron beam techniques, such as, EXFAS and XANES, are underutilized for characterizing the mineralogy, contaminant speciation, and oxidation states of the radioactive components in the waste as well as in the

[15] In this case, "conservative" is meant to imply assumptions that intentionally over-predict release when further information is not available. Multiple levels of conservative assumptions have the cumulative effect of over-predicting contaminant release by 6 or more orders of magnitude (i.e., a factor of 1 million or more). In addition, some assumptions lack the required validation to assure that they are, in fact, conservative.

waste forms and engineered barriers. This information is needed to support contaminant mobility analyses in the required long-term performance assessments.

Test Methods

Numerous test methods are available for measuring physical properties, assessing susceptibility to specific types of degradation, evaluating leaching, and evaluating quality control of cementitious materials.

Issue/Gap: Although test methods are well established for commercial uses of cementitious materials, DOE does not have a set of standard test methods for characterizing waste, waste forms, and engineered barriers or a guidance document on methodology for developing a mechanistic understanding of the waste-engineered barrier-landfill system. DOE does not have a complex-wide database for test method information and data collected from a standardized test program.

Specific characterization and testing needs to support improved material designs and performance assessments are listed below:

Microstructure characterization: Data for actual waste forms is very limited. Additional data is needed to provide a better understanding of contaminant transport through cementitious barriers. The relationships between pore structure and leach rate and pore structure evolution as a function of aging or exposure to certain environmental conditions have not been adequately explored.

Hydraulic Properties: Test protocols for measuring hydraulic properties of cementitious barriers including concretes and waste forms containing large amounts of soluble salts are not available. The potential for using innovative test equipment, such as, the Unsaturated Flow Apparatus-Centrifuge method[16] and Princeton University Pulse-Response technique,[17] to characterize cementitious materials of interest to DOE have not been fully explored for cement waste forms and barriers.

Leaching properties: The methodology and leaching test for generating DOE performance assessment data are not standardized. Standardized leaching tests that reflect practical application of current mechanistic understanding for cementitious materials used in DOE waste disposal applications are needed to produce internally consistent results that can be applied throughout the complex and that are valid over time.

Currently, ASTM, EPA, or other standard methods are used in a manner that lacks internal consistency and rigor. Methods are often modified to adjust to unique materials properties or to satisfy specific test programs, and therefore, results are not transferable throughout the DOE complex or useful in comprehensive databases.

Mineralogy: Phase characterization data for wastes, waste forms, and waste-engineered barrier systems are very limited. This type of data is needed to develop concepts and cases for performance modeling by providing an understanding of the contaminant transport mechanisms.

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[16] See presentation by Jim Conca (Carlsbad Environmental Monitoring and Research Center).
[17] See presentation by George Scherer (Princeton University).

Many of the contaminants of concern are present in small quantities (mg/kg to g/kg), and therefore, may be suitable for nuclear characterization techniques such as EXFAS and XANES. Beam line capabilities and capacity at ANL and LBNL required for these techniques have not been fully utilized for waste and engineered barrier characterization.

Physical Properties: Physical property testing of actual engineered cementitious barrier materials (waste forms, concrete from in-service containments, environmental restoration and D&D activities) is limited. These data are needed to develop concepts, cases, and conditions for performance modeling. Physical property data is also required to support a consistent approach to long-term performance modeling of cementitious barriers.

Accelerated Aging: Guidance on the use of accelerated aging test results and analogous old and ancient material data is needed for a coherent complex-wide approach to using this information in long-term performance predictions.

The expert opinion at the workshop was divided on the possibility of developing useful accelerated aging test methods for evaluating the effects of time and exposure conditions (aging) engineered cementitious barriers. The use of old/ancient analogues was acknowledged as representative of only some of the aging phenomena relevant to engineered cementitious barriers used for radioactive waste disposal.

Long-Term Sample Archive Program

Long-term studies under current and aggressive environments are useful in identifying and understanding coupled chemical and physical mechanisms that impact performance. Such studies have been performed or are underway in other countries including Canada (vault concrete tested over 10 or 15 years), France and Switzerland to support LAW disposal programs.

Issue/Gap: DOE does not have a program to archive laboratory or field test specimens or actual samples of engineered barriers for long-term testing.

Contaminant Retention and Release Mechanisms

Transport Mechanisms

Transport mechanisms for soluble ions through saturated porous media are well established. The movement of liquid and gas through idealized cracks is a fairly routine computational fluid dynamics exercise and descriptions of crack expression in degraded concrete are available. However, these two fields have not been combined to produce an integrated model describing either the movement and exchange of gas and water, or the mass transfer of reactants (e.g., carbon dioxide, oxygen) and constituents of concern (e.g., radionuclides) in the engineered cementitious barrier systems.

Issue/Gap: Knowledge gaps include:

- Understanding liquid and gas phase transport in cementitious materials relevant to DOE under unsaturated conditions;[18]
- Identification of actual field conditions, in contrast to assumed, idealized field conditions;

[18] See presentations of Doug Hooten (University of Toronto) and Andy Garrabrants (Vanderbilt University).

- Interaction of the various mechanisms under laboratory and "field conditions;" and,
- Realistic representation of material structure on the micro- and macro- scale.

Contaminant Stabilization Mechanisms
Stabilization mechanisms for many radioactive isotopes and RCRA hazardous contaminants are well established and consist of chemical stabilization and micro/macro-encapsulation. However, this information is not readily applied to design of waste forms and other engineered barriers.

Issue/Gap: DOE does not have a guidance document on the stabilization chemistry and properties of engineered cementitious materials.

Aging/Durability
The affect of time and dynamic conditions, which vary in response to the local environment, on the ability of engineered barriers to control or influence transport of radionuclides is somewhat understood. Information applicable to time frames of 10s to a few 100s of years under conditions encountered in the construction industry provide a starting place for understanding long-term durability of engineered barriers. However, this information alone is insufficient for understanding and improving the longevity of cementitious materials used for engineered barriers in LAW disposal facilities containing long-lived isotopes that are required to perform for 100s to 1000s of years.

Issue/Gap: Knowledge gaps and needs include:

- Improved understanding of the consequences of multiple simultaneous processes and potential synergistic processes which may be either beneficial or antagonistic to long-term performance,
- Review of applicability of test methodology used to evaluate the susceptibility of cementitious materials to various chemical exposures and conditions encountered in the construction industry, and
- Predictive methodologies for assessing the uncertainty associated with identified aging processes.

Thermodynamic Data and Kinetic Evaluations
A foundation exists for thermodynamic and kinetic modeling of the evolution of cement microstructure and constituent leaching. However, data is not available for cementitious materials (hydrated matrix phases) formed in the presence of radioactive salt wastes and under conditions appropriate to DOE applications. Calculations used in the current thermodynamic predictions often rely on simplifications due to lack of system-specific thermodynamic data and typically do not address kinetic effects.

Issue/Gap: DOE does not have a complex-wide database for thermodynamic data that can be used in support of performance assessment modeling. In addition, DOE does not have a program to generate such thermodynamic and kinetic data or to support the use of such data for performance assessments.

Demonstrated and Measured Performance under Field Conditions

Pilot-Scale Field Testing

Pilot-scale testing and evaluation is an important step to understand the controlling mechanisms and rates of system evolution (e.g., constituent release, oxidation, physical degradation) and to confirm modeling approaches to be used for assessment purposes. The three major waste management sites (Hanford, Idaho, Savannah River) have sufficiently different environmental conditions to warrant pilot-scale testing at each site. Limited pilot-scale field testing has been performed on existing or planned engineered cementitious barriers and engineered cementitious systems for disposal of low-activity radioactive waste. A dramatic reduction in Tc-99 leaching from waste forms that contained slag cement was documented as part of an SRS environmental lysimeter test program which was terminated several years ago.[19] New pilot-scale field test can be expected to provide additional useful information.

Issue/Gap: Pilot-scale programs and field tests conducted in parallel with ongoing operations are needed to develop and refine concepts and cases for performance assessments and to improve design and operational activities. Guidance on designing pilot-scale field tests and on using field test results is also needed.

Monitoring Engineered Cementitious Barriers

Characterization of as-built engineered cementitious barriers and subsequent monitoring to detect changes in properties as a function of time is necessary to improve designs and operational activities and to develop and refine concepts and cases for performance assessments. Monitoring properties of existing engineered barriers as a function of time under operating conditions also enables tracking/comparison of actual and predicted performance over the short-term and provides validation of the base case.

Issue/Gap: Currently, DOE does not require monitoring programs for engineered cementitious barriers and wastes in as-built LAW disposal facilities. Lack of such monitoring has been cited as an important shortcoming by stakeholders, Nuclear Regulatory Commission reviews, and the National Academy of Sciences reports[20].

Defensibility and Credibility

Independent Expert Review

Independent expert review (peer review) is required by stakeholders for acceptance of DOE waste disposal projects. Independent expert review should reduce shortcomings in the current practices caused in part by failure to recognize gaps and/or to use known technology or methods.

Issue/Gap: The complexities of DOE-EM waste management and site restoration programs and the inconsistencies in the current test methodologies and assessment approaches indicate a need

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[19] See Wilhite, E.L., Clark, S.B., 1991. Low-Level Liquid Waste Disposal at the Savannah River Site: A Large Scale Demonstration of Saltstone. Proc. of Waste Management Symposium (WM '91).

[20] See *Tank Waste Retrieval, Processing and On-Site Disposal at Three Department of Energy Sites*, National Research Council, 2006. Also, see Advisory Committee on Nuclear Waste letter to NRC Chairman Klein of December 27, 2006 on the subject of using monitoring to build model confidence, and the letter of October 12, 2006 on evaluating the long-term performance of cement barriers for near-surface waste disposal.

for independent expert review and guidance for peer reviews that includes managing risk over the near term and long term.

Stakeholder Involvement

Active stakeholder involvement is an important programmatic component to insure that stakeholder concerns are appropriately addressed, to provide first-hand knowledge of program design and results to stakeholders, and to facilitate transparency.

Issue/Gap: There is a need to actively engage stakeholders in issue definition and design and implementation of programs to address specific data gaps. A workshop, such as the one reported here, is only one example of many opportunities for stakeholder involvement. Stakeholder involvement is especially important for field demonstration and monitoring programs.

Assessment Responsibility

The current organizational structure for many waste disposal DOE projects often relies on "site-level" management being responsible both for achieving successful operations and assessing performance via PA documents.

Issue/Gap: The current organizational structure that relies on site operations funding and direction of performance assessments has the potential to create the appearance of self-regulation or a conflict of interest both of which can compromise programmatic credibility.

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RECOMMENDATIONS

Programmatic recommendations to improve the understanding of engineered cementitious barriers should recognize and consider the decision making process that leads to the use of these materials in radioactive waste disposal facilities. The value and cost of collecting and analyzing various types of information are typically considered in a data quality objectives approach to identify the most cost effective actions for improving the overall system design basis and risk analysis, and reduce uncertainty. This approach is useful to help prioritize and decide the type of new data to collect and analyze.

The first recommendation is to establish and follow a data-quality-objectives and decision making process to determine the need for and cost effectiveness of new data. Some categories that might require new data to improve the risk assessment include:

- Waste inventory refinements and waste zone/contaminant phase properties;
- Conceptual model development;
- Base case(s) synthesis;
- Data quality (chemical, mineralogical, hydrological, and engineering properties);
- Probability density functions for input parameters for stochastic (uncertainty) analyses
- Release (leaching) mechanisms;
- Integrated systems level long-term barrier performance including caps, engineered cementitious barriers, and metal containers and tanks,
    - Material aging processes under environmental conditions,
    - Structural service-life prediction;
- Improved seismic analyses;
- Transient infiltration analyses, preferential pathways, and groundwater fluctuations; and,
- Special waste forms characterization and criteria

One outcome of this evaluation process is an appreciation for the potential of and relative importance of engineered cementitious barriers in achieving the overall system performance objectives. This evaluation also would highlight the sensitivity of barrier performance to material properties and design features such as thickness of the barriers.

Another practical benefit of an improved understanding of design features and material properties is the potential for cost savings and implementation of innovative technologies through more extensive use of performance specifications rather than materials specifications for procuring engineered materials (concrete vaults, tank fill materials, entombment materials, and environmental restoration treatments).

The following sections contain specific recommendations that are likely to provide high value to the improved design, performance analysis and reduction in uncertainty for the use of engineered cementitious barriers.

Standards of Practice

Guidance and Requirements

Develop guidance and requirements for use of cementitious materials in DOE-EM missions, including low activity waste forms, tank closure, subsurface remediation, and decommissioning and demolition activities. These applications are all shallow land disposal activities, where mitigation of long-lived and highly mobile isotope releases requires special consideration.

A panel of DOE and external experts can be employed to support programmatic risk reduction by defining:

- A checklist of considerations;
- The technical basis for the specified criteria;
- Quantitative standards or guidance to address the criteria; and,
- Rationale for site specificity and the tailored criteria.

Performance Assessments

Standardizing the approach for modeling system performance and engineered cementitious barrier performance and associated contaminant release from shallow land disposal facilities is recommended. Computational models to predict the service life of structures, durability of materials, gas and liquid transport properties, and contaminant release as functions of time and design conditions are available but require adaptation and integration for DOE-EM applications. Model integration requires consistency in the underlying theoretical basis and assumptions, and model components must accommodate evolution in the current state-of-knowledge.

One step in a standardized approach is to identify a set of relevant computational models and then integrate them into an internally consistent product. Based on interactions at the Workshop in December 2006, the following set of models and expertise is recommended for this task:

- 4Sight® (NIST) for evolution of materials properties;[21]
- STADIUM® (SUMMA Consortium) for service life prediction; and,[22]
- LeachXS®/ORCHESTRA® (ECN-DHI-Vanderbilt University) for fate and transport[23]

Updating the components of the integrated code on a 3 to 5 year interval as part of the current performance assessment maintenance program is also recommended.

Design

Design methodologies should incorporate the latest state-of-the-practice and be updated every 3-5 years. For long-term storage structures (greater than 75-year life expectancy), emphasis should be placed on highly durable construction materials and methods. Therefore long-term storage structures should not contain conventional steel reinforcement. Methods for repair and retrofit of existing storage facilities should also be developed. In the case of subcontracts for structural design and construction, a design-build approach with a system of

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[21] See presentation of Ken Snyder (NIST).
[22] See presentation of Jacques Marchand (Laval University).
[23] See presentation of Hans van der Sloot (Energy Research Centre of the Netherlands).

incentives/disincentives should be put in place related to immediate cracking and long-term durability.

Because cracking is a critical aspect of long-term durability for concrete structures, modern techniques for assessing the temperature distribution of mass concrete during hydration should be employed. Similar techniques should be employed to assess the effect of temperature gradients on designs to minimize cracking. Long-term storage structures are more likely to experience a relatively significant seismic event during their life-time and the probability of such an occurrence should be assessed. The degradation of the structure at the time of the event should be taken into account and performance-based design techniques should be used. Reduced scale laboratory testing of structures or components should be carried out to verify design approaches and predictions under simulated seismic activity.

New materials such as self-consolidating, engineered nanocomposite, and shrinkage compensating concrete offer advantages and should be investigated and assessed. To support the acceptance of new materials and methods standardized accelerated test methodologies should be established. The accelerated test methods should be used for purposes of comparison between different materials and methods.

Test Methods

Standardized test methods for generating data used in performance assessments are recommended. Standardized methods will save time, reduce costs, provide internally consistent data for DOE databases, improve acceptance of the data, and support independent peer reviews. The approach recommended for developing a set of standardized test methods appropriate for performance assessments of engineered cementitious barriers includes:

- Identifying a test methods team to identify consensus standard methods (e.g., ASTM or ISO test protocols) and identify development needs;
- Utilizing technical exchanges among the national laboratory personnel, academic experts and technical personnel from other international and government regulatory agencies (e.g., NIST, EPA);
- Developing improved test methods that reflect state of the art understanding and technologies. Examples of resources for developing innovative test methods include:
    - Leaching protocols developed by EPA in coordination with the European Union Directorate General for the Environment;
- Establishing facilities for testing radioactively contaminated materials;
- Developing accelerated testing methodologies for comparative studies between differing engineered concrete mix designs; and,
- Establishing controlled laboratory test methods for purposes of model validation.

Existing peer-reviewed test methods should be used to the greatest extent technically appropriate and practical. All new methods and procedures should be subject to independent peer-review.

Databases and Knowledge Retention

A recommendation is made to develop and maintain databases for:

- Physical and hydraulic properties;
- Materials aging and degradation mechanisms, rates, and consequences;
- Contaminant release modeling parameters (e.g., thermodynamics, kinetics and mass transfer characteristics);
- Field testing and implementation specifications, performance, actual operations, and lessons learned; and,
- Laboratory test results.

These databases will facilitate more efficient and cost effective system design, performance analyses, and operations. Databases should be kept current, peer-reviewed, and readily available to all sites and stakeholders.

Guidance, accountability and discipline are required for database programs. Consequently, establishing a responsible entity (a lead laboratory or organization) is essential. The approach recommended for setting up data bases includes:

- Identifying a database team to assess the current situation, identify gaps and recommend programs to support needs;
- Utilizing technical exchanges among the national laboratory personnel (e.g., SRNL, PNNL, INL), academic experts and technical personnel from other international and government regulatory agencies (e.g., NIST, EPA, NRC); and,
- Interfacing with the team working on standardized test methods.

Field Monitoring and Validation of Performance and Performance Models

Sample Archive Programs

A sample archive program for laboratory samples and as-built or implemented materials throughout the complex is recommended to support current and future durability and aging evaluations. Characterization of aged samples is required for monitoring changes, improving facility designs and predicting of systems service life. A sample archiving program is a cost-effective means of providing aged laboratory and actual samples.

Sample archive programs are needed at the Hanford reservation, the Idaho Site, and the Savannah River Site. The approach recommended for setting up an archive program includes:

- Developing a guidance document for archive programs including archiving protocols;
- Identifying organizations/personnel at each site to assess options and needs and to set up and run a site archive program; and,
- Providing facilities and programs for long-term sample retention.

Pilot-Scale Field Tests

Pilot-scale testing and field tests are recommended to evaluate assumptions used to construct base cases for performance modeling. If practical, field tests can be constructed along side operating facilities to evaluate site specific exposure conditions beyond those experienced by the actual engineered barriers, and improve/validate assessment models.

Pilot-scale tests can be used to evaluate response to seismic events and to the consequences of concurrent and sequential degradation mechanisms on materials and structural units. Pilot-scale and field tests also provide the opportunity to develop and test monitoring approaches and equipment.

Environmental conditions are sufficiently different at Hanford, Savannah River Site and the Idaho Site to warrant coordinated studies at each location. The approach recommended for setting up a pilot-scale and field testing program includes:

- Developing a brief guidance document on designing field tests including essential measurements and data collection to optimize the test value;
- Identifying organizations/personnel at each site responsible for assessing options and needs;
- Identifying opportunities for participation by independent research groups such as universities and NIST;
  - For example, the University of South Carolina has an environmental test bed with capabilities of simulating seismic forces on pilot-scale structures. Information obtained from such a facility can be used improve assumptions in the current performance assessment.
- Providing life cycle funding for field tests and pilot-scale tests.

Monitoring Program for Engineered Cementitious Materials

A program for monitoring the component materials and structures of existing disposal facilities, e.g., SRS saltstone and SRS E-Area Vaults, during the operational phase is recommended. The resulting information is needed to validate the base case(s) in the performance assessment modeling. In addition, monitoring of the as-built systems provides for early interventions, if necessary, to maintain acceptable system performance.

The monitoring systems should be tailored to the needs of the particular structure and should be robust and suited for the long-term. Data interpretation is a key aspect of long-term monitoring that should be addressed at the outset. In-situ evaluation techniques of storage facilities should be incorporated and further developed. In-situ evaluation (determining key response parameters under mechanical or thermal loading) provides key insight into the state of degradation that cannot be assessed with long-term monitoring. In-situ evaluation can be used in combination with long-term monitoring to better track the degradation mechanisms over time.

Guidance, accountability and discipline are required for monitoring programs. Consequently, establishing a responsibility and committing funds are essential. The approach recommended for setting up monitoring programs includes:

- Setting up a team with representatives from the DOE complex and consulting with international experts to develop a brief guidance document on monitoring and use of monitoring data;
- Setting up monitoring programs and identifying principal investigators;

- Identifying requirements for monitoring and monitoring techniques and methods;
- Identifying opportunities for participation by independent organizations such as universities and NIST and for developing and using innovative monitoring technology; and,
- Identifying funding options for long-term monitoring programs.

Defensibility and Credibility

Independent Review and Knowledge Exchange

Independent expert peer review at every stage in performance assessments is recommended. Embedding independent peer review as a program component is essential to assure application of the available state-of-knowledge, transparency and stakeholder acceptance.

Knowledge Exchange

More emphasis on technical exchanges among research scientists, risk assessment modelers, and operations personnel within the DOE complex and with independent experts is recommended. Opportunities for intra DOE-EM exchanges should be developed in addition to initiating and/or taking advantage of established radioactive waste disposal/management national and international technical exchanges and forums.

Stakeholder Involvement

Active stakeholder involvement is recommended to be included as an integral part of broad program planning and specific program components such as developing performance specifications, field demonstrations, and performance assessment base cases/conceptual models to insure that critical questions are identified and addressed, and to improve stakeholder understanding of program outcomes through direct interactions.

Independent Funding

Review and possible modification of the current approach to funding performance assessment is recommended to provide transparency and reduce the potential for perceived conflicts of interest. Currently, performance assessments are funded by site operations departments which have a vested interest in the outcome of the analysis. Possible alternatives to the current practice include:

- Funding performance assessments and related data acquisition with a combination of fund matching from headquarters and redirected operations funds; and,
- Better utilizing already committed funds to address some of the specific needs identified in this report.

Leveraging Resources

Leveraging DOE investments to advance the state-of-knowledge and practice for the use of engineered cementitious materials is strongly recommended. One approach to leveraging technology is to take advantage of parallel or related efforts at other Federal Agencies and International Radioactive Waste Management Agencies.

Needs that can be supported by leveraging programs and expertise at other Federal Agencies and Organizations include:

- Standardized performance assessment approaches (NIST and NRC);
- Standardized leaching assessment approaches (EPA); and,
- Improved fundamental understanding of material structure, durability and aging (NIST and the US Army Corps of Engineers).

Needs that can be supported by leveraging international radioactive waste management expertise include access to:

- Basic data (radiochemical and cementitious materials data) and technology exchange by collaborating with the French nuclear waste management research organizations (C. Gallé, French Atomic Energy Commission, CEA-Seclay);
- Service life prediction models used in the construction industry to support physical durability of containments structures by participating in the SUMMA Consortium (J. Marchand, Laval University, Canada);
- Mechanistic leaching test protocols and systems modeling codes that can support and improve the current performance assessments by participating in an existing European Union–US partnership (Energy Research Centre of the Netherlands, DHI Water & Environment, Denmark, and Vanderbilt University).[24]
    - The foundation exists for a very effective and efficient collaborative partnership between SRNL, NIST, Laval University, Vanderbilt University and ECN to develop a tool to support design and performance assessment of cementitious engineered barriers. Currently, these organizations each provide leadership in specific modeling and implementation areas. The proposed product of this partnership is a fully integrated set of modules which would provide an internally consistent approach for structural service life, material durability and contaminant release assessment that could be used at all of the DOE sites. The intent is to provide a next-generation-design basis and source term information for DOE system performance assessments.
- Support partnerships with local universities, for example, SRNL and the University of South Carolina in the development and implementation of long-term monitoring, in-situ evaluation, improved design of containment structures and development of accelerated test methods.

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[24] The authors make this recommendation while clearly acknowledging that they have institutional and other relationships that will benefit from its adoption. We do so because we believe the foundation already exists for a unique and very effective and efficient collaborative partnership between SRNL, NIST, Laval University, Vanderbilt University and ECN to develop a tool to support design and performance assessment. These organizations each currently provide leadership in specific model areas and implementation. The product of this partnership would be a fully integrated set of modules that provide a consistent approach for structural service life, material durability and contaminant release assessment that could be used at all of the DOE sites. This would provide a next generation design basis and source term information for system performance assessment.

Additional opportunities for leveraging funds, expertise and manpower may be realized by re-directing focus and funds already committed in related DOE programs such as:

- EM International Russian Program;
- Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University;
- Florida International University;
- MSE Technology Applications Inc., Butte, MN; and,
- Local universities with applicable expertise and facilities such as the University of South Carolina utilizing ORISE, EPSCoR, and other academic support programs.

Finally, there is extensive research being carried out at U.S. DOE National Laboratories, and foreign universities that is relevant to the DOE mission. A recommendation is made for DOE-EM in conjunction with the DOE-OS to identify basic research needs and support programs through an EM basic needs grant program.

ATTACHMENT 1. WORKSHOP PROGRAM

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Cementitious Materials for Waste Treatment, Disposal, Remediation and Decommissioning Workshop

Decemeber 12-14, 2006

Center for
Hydrogen Research

Aiken SC

VANDERBILT UNIVERSITY

Dear Participant,

On behalf of the Department of Energy, Savannah River National Laboratory, Vanderbilt University, and the Consortium for Risk Evaluation with Stakeholder Participation (CRESP), welcome to the Cementitious Materials for Waste Treatment, Disposal, Remediation and Decommissioning Workshop.

Each of you brings technical expertise and processing knowledge that will be essential to the successful completion of the of the many related projects and programs. You are tremendous assets to the Department of Energy and you have our thanks for investing your time and talents in this workshop.

By working together, we can effectively use this workshop and the relationships established here to further the technical projects and programs necessary for the use of Cementitious Materials for Waste Treatment, Disposal, Remediation and Decommissioning.

We look forward to enthusiastic sharing of information and generation of ideas during our time together to the benefit of each of us and The Department of Energy.

M. A. Gilbertson
Department of Energy Deputy Assistant Secretary for Engineering and Technology, Office of Environmental management, EM 20

Dr. G.T. Wright
Laboratory Director, Savannah River National Laboratory

Dr. J.E.Marra.
Associate Laboratory Director, Savannah River National Laboratory

Technical Review Committee

M. A. Gilbertson
Department of Energy Deputy Assistant Secretary for Engineering and Technology, Office of Environmental Management, EM 20

Dr. G. T. Wright
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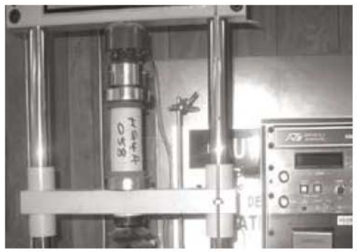

Program Organizers

Dr. C. A. Langton
Savannah River National Laboratory

H. F. Sturm
Savannah River National Laboratory

Dr. D. S. Kosson
Vanderbilt University

Dr. A. C. Garrabrants
Vanderbilt University

Reception and Mixer Sponsors

A very special thanks to CH2M-Hill, Vanderbilt University and Washington Group International , sponsors for the Tuesday and Wednesday Night Reception and Mixer.

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CRESP

Agenda *

Monday- December 11, 2006

Leach XS training (optional) 8:00 am to 5:00pm

Early registration 9:00am to 4:00pm

TUESDAY- December 12, 2006
Morning Sessions

Welcome and Plenary Speaker

Time	Title	Authors/*Speaker	Org.
7:30a	REGISTRATION		
8:30a	Introductions	C. Langton[1], D. Kosson[2], H. Sturm[1]	[1]SRNL, [2]VU
	Welcome	W. Spader[1], G.T. Wright[2]	[1]DOE-SR, [2]SRNL
	Workshop Objectives	C. Langton[1], D. Kosson[2]	[1]SRNL, [2]VU
9:00a	Plenary Session	M. Gilbertson	DOE-EM
9:30a	Questions		

Session 1A

Role of Cementitious Materials in Meeting Regulatory and Stakeholder Requirements for DOE LLW Disposal: Panel

Session Chair: Susan Thorneloe, EPA-ORD*
Session Co-Chair: Howard Pope, DOE-SRS*
Session Co-Chair: Michelle Ewart, DOE-SRS*

Time	Title	Authors/*Speaker	Org.
9:45a	Decommissioning Project Remnant Considerations	G. Hannah	DOE-SR
10:00a	Hanford Tank Farm Closure Mission	M. Jaraysi	CH2M-Hill Hanford
10:15a	Impacts of Secondary Waste on Near-Surface Disposal Facility at Hanford	B. Mauss	DOE-ORP
10:30a	Grout Attributes Important to SRS HLW Tank Closure	S. H. Reboul, J. L. Newman	WSRC-SRS
10:45a	Break		
11:00a	Citizens Advisory Board Perspective	J. Ortaldo	CAB-SRS
11:15a	South Carolina DHEC Perspective	S. Sherritt	SCDHEC
11:30a	Regulatory Considerations for Use of Cementitious Materials in High Level Waste Tanks at Hanford	*J. Lyon, M. Barnes	WA Dept. of Ecology
11:45a	EPA Perspective	G. Helms	EPA Office of Solid Waste
12:00p	NRC Perspective on the Use of Cementitious Materials in Radioactive Waste Management	D. Esh	NRC
12:15p	Questions		
12:30p	Lunch		

**Chair and Co-Chair will prepare summaries of information from their sessions which will be presented at the Thursday morning session.*

TUESDAY- December 12, 2006
Afternoon Sessions

Session 1B
Chemical and Mineralogical Properties and Containment Transport Properties in Cementitious Materials

Session Chair: David Kosson, Vanderbilt University*
Session Co-Chair: Miles Denham, Savannah River National Laboratory*

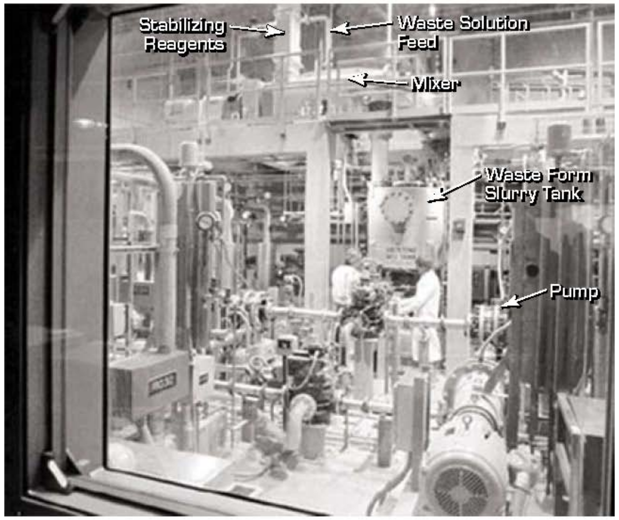
Time	Title	Authors/*Speaker	Org.
1:30p	Conceptual Models and Approaches to Understanding Long-Term Performance of Cementitious Waste Forms	*F. Sanchez[1], D. S. Kosson[1], A. Garrabrants[1], H. van der Sloot[2], C. Langton[3], G. Flach[3]	[1]VU, [2]ECN, [3]SRNL
2:00p	Estimated Contaminant Release Concentrations from Closed Hanford Tanks	*W. Deutsch, J. Serne, K. Cantrell, K. Krupka, M. Lindberg, C. Brown	PNNL
2:30p	Modeling and Thermodynamic Properties of Cement Hydrates to Estimate Their Stability in a Temperature Range 0-100°C: Implication in Terms of Degradation	*B. Huet, G. Scherer	Princeton U
3:00p	Break		
3:15p	Predicting the Service-Life of Concrete Structures Exposed to Chemically Aggressive Environments	J. Marchand	Laval U
3:45p	Reactive Transport Modeling of Leaching Tests and Long-term Processes Applied to Cementitious Waste Disposal	*L. De Windt[1], R. Badreddine[2], J. van der Lee[1]	[1]EMP, [2]INERIS France
4:15p	Modeling Chemical Speciation and Release from Cement Stabilized Wastes Using LeachXS	H. van der Sloot	ECN

Session 1B continued

Time	Title	Authors/*Speaker	Org.
4:45p	Estimated Duration of the Subsurface Reducing Environment Produced by the Z-Area Saltstone Disposal Facility	*D. Kaplan, T. Hang	SRNL
5:05p	Questions		
5:15p	Poster Session and Reception - Sponsored by CH2M Hill		

**Chair and Co-Chair will prepare summaries of information from their sessions which will be presented at the Thursday morning session.*

Session 1A & 1B Follow-Up
Time and location will be provided for additional input and follow-up on topics covered in Session 1A and Session 1B. Discussion will be informal and coordinated by session chair and co-chair.



WEDNESDAY- December 13, 2006
Morning Sessions

Session 2A
Water and Gas Transport Through Cementitious Materials

Session Chair: Florence Sanchez, Vanderbilt University*
Session Co-Chair: Gregory Flach, Savannah River National Laboratory*

Time	Title	Authors/*Speaker	Org.
8:00a	Intermediate Long-Lived Nuclear Waste Management: An Integrated Approach to Assess the Long-Term Behavior of Cement-Based Materials in the Context of Deep Disposal	*C. Galle, H. Peycelon, P. Le Bescop, S. Bejaoui, V. L'Hostis, B. Bary, P. Bouniol, P. Richet	DANS/ DPC/ SCCME France
8:30a	Measuring Liquid Permeability in Saturated Cement Paste and Concrete	G. Scherer	Princeton U
9:00a	Measuring Transport Properties in Grout	*J. L. Conca[1], J. Wright[2]	[1]NMWU, [2]UFA Ventures
9:30a	Testing and Standards Related to Fluid and Chemical Transport	D. Hooton	U of Toronto
10:00a	Break		
10:15a	The Impact of Moisture Transport on the Release of Constituents from Cement-Stabilized Materials Stored in Intermittently Saturated Environments	*A. Garrabrants, F. Sanchez, D. Kosson	VU
10:45a	Diffusion of Cementitious Pore Fluids into Boom Clay from a Deep HLW Disposal Site: Modeling of a Laboratory Experiment and Long-Term Interaction	*J. Diederik, L. Wang, P. De Canniere	SCK-CEN Belgium
11:15a	Leaching of Trace Elements from Materials Stabilized with Cementitious Coal Fly Ash	C. Benson	U of Wisconsin

Session 2A continued

Time	Title	Authors/*Speaker	Org.
11:45a	Studies of Tritium Characterization in Concrete at the Savannah River Site	R. Hochel, *E. Clark	SRNL
12:05p	Lunch		

**Chair and Co-Chair will prepare summaries of information from their sessions which will be presented at the Thursday morning session.*

WEDNESDAY- December 13, 2006
Afternoon Sessions

Session 2B
Degradation Mechanisms and Test Methods, Durability Criteria and Long-Term Degradation Evaluation

Session Chair: Christine Langton, Savannah River National Laboratory*
Session Co-Chair: Mark Phifer, Savannah River National Laboratory*

Time	Title	Authors/*Speaker	Org.
1:00p	Re-Use of Waste and Behaviour of Heavy Metals: A Molecular Approach of the Transfer Mechanisms	J. Rose[1], P. Chaurand[1], A. Benard[2], J. Bottero[1]	[1]CEREGE [2]INERIS France
1:30p	A Review of Diffferent Forms of Sulfate Attack	D. Hooton	U of Toronto
2:00p	Microbial Induced Degradation of Cement-Solidified Waste Forms for Radioactive Waste Disposal	*N. Egiebor, M. Idachaba	Tuskegee U
2:30p	Break		
2:45p	Technical Issues on Laboratory Study Methodology to Assess Long-Term Release of Contaminants from Grout/ Cement in the Vadose Zone	R. Serne	PNNL

Session 2B continued

Time	Title	Authors/*Speaker	Org.
3:15p	Numerical Simulation of Concrete Durability Under Coupled Deterioration Processes	D. Chen, S. Mahadevan, *D. Kosson	VU
3:45p	Past, Present and Future Research on Concrete Degradation Modeling at The National Institute of Standards and Technology	K. Snyder	NIST
4:15p	Fluidized Bed Steam Reforming (FBSR): A Novel Process for Mineralizing Wastes	C. Jantzen	SRNL
4:45p	Alternatives for Low-Temperature Waste Immobilization	J. Westsik, Jr., *R. Serne	PNNL
5:15p	Questions		
5:30p	Poster Session and Mixer - Sponsored by CRESP, VU and WGI		

**Chair and Co-Chair will prepare summaries of information from their sessions which will be presented at the Thursday morning session.*

Session 2A & 2B Follow-Up

Time and location will be provided for additional input and follow-up on topics covered in Session 2A and Session 2B. Discussion will be informal and coordinated by session chair and co-chair.

THURSDAY- December 14, 2006
Morning Sessions

Session 3A

Long-Term Performance Predictions and Risk Assessment Integration of Cementitious Materials in PA Modeling

Session Chair: Andrew Garrabrants, Vanderbilt University*
Session Co-Chair: David Esh, Nuclear Regulatory Commission*

Time	Title	Authors/*Speaker	Org.
8:00a	Risk-Based Radionuclide Derived Concentration Guideline Levels for Concrete Slab End States	T. Jannik	SRNL
8:30a	Probabilistic Assessment of Long-Term Concrete Vault Durability in a Sulfate Bearing Waste Environment	*G. Flach, M. Denham, M.Phifer	SRNL
9:00a	Initial Single Shell Performance Assessment for the Hanford Site	*M. Connelly[1], M. Jaraysi[1], M. Wood[2]	[1]CM2Hill, [2]Fluor Hanford
9:30a	Kalman Filtering as Part of a Long-Term Monitoring Strategy	K. Shyder	NIST
10:00a	Cement Condition of Nuclear Waste; Where Do We Go?	F. Glasser	U of Aberdeen Scotland
10:30a	Break		

**Chair and Co-Chair will prepare summaries of information from their sessions which will be presented at the Thursday morning session.*

Session 3B

Path Forward: Key Gaps in Knowledge and Practice, Opportunities for Alternative Approaches and Improvements

Session Chair: David Kosson, Vanderbilt University*
Session Co-Chair: Christine Langton, Savannah River National Laboratory*

Time	Title	Authors/*Speaker	Org.
10:45a	Session 1A Overview	S. Thorneloe[1], H. Pope[2], M. Ewart[2]	[1]EPA-ORD [2]DOE-SR
11:00a	Session 1B Overview	D. Kosson[1], M. Denham[2]	[1]VU [2]SRNL
11:15a	Session 2A Overview	F. Sanchez[1], G. Flach[2]	[1]VU [2]SRNL
11:30a	Session 2B Overview	C. Langton, M. Phifer	SRNL
11:45a	Session 3A Overview	A. Garrabrants[1], D. Esh[2]	[1]VU [2]NRC
12:00	Closing Remarks	D. Kosson[1], C. Langton[2]	[1]VU [2]SRNL
12:15p	Adjourn	J. E. Marra	SRNL

**Chair and Co-Chair will prepare summaries of information from their sessions which will be presented at the Thursday morning session.*

Poster Session

Session Chair: Amitava Ganguly, Bechtel Savannah River, Inc.*
Session Co-Chair: Dan Kaplan, Savannah River National Laboratory*
Session Co-Chair: Ken Dixon, Savannah River National Laboratory*

Poster Title	Author(s)	Org
Application of Cement Grout for In-Situ Treatment of Radioactive Wastes in Seepage Basins at SRS	A. Ganguly	Bechtel Savannah River Co, Inc.
Consolidated Tank Closure System Demonstration	J. Faldowski	AEA
Hanford Site Cement-Based Waste Stream Solidification Studies	*B. Clark[2], L. Lockrem[3], G. Cooke[3], M. Avila[1], R. Westberg[1], M. Silsbee[2], R. Lee[2]	[1]Center for Laboratory Sciences, Pasco WA [2]RJLee group, Inc., [3]CH2M Hill Hanford Group, Inc., [4]Fluor Hanford, Inc., [5]Fluor Federal Services
Spatial Distribution of Contaminants in Shallow Landfills	L. Collard	SRNL
Cement Solidification of Ammonium Sulfate Rich Basin 42 waste Water from the Hanford Effluent Treatment Facility	*G. Cooke[3], L. Lockrem[3], M. Avila[1], R. Westberg[1], M. Silsbee[2], M. Guthrie[4], G. Koci[5], K. Lueck[4]	[1]Center for Laboratory Sciences, Pasco WA [2]RJLee group, Inc., [3]CH2M Hill Hanford Group, Inc., [4]Fluor Hanford, Inc., [5]Fluor Federal Services
Review of Radiolysis Studies on Cementitous Waste	*C. Crawford, N. Bibler	SRNL
Pretreatment of Tc-Containing Waste and Its Effect on 99Tc Leaching from Grouts	A. Aloy[1], E. Kovarskaya[1] J. R. Harbour[2], C.Langton[2], E. Holtzscheiter[2]	[1]KRI Russia [2]SRNL
Remediation of the SRS P-Area Reactor Seepage Basins	J. Bradley	BSRI

Poster Session continued

Poster Title	Author(s)	Org
Results on Cementitious waste Forms – Collaboration Between Khlopin Radium Institute and SRNL	*J. Harbour[1], A. Alloy[2]	[1]SRNL, [2]Khlopin Radium Institute
Groundwater Barriers & Base Injection "A Low Cost Solution to Manage Radioactive Contaminants at SRS"	M. Hartz	BSRI
Novel Methods to Characterize Cementitious Materials for Performance Assessment Calculations	E. Mattson[1], *K. Dixon[2], *M.Phifer[2]	[1]INL, [2]SRNL
Analysis and Solidification of Tritiated Water – Evaluation of SRS Vault Limits and Investigation of Polymers, Zeolites and Various Cementitious Matrices	*L. Oji, C. Crawford, C. Langton	SRNL
Integral Waterproofing Admixtures	J. Taylor	Kryton International Inc.
Applications for Shrinkage Compensating Concrete	L. Valentine	CONEX, Inc.
Toxicity Characteristic Leaching Procedure Applied to Radioactive Saltstone Containing Tetraphenylborate: Development of a Modified Zero-Headspace Extractor	*K. Crapse, A. Cozzi, C. Crawford, A. Jurgensen, J. Zamecnik, C. Langton, D. M. Missimer	SRNL
Emergency Pump Well Mitigation and Decommissioning in L-Area Complex Basin at SRS by Underwater Placement of Controlled Low Strength Material: Mix Design and Demonstration	*A. Duncan[1], W. Hinz[1], C. Olson[2], W. Mhyre[3], J. Cook[3]	[1]SRNL, [2]BSRI, [3]WGI
Structural Engineering Support of SRS Waste Disposal Projects	W. Kennedy	WSRC

Poster Session continued

Poster Title	Author(s)	Org
Measurement of Hydraulic Conductivity of Cementitious Materials Using Radioactive Tracer Methods	*D. Taylor, D. DiPrete, C. Langton	SRNL
Evaluation of Organic Vapor Release from Cement-based Waste Forms, Part I: Testing	*A. Cozzi, R. Eibling, J. Zamecnik	SRNL
Evaluation of Organic Vapor Release from Cement-based Waste Forms, Part II: Analysis	*R. Eibling, A.Cozzi, J. Zamecnik	SRNL
Evaluation of Organic Vapor Release from Cement-based Waste Forms, Part III: Modeling	*J. Zamecnik, A. Cozzi, R. Eibling	SRNL,

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ATTACHMENT 2. SUMMARY OF WORKSHOP PRESENTATIONS

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Session 1A. Role of Cementitious Material in Meeting Regulatory and Stakeholder Requirements for DOE LLW Disposal: Panel

This session was chaired by Susan Thorneloe of the Environmental Protection Agency Office of Research and Development, with Howard Pope and Michelle Ewart of the Department of Energy Savannah River Office serving as co-chairs.

The first presentation by Ray Hannah of the DOE-SR Closure Project was titled, "Decommissioning Project Remnant Considerations". The scope of D&D at SRS is that over 1000 facilities have been identified for decommissioning, with 270 having been completed. Work is scheduled to be completed by 2025. For the simple, less complicated facilities the decommissioning end point is to remove the facility down to its concrete pad. For large, hardened facilities such as reactors and canyons a choice needs to be made between complete removal or an in-situ endpoint. Cementitious materials play a role in either choice. The concrete pad may contain residual contamination. The in-situ option can use cementitious materials to provide structural stability, reduce contaminant mobility and to provide contaminant isolation. The decision as to which option to choose and how to best use cementitious material will be made by considering risk to workers, the general population and the environment. Opportunities exist to improve our understanding of concrete as a material to reduce contaminant mobility and the long-term durability of cementitious materials.

Moses Jaraysi of CH_2MHill at the Hanford Site presented "Hanford Tank Farm Closure Mission". He began with an overview of the hydrology and geography of the Hanford site. The current tank closure program focuses on the 149 single shell tanks built between 1949 and 1964 that contain 33 million gallons of radioactive waste and are not in compliance with regulations. The conceptual design to stabilize and isolate the single shell tanks uses three layers of grout. The first layer is 30 to 90 cm thick and consists of a free-flowing grout that will cover the residual materials at the bottom of the tank. The next layer of grout will enhance the stability of the tank and will fill the majority of the tank. The final layer will consist of a high compressive strength grout that will fill the remaining tank space and act as a deterrent to future intruders. The tanks will be covered with a multi-layer cap to provide defense in depth. Technology needs exist in the areas of grout properties for tank stabilization, retrieval of residuals in ancillary equipment, residuals characterization and defining closure alternatives for ancillary equipment. Closure decisions will be made as part of the Tank Closure and Waste Management EIS, DOE Order 435.1 compliance and RCRA permitting. Awaiting these decisions, the C-200 Demonstration Project was formed as a collaborative DOE/Regulatory Agency project to identify and implement D&D needs for closure of a tank farm.

Billie Mauss of the DOE Office of River Protection next presented "Impact of Secondary Waste on Near-Surface Disposal Facility at Hanford." At Hanford the Integrated Disposal Facility will be used to dispose of Immobilized Low Activity Waste (ILAW), which is vitrified low-level waste, secondary waste from the production of the ILAW and other Hanford site and DOE low-level waste. Performance assessment work has shown that the most significant waste is the secondary waste, primarily I-129 produced during the vitrification process. There is a need for a low-temperature waste form that will improve retention of the secondary I-129. Four waste forms are being tested, 1) Alkali Aluminosilicate Hydroceramic, 2) Phosphate Bonded Ceramic, 3) Alkali Aluminosilicate Geopolymer and 4) Cast Stone (grout).

Scott Reboul, Washington Savannah River Company, presented "Grout Attributes Important to SRS HLW Tank Closure." At SRS, the Tank Farm lifespan is nearing completion. The tanks will be emptied, grouted and closed to reduce risk and retard environmental releases. The attributes of the grout to be used are the key to the long term performance. The approach being used is to identify the grout attributes that are important to tank closure, prepare grouts with these attributes for laboratory testing, identify attribute variations and use modeling to predict potential impacts. In order of decreasing priority, the attributes of most interest are low hydraulic conductivity, degradation resistance, pore water chemistry (high pH, low Eh) strength and flowability. The path forward is to perform near-term testing to measure attributes, analyze the results and incorporate the test results into modeling.

Joe Ortaldo of the SRS Citizen's Advisory Board gave a talk "Citizens Advisory Board Perspective." The SRS CAB consists of 25 members of the public and 7 ex-officio members from DOE, EPA, SCDHEC and GaDNR. The CAB has been in existence for 10 years and in that time has made 240 recommendations to DOE. The CAB is organized into five committees, Administrative, Facilities and Legacy Management, Nuclear Materials, Strategic and Site Remediation and Waste Management. The CAB perspectives are 1) Regulatory-accepted monitoring with appropriate oversight, 2) Peer-reviewed technology demonstrated at an adequate scale, 3) Peer-reviewed performance prediction model and 4) Contingency plan of performance does not meet requirements or predictions.

Shelly Sherritt, SCDHEC, gave a talk "South Carolina DHEC Perspective." Her talk was based on three characteristics of concrete, it is hard, grey and it cracks. Because concrete is hard it can be used for many purposes in waste management, including keeping solids in or out, as an intruder barrier, as disposal containers, to fill voids, to prevent subsidence, as secondary containment for liquids, for tank construction and to make large disposal vaults, such as for Saltstone. The color of the concrete indicates that the mix formulation can be adjusted to suit difference purposes. The fact that concrete cracks indicates that it should not be used for closure caps where soil, clay and High Density Polyethylene are better choices.

"Regulatory Considerations for Use of Cementitious Materials in High Level Waste Tanks at Hanford" was given by Jeffery Lyon of the State of Washington Department of Ecology. The high level waste tanks at Hanford are regulated by both Federal and State agencies. The current status of the tank farms is that the tanks are considered "Unfit for Use", 33% of the 149 single shell tanks are considered leakers, many tanks have spills associated with them, all of the tanks farms have significant soil contamination and indications of groundwater contamination. The considerations for use of cementitious materials for tank closure include the condition of the tanks, access into the tanks, different waste types, retrieval effects, placement effects on waste residuals, demonstration and research needs and short and long term needs.
Demonstration/research needs with respect to the chemistry of the cementitious material incorporation of technetium and uranium, leach rate testing methods, development of meaningful, predictive tests, maximized retardation and minimize impacts and control of release

rates. Wastes from a variety of processes were stored in the Hanford tank farms including: PUREX, Hot Semi Works, RedOx, bismuth phosphate reprocessing, and uranium and fission product recovery.

Susan Thorneloe of the US EPA Office of Research and Development presented "Developments in Leach Testing." EPA regulates waste management under RCRA. Leach testing has been used in regulatory programs to help determine what waste is hazardous and what treatment is adequate. TCLP is the most used leaching test. The TCLP test was designed as a screening test to consider leaching that may occur in a municipal solid waste landfill. Radiological wastes are not regulated under RCRA, but mixed waste is. The TCLP evaluation method is used when it is not required, as in beneficial reuse programs. The EPA Science Advisory Board has expressed concerns about the over-broad use of TCLP and urged research and development work toward new tests. New tests should consider the factors that affect leaching, such as waste form, pH, infiltration redox conditions and others. The tests should be capable of field validation.

David Esh of the US Nuclear Regulatory Commission Division of Waste Management and Environmental Protection presented "Regulatory Perspective on the Use of Cementitious Materials in Radioactive Waste Management." The NRC is interested in the application of cementitious materials to waste management, in particular in the main functions that the materials play such as limiting water contact with waste, limiting intrusion, chemical retention of radionuclides, shielding and waste stabilization. The issues with cementitious materials depend upon the duration, magnitude and characteristics of the hazard being mitigated. Justification of performance beyond 500 years may be very challenging. Long time frames create uncertainty which may or may not be addressed by research. The primary applications of cementitious materials that are of interest to the NRC are grouting of tanks, disposal vaults, sealing and filling of voids and cementitious waste forms. Uncertainties associated with cementitious materials in waste isolation include hydraulic properties of long times, unsaturated properties, retention properties, degradation mechanisms, the influence of fractures on degradation, oxidation of reducing waste forms and the extension of laboratory-scale short-term tests to large-scale, long-term applications. Some areas of research that may be tractable include development of accelerated laboratory-scale tests methods, compilation of a data base of international experiences, experiments to estimate retention properties for lesser studied radionuclides and experiments to evaluate potential synergisms between degradation mechanisms including the impact of fractures.

Session 1B. Chemical and Mineralogical Properties and Contaminant Transport Properties in Cementitious Materials

This session was chaired by David Kosson of Vanderbilt University and Miles Denham of the Savannah River National Laboratory.

"Conceptual Models and Approaches to Understanding Long Term Performance of Cementitious Waste Forms" was presented by Florence Sanchez of Vanderbilt University. The work was a collaboration with Vanderbilt, Netherlands Energy Research Centre, DHI (Denmark), SRNL and PNNL. The primary factors affecting constituent release by leaching from cementitious waste forms are the integrity of the engineered and institutional systems and the waste form performance. The constituents of most concern are the long-lived and mobile radionuclides, such as Tc-99, Np-237, Se-79, I-129, C-14 and the uranium isotopes, as well as the mobile constituents Cs-137, Sr-90, nitrate and H-3. The conceptual model of physical integrity and water contact of the waste forms is that cracks develop that increase the solid-liquid surface are, bridging of micro-cracks create macro-cracks that develop into through cracks which lead to convective flow. The conceptual model of moisture transport is that the waste form consumes water via hydration reaction, but exchanges water with the surrounding environments by evaporation/condensation, capillary suction and intermittent wetting by infiltration. The resulting water content then determines the gaseous degradation processes such as oxidation and carbonation and the constituent diffusion pathways. The conceptual model of oxidation rate and extent is that the waste form pores are a two phase system – gas and water - that depends on the degree of saturation of the waste form. The conceptual model of leaching of major and trace constituents is that it is described by moving dissolution fronts that are affected by precipitation/reaction processes near the external boundaries and $Ca(OH)_2$ and CHS control of water pH. Long term degradation is an integrated process of chemical and physical effects. LeachXS is a software tool that has been developed for integrating experimental data, model development, parameter estimation and prediction. It incorporates multiple processes and system configurations, has data management and interpretation features, provides geochemical analysis and has a data base of material leaching information. Processes are not included in current DOE performance evaluations that can impact constituent release. CRESP and SRNL are currently working together to provide the needed evaluation system components.

Bill Deutsch of Pacific Northwest National Laboratory presented "Estimating Contaminant Release Concentrations from Hanford Tanks." Contaminant release models quantify the release from residual waste to the environment. These are important because slow release may limit risk to an acceptable level. Knowledge of the waste and the contaminant release mechanisms provides confidence in a performance assessment and can reduce uncertainties and conservatism. Hanford has a program to test residual waste that uses leaching tests, X-Ray diffraction, scanning electron microscope/energy dispersive spectroscopy and selective chemical extractions. The data is used to develop a contaminant release model that identifies the controlling solids using chemical equilibrium calculations and analytical data. Mechanistic models are more defensible than empirical models, however empirical models are necessary when the release mechanisms cannot be determined. They have a program to determine total contaminant concentrations in residual sludge sample to provide an upper limit on future releases. They also perform single contact and sequential contact leach tests using double deionized water, $Ca(OH)_2$ saturated solutions and $CaCO_3$ saturated solutions because the composition of infiltrating water will alter the release model. One of the results is a uranium mechanistic release model for tank C-203 sludge in which cejkaite solubility and uranium release is limited by the presence of soluble $NaNO_3$. Releases from a tank must consider contaminant interactions with the tank filler grout and tank components such as steel and concrete.

"Thermodynamics of Cement Degradation" was given by Bruno Huet of Princeton University. The work looked at the thermodynamic properties of cement the hydrates calcium silica hydrate, calcium aluminate trisulfate, calcium aluminate monosulfate and hydrogarnet. There is a lack of exhaustive data sets of this information. The work of Helgeson 1979 was used to estimate heat capacities and entropies. The substitution of Cl^-, OH^- and SO_4^{-2} into hydrate phases was investigated. Water is released for hydrates as they degrade, which leads to diffusion driven advection.

Jacques Marchand of Laval University in Canada presented "Predicting the Service-Life of Concrete Structures Exposed to Chemically Aggressive Environment." The talk covered work to develop a modeling tool to predict concrete degradation STADIUM. This is a multi ionic reactive transport model that handles diffusion, electrical coupling, chemical activity and advection. It is a one-dimensional, finite element model with 11 equations in 11 unknowns. The input parameters are concrete mix properties and binder composition, porosity, pore solution chemistry, diffusion coefficients and water diffusivity. Eight years of experimental data has been collected and is used to validate the model leaching, sulfate attach and chloride attack predictions of the model.

The paper "Reactive Transport Modeling of Leaching Tests and Long-Term Processes Applied to Cementitious Waste Disposal" was given by Laurent DeWindt of the Ecole des Mines in France. Dynamic leach tests can be used to better characterize the long-term evolution of cementitious waste forms. Understanding leaching mechanisms can allow extrapolation of laboratory results to engineered systems. The objective of the work is to develop a common modeling approach and code that can be applied to different scale and is as mechanistic as possible. Reactive transport codes are good candidates to meet the objective. This work used the HYTEC reactive transport code with a three dimensional cylindrical geometry. The work consists of three stages. The first is the Initial State. This was addressed by comparing model runs with batch leaching tests of cementitious samples containing 1% lead. Stage 2 is dynamic leaching. This was investigated looking at the edge effect, the interface of the outside surface of the sample with the leach solution using sodium release. Stage 3 is On-site Evolution vs. Scenarios. In this stage three cases were studies, intact, macro-fractures and a micro-crack network. The conclusions presented were: 1) modeling of the initial state required preliminary analyses and batch leaching tests, 2) the core source term model lead to the development of a dynamic leaching 3D simulations considering simultaneously pore water evolution, mineralogical alteration fronts and the concomitant release of elements, which showed efficient containment of lead, 3) process modeling is time consuming and the waste evolution was not fully addressed because of the complexity of cementitious materials and the lack of sorption data, 4) reactive transport codes can be used to extrapolate laboratory to site scenarios, 5) reactive transport codes can support performance and environmental impact assessments, and 6) the major perspectives for further work are for unsaturated modeling, sorption data and redox states.

Hans van der Sloot of ECN in The Netherlands presented “Modeling Chemical Speciation and Release from Cement Stabilized Waste Using LeachXS.” A database/expert system called LeachXS has been developed to facilitate data retrieval, test comparison, modeling and scenario evaluation. For geochemical speciation/transport ORCHESTRA is the modeling framework used. LeachXS has three data bases, material leaching, scenarios and regulatory. ORCHESTRA contains a thermodynamic database. The steps in chemical speciation modeling are: 1) pH dependence leaching tests on granular material or size reduced monolithic material, 2) measurement of release from granular materials in percolation tests or from a monolithic specimen in a tank test, 3) speciation modeling using LeachXS and ORCHESTRA to identify relevant mineral phases, 4) prediction of leaching behavior in a pH dependence test providing a chemical speciation fingerprint, 5) resulting speciation used as input for the chemical/transport modeling to describe releases, and 6) full mechanistic model of the field scenario with external scenarios and realistic infiltration estimates. The leaching test methods in CEN/TC 292 and ISO/TC 190 are applicable to a wide variety of materials. An integrated approach of assessing environmental impact for a broad range of materials is the way to proceed. Characterization will provide better understanding of material behavior and partitioning. The chemical fingerprint derived from a pH dependence test provides a chemical speciation fingerprint suitable to predicting laboratory tests and more complex modeling. Insights from modeling can provide the means to developing better compliance test procedures. Placing compliance test data in conjunction with characterization data allows for more far reaching conclusions. The full mechanistic approach is an ambitious approach but seems to be the best way forward for a wide variety off materials and scenarios.

“Estimated Duration of the Subsurface Reducing Environment Produced by the Z-Area Saltstone Disposal Facility” was presented by Dan Kaplan of the Savannah River National Laboratory. Reactive transport modeling based on a conceptual model based on field study and laboratory measurements was used to answer the question of how long the Saltstone facility will remain in a reducing state which immobilized several key waste constituents, primarily Tc-99. Blast furnace slag is used in Saltstone as a reducing agent. A multi-year field lysimeter test showed that Saltstone with slag essentially eliminated Tc release. A reactive transport model was developed using parameters from the field and laboratory tests of Saltstone that showed the reducing capacity would remain for time greater than 10,000 years. Almost identical results were obtained independently by a completely different approach.

Session 2A. Water and Gas Transport Through Cementitious Materials

The session was chaired by Florence Sanchez of Vanderbilt University and Gregory Flach of the Savannah River National Laboratory.

Christophe Galle of the French Atomic Energy Commission gave the first paper, “Intermediate Long-Lived Nuclear Waste Management: An Integrated Approach to Assess the Long-Term Behavior of Cement-Based Materials in the Context of Deep Disposal.” A French law passed in 1991 set three lines of research for intermediate and high level waste 1) partitioning and transmutation, 2) deep geological repository, and 3) waste conditioning and long-term interim storage. Since June 2006 a new law determines waste management research along three lines, 1) partitioning and transmutation of spent fuel, 2) retrievable disposal in a deep repository, and 3) conditioning of waste and temporary storage. A functional analysis of the interim storage and disposal consists of a Safety Assessment and Performance Analysis of the facilities, and operational analysis that includes the role of concrete and waste package performance functions, and a number of scientific questions such as waste package degradation by underground leaching. Key phenomena that affect concrete evolution in saturated and unsaturated systems, such as alkali-aggregate reactions and freeze-thaw were given. The key issues with long-term storage in an unsaturated environment are radiolysis, air carbonation and rebar corrosion. Issues in a saturated environment are concrete leaching, leading to chemical degradation, dissolution and precipitation processes, microstructure and transport property evolution, mechanical effects and impacts on radon transport. Future work will focus on coupling mechanical and chemical transport, a microstructure-diffusion model, studying blended cements, and various aspects of corrosion.

“New Methods to Measure Permeability” was given by George Scherer with Princeton University. Five methods were discussed, direct flux measurement, pressure relaxation, beam-bending, thermopermeametry and dynamic pressurization. Direct flux measurement is the traditional method. A pressure difference is applied to the sample and the water flux is measured. The method is slow and subject to leaks. In the pressure relaxation method a pressure is applied to one side of a sample, and the change in pressure with time is monitored as the liquid moves into the sample. This method is faster than direct flux but is also subject to leaks since high pressure is used. Beam bending compresses the pore liquid in the upper half of the beam and creates suction in the bottom half. The liquid then moves with the rate of flow dependent on the hydraulic conductivity and the elastic modulus of the beam material. Beam bending is fast and inexpensive, requires a slender sample, requires a saturated sample and provides elastic and viscoelastic properties in addition to permeability. Thermopermeametry is based on thermal expansion of a liquid causing expansion of a solid. The kinetics of expansion and contraction reflect the rate at which liquid in the solid exchanges with liquid in the surrounding bath. Poromechanics analysis if dilation kinetics yields permeability. Thermopermeametry is suitable for large heterogeneous samples, however large samples may be hard to saturate and the process can be slow for large samples with low permeability. The dynamic pressurization test uses strain gauges embedded in the samples. A pressure of 3 – 10 MPa is applied in less than 2 seconds. Measurements are made during loading and unloading cycles. This test yields the bulk modulus of the solid phase as well as permeability. Entrapped air must be reduced below 0.1% or it will profoundly affect kinetics. Preliminary results are promising; a measured permeability of 10^{-21} m^2 was obtained in about 24 hours for a sample with a radius of 4.9 cm. The measurement time scales as the square of the radius. For homogeneous materials, beam bending is the most efficient means of measuring permeability. Dynamic pressurization is promising for concrete. All of the methods discussed require fully saturated samples, which is difficult for materials with small pore sizes.

Jim Conca, Director of the Carlsbad Environmental Monitoring and Research Center, presented "Measuring Transport Properties in Grout and Cement. The primary transport parameters in porous media are hydraulic conductivity, diffusion coefficient and retardation factor. The center uses an unsaturated flow apparatus (UFA) to measure the hydraulic conductivity of cementitious samples. A core sample of cementitious material running at 2000 rpm with a flow rate into the sample of 0.1 ml/hour reached hydraulic steady state in 14 hours with a hydraulic conductivity of 9.4 x 10^{-9} cm/s and a volumetric water content of 9.8%. By changing the setup of the UFA it can also be used to measure the matric potential of a sample. Measured steady-state diffusion coefficients for dissolved species in a porous medium that are below 10^{-6} cm^2/sec result from physical properties of the medium itself, particularly those that affect path length, such as the number and sizes of dead end pores of the free volumetric water content. A plot of the diffusion coefficient versus the volumetric free water content is the same for all natural materials. The test UFA can be used to measure retardation factors directly. This is better than calculating the retardation factor from a measured K_d because the K_d measurement does not account for processes such as precipitation, redox reactions, biologic interactions of water-rock sensitivities.

"Testing and Standards Related to Fluid and Chemical Transport" was given by Doug Hooton of the University of Toronto. Since fluid penetration, both gasses and liquids, is in most cases the first step in any degradation process, reliable and reproducible performance tests are needed for measuring the relevant fluid transport properties of concrete. The test results will vary depending upon when and where the samples are taken. All test methods have variability, so statistical acceptance limits need to be set. The mechanisms that can move fluids into concrete are permeability, diffusion, sorption, and wick action. Each of these is modified by time-dependence, binding and chemical reactions, cracking and other defects, and spatial dependence such as curing. Capillary absorption into unsaturated concrete can allow fluid ingress in the time frame of minutes and hours, with the affected depth ranging from a few millimeters to several centimeters, which is much faster the for saturated diffusion. Chlorides do not damage the concrete matrix but do cause corrosion of steel. Sulfates chemically interact and damage the matrix through the formation of expansive phases or de-calcification. In DOE waste there is potential for interaction between soluble species in the waste and the cementitious matrix. A number of test methods were described. Test under development include a conductivity test, a rapid chloride migration test, a field rate of absorption test and a water permeability test.

Andrew Garrabrants of Vanderbilt University gave "The Impact of Moisture Transport on the Release of Constituents from Cement-Stabilized Materials Stored in Intermittently Saturated Environments." The environmental performance of cement-based materials used in disposal or containment of waste materials can be significantly altered by interaction with an intermittently saturated environment. The objective of the work was to develop a mathematical representation of moisture transport for a cementitious matrix. It would integrate moisture transport into mass transport models and couple dissolution and diffusion, creating the Intermittent Mass Transport model, that would be validated versus an independent data set and compared with wetting/drying scenarios and current saturated modeling approaches. The results of water vapor transport experiments were used to validate parts of the model. The model uses a two regime (funicular and isothermal) drying model as its basis. Saturated diffusion models over-predict releases because they do not account for dry times when diffusion does not operate. Simple models do not account for pH and other chemical effects. Long term release estimates from cementitious matrices are influenced by the formulation of the model, the scenario conditions and external stresses. The IMT model is useful since it combines chemistry with mass transport, accounts for drying as a function of isotherm and external relative humidity and calculates release as a function of wetting frequency. Future work will focus on gas phase phenomena, validation of predicted moisture transport and profiles including degradation evaluation.

"Diffusion of Cementitious Pore Fluids into Boom Clay from a Deep HLW Disposal Site: Modeling of a Laboratory Experiment and Long Term Interaction was presented by Diederik Jacques of SCK-CEN in Belgium. The objective of the work was to model laboratory experiments of the advection of young concrete water through Boom Clay cores to assess the possible extent of alterations in the clay due to interactions with alkaline fluids over 25,000 years. The Boom Clay is the host formation being studies for geologic disposal of high level nuclear waste. The experimental set up used Boom Clay cores and water in equilibrium with fresh concrete which had a pH of 13.1 and high potassium and sodium content. Steady state conditions were maintained for 1000 days while measurements were made of the outflow water chemistry. A reactive transport model was set up using PHREEQC. Three types of models were developed: 1) fixed cation exchange capacity (CEC), 2) fixed CEC plus pH dependent CEC and 3) fixed CEC plus pH dependent CEC plus surface complexation. The model was calibrated against experimental results for NA, K, Al and Si. The findings were that exchange processes are important and that secondary phases are of lesser importance. The approach for the long-term diffusion modeling was to consider only equilibrium reactions, use a simplified model of concrete mineralogy, use radial diffusion and neglect the effect of chemical change on porosity and diffusivity. Further work is needed to quantify the sensitivity of the model assumptions for the concrete model, secondary minerals and the Boom Clay model.

Craig Benson, University if Wisconsin-Madison, gave the paper titled, "Leaching of Trace Elements from Highway Materials Stabilized with Coal Fly Ash." Over half of Wisconsin has "poor" subgrade soils that need improvement for road construction. One alternative to crushed rock is cement of fly ash. Coal fly ash is a fine-grained byproduct of coal fired power plants produced in vast quantities. M any ashes have properties that are desirable for soil stabilization. One concern in this use is that trace elements in the ashes will leach out and contaminate ground water. A study was carried out with four elements: 1) water leach tests on soil and soil-fly ash mixtures, 2) column leach tests on soil and soil-fly ash mixtures, 3) field tests, and 4) chemical transport modeling. Soils were obtained from 6 sources and fly ashes from 5 sources for the tests. Characterization tests were conducted on all samples. Findings of the studies were: 1) leaching of Cd, Cr, Se and Ag from inorganic soils stabilized with fly ash is predictable using conventional theory obtained from laboratory tests, 2) transport parameters can be estimated of measured using conventional test methods, 3) pH is a master variable affecting release, but it appears to remain persistent within the time frame of interest for infrastructure projects, and 4) field conditions can be predicted if the leaching source term can be well defined. Several questions remain to be addressed. 1) “Over what range of materials can these findings be applied – not organic soils or recycled asphalt?” 2) “How does weathering (freeze-thaw, wet-dry, repeated loading) affect behavior?” 3) “Do other trace elements of concern follow the patterns observed so far?” and 4) “What of long term performance – there is a need for continued monitoring?”

The paper “Studies of Tritium Characterization on Concrete at the Savannah River Site” was given by Elliot Clark of the Savannah River National Laboratory. Tritium was produced and processed in several facilities at SRS that have been or are scheduled to be dismantled or deactivated. Tritium readily exchanges with normal hydrogen in concrete and becomes almost undetectable because of tritium’s weak beta emission. Exposure of concrete to tritiated liquid produces a relatively constant tritium concentration with depth profile. Exposure of concrete to tritium in the vapor phase produces a diffusive type concentration variation from the exposure surface inward. SRNL developed a simple and low cost method of assaying for tritium in concrete using a hammer drill to core concrete followed by a nitric acid dissolution technique that allows liquid scintillation counting to characterize tritium. Several surface detection methods were investigated. It must always be assumed that tritium penetrates throughout concrete.

Session 2B. Degradation Mechanisms and Test Methods, Durability Criteria and Long-Term Degradation Evaluation

The session was chaired by Christine and Mark Phifer, both of the Savannah River National Laboratory

The first paper in the session was "Re-Use of Waste and Behavior of Heavy Metals: A Molecular Approach of the Transfer Mechanisms" by Jerome Rose of CEREGE, France. This work uses a mechanistic approach to study the speciation of metals and metalloids in cement and slag phases. A multi-scale structural study was done which used x-ray diffraction, scanning electron microscopy and light scattering for macro scale work, x-ray scattering for semi local scale investigation and nuclear magnetic resonance for local scale characterization. A study of Cr(VI) in cement phases showed that it is less mobile than predicted by models. Lead in cement was found to be fixed by the calcium silica hydrate phase. The conclusion was that a mechanistic approach can be used at the molecular level. Large scale leaching experiments are a necessity. The role of iron phases is very important.

Doug Hooton of the University of Toronto gave the paper "A Review of Different Forms of Sulfate Attack." Internal sulfate attack can occur if there are excess sulfates from constituent materials which can dissolve into the pore solution in service conditions. In the case of DOE wastes, there is a concern that if moisture enters the waste precipitated sulfate in the waste could become soluble and cause internal sulfate attack. Ettringite formation can be addressed by limiting sources of reactive alumina, but there forms of sulfate attack exist, namely salt crystallization and thaumasite.

Sulfate resistance of concrete is addressed by setting limits on tricalcium aluminate, using supplemental materials such as silica fume or fly ash, setting limits on the water to cement ratio, ensuring proper compaction and curing and using entrained air to provide space for expansion. Two tests are used to determine sulfate resistance, ASTM C452 and C1012. Type V cements are resistant to sulfate attack, but not immune. Blended materials may work better than Type V cement. A Type I cement with 72% slag was undamaged after 24 years in a $MgSO_4$ solution.

Some Pacific Rim slags have high alumina contents that may not work well for sulfate resistance, though the addition of gypsum may help. There are no standard concrete tests for assessing sulfate resistance because even using highly concentrated solutions the tests take several years to produce visual damage. Therefore, the ACI 318 code limits the cement binder type and places a maximum on the water to cement ratio that depends on the severity of the expected exposure.

In locations with low relative humidity and high-sulfate soils evapotranspiration can bring sulfate salts in contact with concrete. Delayed Ettringite formation seems to be caused by high early temperature, a source of alkali consumption and subsequent exposure to moisture, which causes reformation of Ettringite and severe cracking. This is currently dealt with by keeping temperatures below 65° C. or by using enough pozzolan or slag to keep the temperature below 85° C. Thaumasite is a relatively unusual form of sulfate attack associated with low temperatures and very wet environments, where CSH and $Ca(OH)_2$ are converted to gypsum and thaumasite, which turn the concrete matrix to mush. To provide for sulfate resistant concrete the exposure conditions must be understood and good quality concrete must be used. Relying solely on binder type is not sufficient. There is a need to develop guidance to avoid thaumasite sulfate attack.

"Microbial Induced Degradation of Cement-Solidified Waste Forms for Radioactive Waste Disposal" was presented by Nosa Egiebor of Tuskegee University. NRC Regulation 10 CFR 61 requires evaluation of waste forms for microbial stability. The established NRC test protocol has been controversial die to several technical limitations, one of which is the inability to account for the effects of low pH on sample stability. The project used a sulfur oxidizing bacteria that produces sulfuric acid. The resulting leachate solution had a pH of 2 which released more constituents from the test sample than found using the standard NRC protocol. The identified technical problems with the NRC test protocol were 1) the waste form degradation observed during the experimental microbial induced degradation test is due to initial high acidity in the pre-test microbial broth, 2) the microbial broth used is substrate-limited, as available sulfur substrate is oxidized before contact with the sample, and 3) the substrate limitation is due to the batch mode employed in the NRC test protocol. An alternative protocol was developed that uses a two-stage Biofilm formation. The first stage is to grow a microbial biofilm on the waste form surface before the evaluation. Stage 2 is to take the sample with the established biofilm and conduct the microbial induced degradation test using a continuous flow of fresh medium at pH 4. The new protocol clearly defines the role of microbes during microbial induced degradation of cement-solidified waste forms.

Jeff Serne of the Pacific Northwest National Laboratory presented the paper "Technical Issues on Laboratory Methodology to Assess Long-Term Release of Contaminants from Grout/Cement in the Vadose Zone." There are difficulties in extrapolating short-term laboratory tests to long-term performance predictions. Three areas of particular concern are diffusion experiments, cement/concrete aging and reducing capacity of grouts. To address the diffusion issue PNNL workers have developed soil-soil and concrete-soil half cell diffusion experiments. The apparatuses are kept in unsaturated conditions. At the end of the experiment the cells are frozen and thin sections to determine the diffusion profile. They have found that Tc and I diffuse 4 times slower in soil when the water content changes from 7% to 4%. The change in concrete is 1 to 2 orders of magnitude for the same change in water content. They found I to diffuse 1 to 3 orders of magnitude more slowly that Tc in concrete. The concrete-soil half cell experiments gave results 4 to 6 orders of magnitude lower that ANS 16.1 leach tests. To investigate carbonation, the researches used super critical CO_2 to accelerate the test. Higher than expected leaching resulted were observed. They suspected cracking caused by release of pressure when the sample was removed. They now use a saturated $NaCO_3$ solution. They are now looking at carbonation in old buildings at the Hanford site. There have been several studies on the reducing capacity issue, but the issue remains. Questions remain: "Are "water immersion" leach tests appropriate for concrete/cement waste forms in shallow land burial environment?" "Can one overcome method difficulties un using unsaturated half-cell test methodologies and what data reduction equations are correct?" "How do you accelerate the aging of specimens and then characterize the solids without introducing artifacts?" "Do micro-cracks that are ~1 μM in diameter and not very long or randomly connected really matter for mass transport?" "How do you accurately measure the "reducing" capacity of cement and common additives?"

David Kosson presented the work of D. Chen and S Mahadevan of Vanderbilt University "Numerical Simulation of Concrete Durability under Coupled Deterioration Processes." A model framework was set up using the ANSYS finite element structural analysis software that sequentially applied heat transfer, moisture transport and carbon dioxide transport to a concrete structure to produce degradation by expansion/contraction, drying shrinkage/wetting and carbonation, then reapplied the processes to the resulting degraded structure. The methodology included chloride penetration and resulting corrosion and expansion. A time-dependent reliability analysis was performed. The uncertainty sources were the variability in time-dependent deterioration processes such as environmental loadings, variability in concrete materials and geometry and uncertainties in the model and its parameters. The random variables used were: the concrete cover depth, chloride diffusivity, the surface chloride content and the chloride threshold value. A sensitivity analysis was done to quantify the influence of the random variables.

"Concrete Degradation Modeling Research at NIST" was given by Ken Snyder of the National Institute of Standards and Technology. For more than a decade, a computer model for concrete degradation has been under development at NIST. The underlying philosophy is to incorporate all of the relevant physics and chemistry of transport and reaction in cementitious systems. The NIST model is similar to other models in that it incorporates pore water chemistry, dissolution/precipitation reactions, empirical porosity dependence of transport coefficients, the physics and chemistry are treated separately and chemical reaction is a boundary condition to transport. The NIST model is unique in that it handles concentrated electrolytes. The transport model has been validated using parameter-free calculations of binary diffusion coefficients, solution conductivity, transference number, and diffusion potential. Future work will address redox reactions and kinetics, osmotic effects, moisture transport, temperature dependence and binding.

Carol Jantzen of the Savannah River National Laboratory gave the paper "Fluidized Bed Steam Reforming (FBSR): A Novel Process for Mineralizing Organic and Halide Containing Wastes." FBSR is being considered as an alternative technology for the immobilization of a wide variety of aqueous high sodium containing radioactive wastes at various DOE facilities in the United States. It is a robust technology that can accommodate a wide range of feeds. It is a moderate temperature process whose reactions include organic destruction, denitrification, evaporation, dehydration and hydrothermal reactivity. The process produces mineral as durable as borosilicate glass that passes TCLP when the ferrite spinel phase is provided by use of a catalyst. The product mineralogy is anhydrous analogs of zeolites.

The work of Joe Westsik of the Pacific Northwest National Laboratory "Alternatives for Low-Temperature Waste Immobilization" was given by Jeff Serne. The scope of the work was to seek solutions from the private sector to demonstrate low-temperature immobilization technologies for mixed radioactive and hazardous waste. The wastes to be used in the demonstrations were Hanford off gas caustic scrubber and Idaho sodium bearing waste. Three waste forms were selected for evaluation. Alkali Aluminosilicate Hydroceramic Cement from the Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University, Phosphate Bonded Ceramic from CH2MHill and Alkali Aluminosilicate Geopolymer from the Vitreous State Laboratory at The Catholic University. Each of the vendors was giver simulated waste and they prepared and characterized the waste forms in terms of chemical composition, waste loading TCLP and compressive strength. PNNL did additional testing on specimens provided by the vendors, Product Consistency Test, ANSI/ANS 16.1 Leachability and compressive strength after irradiation. The phosphate bonded ceramic and alkali aluminosilicate geopolymer show potential based on TCLP, compressive strength and Na leachability index requirements. The ANS 16.1 immersion test revealed formulation issues that need to be addressed. Out-year activities will be based upon ORP and ID decisions whether of not to pursue this type of technology.

Session 3A. Long-Term Performance Predictions and Risk Assessment: Integration of Cementitious Materials and PA Modeling

The Session was chaired by Andrew Garrabrants of Vanderbilt University and David Esh of the Nuclear Regulatory Commission

Tim Jannik of the Savannah River National Laboratory gave the first paper, “Risk-Based Radionuclide Derived Concentration Guideline Levels for Concrete Slab End States.” A concrete slab is the common planned end state at SRS for the deactivation and decommissioning of buildings. An integral part of the risk calculations used to determine the potential impact to workers and members of the public are derived concentration guidelines levels. At SRS these are site-specific values calculated based on the unique properties and exposure scenarios expected for concrete slabs. The risk factors used are from the Environmental Protection Agency Federal Guidance Report 13. The use of site specific parameters gives higher derived concentration guideline levels than using default values, largely due to the lower dust generation for concrete than for soil.

“Probabilistic Assessment of Long-Term Concrete Vault Durability in a Sulfate-Bearing Waste Environment” was given by Greg Flach of the Savannah River National Laboratory. At SRS about 50 million gallons of low level liquid waste will be mixed with dry cement, fly ash and blast furnace slag and pumped into concrete vaults to produce an entombed solid called Saltstone. Each Saltstone vaults functions as a hydraulic barrier to advective and diffusive release of radionuclides and nitrate to the environment. The low level liquid waste has a sulfate concentration of 0.1M. The work investigated to effect of sulfate attack resulting from this level of sulfate within the cementitious waste form on the vault structures. Three methods of sulfate delivery were considered, early movement of wet mix into cracks in the vault inside surface, capillary suction into and diffusion. The vaults are made with a sulfate-resistant mix. Physical damage to concrete from sulfate intrusion involves coupled transport, chemical reaction and fracture mechanics processes that are not completely understood and are not fully represented in current predictive models. This suggests that a probabilistic approach should be used. This was done using the GoldSim software platform. The results showed a range in vault life spans from 1000s to 100,000s of years and indicate that longevity can be significantly increased through the application of a waterproof coating on the vault interior. Dry mix composition did not appear to significantly affect equilibrium expansion, but can slow the rate of sulfate attack through lower permeability and diffusion coefficient, and possibly slower chemical kinetics.

Michael Connelly of CH2MHill at Hanford gave the paper “Initial Single Shell Tank System Performance Assessment for the Hanford Site.” The initial SST PA is based on current “State of Knowledge” and analyzes for future human-health impacts from waste remaining in the tanks following retrieval, deep vadose contamination and ancillary equipment left in the tank farms following closure. The PA supports pre- and post-retrieval documentation, interim activities and characterization activities pending the completion of the Tank Closure and Waste Management Environmental Impact statement and its Record of Decision. The PA will be used as a communication tool. The goal for tank farm closure utilizes the “Defense-in-Depth” concept put forth by the NRC, using natural and man-made barriers, institutional controls, a thick vadose zone and the processes of retardation and decay. The PA considers groundwater, air and intruder pathways of potential exposure. The groundwater model STOMP is used. The potential tank closure system modeled is a three-layer grouted tank. There is limited data on long-term grout performance inside a tank in an arid environment. A formalized sensitivity analysis was used to identify the most significant parameters and examine "what if" cases. Laboratory testing of residual waste samples have begun. Key assumption in the Initial PA include: diffusion dominated release from the tanks and no credit is taken for other barriers such as tank steel. The reference case analyzed represents the current version of the "central tendency" and is expected to be refined over time. The major sources of uncertainty are long term stewardship, design decisions and geologic/hydrologic variables. Initial results are that groundwater impacts related to single shell tank residuals are below the performance objectives provided the tanks are retrieved to the goal of 360 ft^3 for tanks with a capacity greater than 500,000 gal and 30 ft^3 for 55,000 gal tanks. The Initial PA will be used to begin an open and transparent process with the regulatory agencies, tribal nations, and stakeholders to collaborate on the approaches, assumptions and methodologies used in the SST PA.

"Long-Term Monitoring Strategy using Nonlinear Kalman Filtering" was presented by Ken Snyder of the National Institute of Standards and Technology. This talk reported on work that has just begun. The present state is that existing computer models are limited, monitoring provides assurance, and that a model revision rationale is needed. The objective of the work is to combine models and measurements with a rational strategy to improve both. Kalman filtering is being investigated as a way of achieving the objective. The process was described and two examples using Fickian diffusion were given. Future work will look at other nonlinear Kalman filters, seek an optimum state vector vases set and examine state vector constraints.

The final presentation, "Cement Conditioning of Nuclear Wastes – Where Do We Go?" was given by Fred Glasser of the University of Aberdeen. The basic properties of Portland cement relative to immobilization were given; high pH buffered by reserves of solids, slightly oxidizing Eh that is unbuffered, high chemical potentials for Ca with high surface area of solids available for sorption and precipitation. The additional chemical potential for reactions resulting in immobilization makes cement unique as a reactive barrier and can also act at a distance as an alkali plume. The bonding of +1 ions is weak, but stronger for species with higher charge. We suffer from a lack of basic knowledge about the redox behavior at high pH of some species such as Tc and the actinides. The nuclear industry uses modified blend which have little long-term performance data. Shrinkage always occurs and should be managed to avoid a few large cracks. Aggregates reduce heat and shrinkage and also the concentration of pH conditioning mass. Potential problems due to aggregate can be eliminated at the design stage. Cement formulation is a compromise. The logic underlying selection needs to be presented with a convincing case for the priorities presented.

The NAS has recommended "test beds". Grout designers and modelers should be involved with these tests. Cracks heal, though the process is understudied. The NAS has also recommended development of accelerated test methods. These are likely to not succeed. In the present state of knowledge, we are going to have to depend on models and modeling, perhaps supplemented by focused experimental work. Models of chemical evolution are arguable at a more advanced state than models of physical performance. Models are likely to be limited by available data, so parallel efforts to improve the data base are needed. We should not totally rely on modeling – it is best used to focus experiments. An action check list includes the following topics for further work: matrix properties – evolution of pH and electroactivity of redox couples, bonding mechanisms of radwaste species in fresh and altered matrices, formulation priorities- establish protocols including changing nature of cement and aggregates, scale up effects, cracking and crack healing – impacts on permeation, role of accelerated testing and development of modeling protocols – verification/validation of model predictions and integration of models for physical and chemical attributes of performance.

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ATTACHMENT 3. ELECTRONIC PROCEEDINGS (DVD)

Workshop on Engineered Barriers for Low-Activity Radioactive Waste Treatment, Containment, Environmental Restoration and D&D

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WSRC-RP-2007-00210
March 28, 2007

Electronic Proceedings (DVD)

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