Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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CEMENTITIOUS BARRIERS PARTNERSHIP
FY2014 END-YEAR REPORT

CBP-TR-2015-009, Rev. **0**

CEMENTITIOUS BARRIERS PARTNERSHIP FY2014 END-YEAR REPORT

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December 2014

ACKNOWLEDGEMENTS

This report was prepared for the United States Department of Energy under the Savannah River National Laboratory Cooperative Research and Development Agreement (CRADA) No. CR-08-001. The Cementitious Barriers Partnership is sponsored by the U.S. DOE Office of Tank Waste Management in collaboration with the U. S. NRC and administered through the Savannah River National Laboratory CRADA. 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 Savannah River Nuclear Solutions, Vanderbilt University 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. This report is part of a larger multi-investigator project supported by the U. S. Department of Energy entitled the Cementitious Barriers Partnership. The opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily represent the views of the U.S. Department of Energy. This work was also partially supported by the National Institute of Standards and Technology Sustainable, High Performance Infrastructure Materials program.

Printed in the United States of America
United States Department of Energy
Office of Environmental Management
Washington, DC

This document is available on the U.S. DOE Information Bridge and on the CBP website: http://cementbarriers.org/
An electronic copy of this document is also available through links on the following website: http://srnl.doe.gov/

FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Tank Waste Management. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP partners are the Savannah River National Laboratory (SRNL), Vanderbilt University (VU), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc. The Nuclear Regulatory Commission (NRC) is providing support under a Memorandum of Understanding. The National Institute of Standards and Technology (NIST) has provided research previously under an Interagency Agreement. Neither the NRC nor NIST are signatories to the CRADA.

The periods of cementitious performance being evaluated are up to and >100 years for operating facilities and > 1000 years for waste management. The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems, e.g., wasteforms, containment structures, entombments, and environmental remediation, including decontamination and decommissioning analysis of structural concrete components of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (wasteform in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a multi-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.

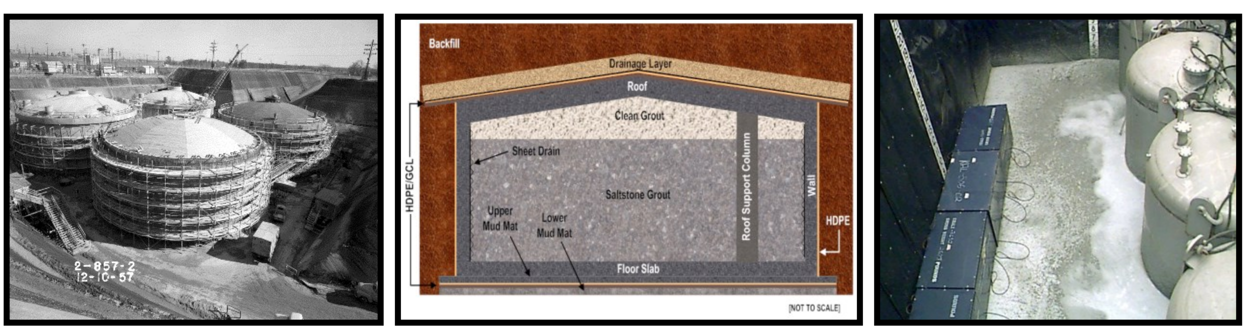
CEMENTITIOUS BARRIERS PARTNERSHIP
2014 END-YEAR REPORT

SUMMARY

The DOE-EM Office of Tank Waste Management Cementitious Barriers Partnership (CBP) is chartered with providing the technical basis for implementing cement-based waste forms and radioactive waste containment structures for long-term disposal. Therefore, the CBP ultimate purpose is to support progress in final treatment and disposal of legacy waste and closure of High-Level Waste (HLW) tanks in the DOE complex. This report highlights the CBP 2014 Software and Experimental Program accomplishments that support the Department of Energy needs in environmental cleanup and waste disposal. DOE needs in this area include:

- Long-term performance predictions to provide credibility (i.e., a defensible technical basis) for regulator and DOE review and approvals,
- Facility flow sheet development/enhancements, and
- Conceptual designs for new disposal facilities.

In 2014, the Cementitious Barriers Partnership demonstrated continued tangible progress toward fulfilling the objective of developing a set of software tools and experimental programs to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications. Both the modeling tools and the experimental data have already benefited DOE sites in the areas of performance assessments by increasing confidence backed up with modeling support, leaching methods, and transport properties developed for actual DOE materials. In May of 2014, the CBP released the CBP Software Toolbox – "Version 2.0" which provides concrete degradation models for: 1) sulfate attack, 2) carbonation, 3) chloride initiated rebar corrosion and constituent leaching, and 4) percolation with radial diffusion (for leaching and transport in cracked cementitious materials). These models are applicable and can be used by both DOE and the Nuclear Regulatory Commission (NRC) for service life and long-term performance evaluations and predictions of nuclear and radioactive waste containment structures across the DOE complex (Figure 1) including:



Tank Closure | Saltstone Disposal | Low Level Waste Vault Grouted

Figure 1: Various DOE Cementitious Barriers in Waste Management

- Future SRS Saltstone and HLW tank performance assessments and special analyses
- Hanford site HLW tank closure projects, secondary waste treatment, and other projects in which cementitious barriers are used
- The Advanced Simulation Capability for Environmental Management (ASCEM) project, which requires source terms from cementitious containment structures as input to their flow simulations
- Regulatory reviews of DOE performance assessments
- Nuclear Regulatory Commission reviews of commercial nuclear power plant (NPP) structures which are part of the overall US Energy Security program to extend the service life of NPPs

In addition, the CBP experimental programs have had a significant impact on the DOE complex by providing specific data unique to DOE sodium salt wastes at both Hanford and SRS which are not available in the open literature. The programs have also produced significant data shedding light on the performance of the concretes selected for disposal of DOE salt waste forms at SRS. Experimental programs on technetium (Tc) mobility, cement phase characterization, and concrete performance after exposure to aggressive conditions have provided significant conclusions as summarized below:

- SRNL experimental studies related to Tc mobility indicate that conventional leaching protocols may not be conservative for direct disposal of Tc-containing waste forms in vadose zone environments. These results have the potential to influence the current Hanford supplemental waste treatment flow sheet and disposal conceptual design.

- SRNL mineralogy characterization discussed in this paper illustrates that sodium salt waste form matrices are somewhat similar to but not the same as those found in blended cement matrices which to date have been used in long-term thermodynamic modeling and contaminant sequestration as a first approximation. Utilizing the CBP generated data in long-term performance predictions provides for a more defensible technical basis in performance evaluations.

- In 2014, SIMCO Technologies, Inc. (SIMCO) completed a two phase study with surprising results in the second phase study. The SIMCO experimental work was aimed at supporting the assessment of long-term durability of concrete barriers containing sulfate-bearing salt wasteform, present at both SRS and Hanford. In the Phase 1 experimental study, ordinary Portland cement hydrated cement pastes were exposed to aggressive solutions. In the 2014 Phase II study, the scope was extended to include hydrated cement blend pastes representative of DOE cementitious barrier materials that included slag and flyash. Also, the range of aggressive contact solutions was expanded. The experimental program was aimed at testing aggressive contact solutions that more closely mimic the chemical composition of saltstone pore solution. Phase I experimental results showed that damage does not occur in high pH solutions in the presence of sulfate. However, Phase II results showed that this was not the case (i.e., damage was observed) for concrete barriers that contained additional silica fume.

- Vanderbilt University experimental studies characterized changes in the microstructure and chemical speciation from carbonation in cementitious materials (a primary waste tank degradation mechanism) as a function of material alkalinity and exposure conditions to evaluate the carbonation front, transport of gases, and reaction chemistry. The improved LeachXS/ORCHESTRA carbonation model was then used to assess impact of carbonation on contaminant migration for a representative tank closure scenario.

In 2014, the CBP released its new Software Toolbox - Version 2.0, a software package providing new concrete degradation models that assist in lifetime predictions for cementitious structures. The experimentally-based software is used to predict degradation depths and damage due to sulfate attack, chloride attack, and carbonation for actual DOE cementitious waste structures. The software provides analyses to evaluate the integrity of the concrete barrier for various model constructs with an example for a HLW tank shown in Figure 2.

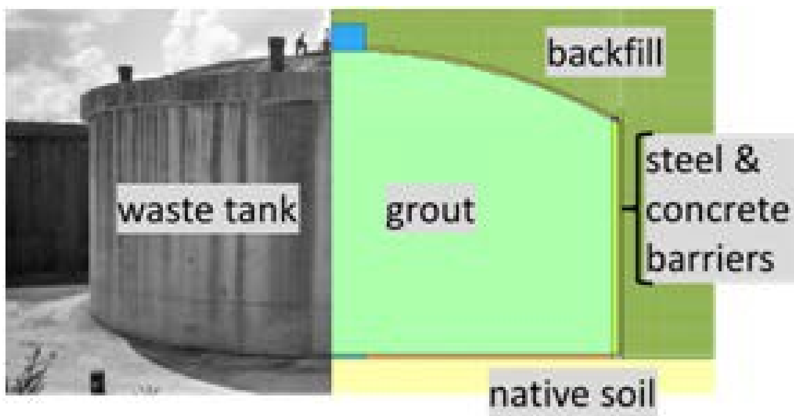


Figure 2: Cementitious Barriers – Tank Integrity and Closure Model Constructs

The CBP modeling and experimental products have already had a beneficial impact to DOE disposal and closure efforts, with some of the highlights discussed in this paper. The CBP software tools and experimental programs have been used to support DOE Performance Assessments (PAs) such as the Saltstone Disposal Facility at the Savannah River Site and have the potential to impact the design of new facilities. Also in 2014, the CBP hosted workshops across the DOE-complex to familiarize the end-users to the existing benefits of the software and experimental programs and to hear first-hand of areas of uncertainty that CBP could respond to in future development work.

CBP SOFTWARE TOOLS AND IMPACT

The CBP Software Toolbox is a suite of software for simulating reactive transport in cementitious materials and certain important degradation phenomena. The primary software components are STADIUM, LeachXS/ORCHESTRA (LXO), and a GoldSim interface for probabilistic analysis of selected degradation scenarios. The current version released in 2014, “Version 2.0”, supports analysis of external sulfate attack, carbonation degradation analysis, chloride attack, and dual regime modeling for fractured and in-tact cementitious materials. The integrated software is shown in Figures 3 and 4 with the various software components and modules, respectively, which simulate various degradation and leaching mechanisms in DOE-specific cementitious materials.

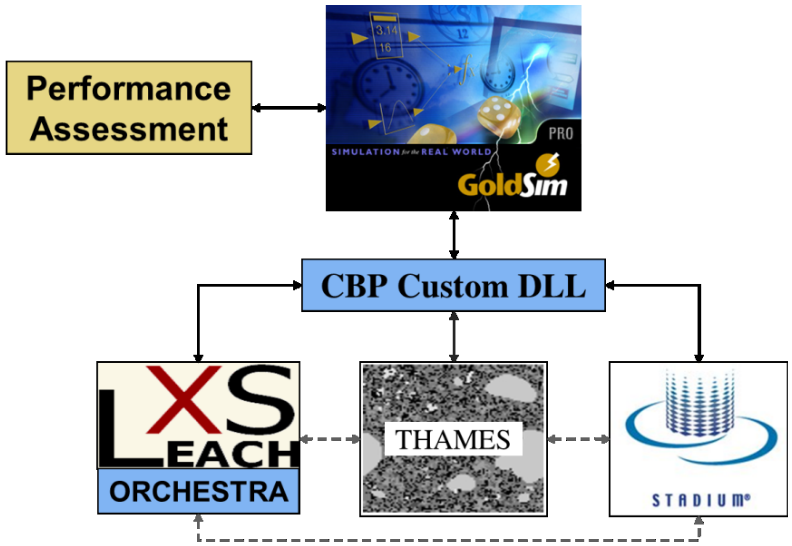


Figure 3: CBP Partner Software Components

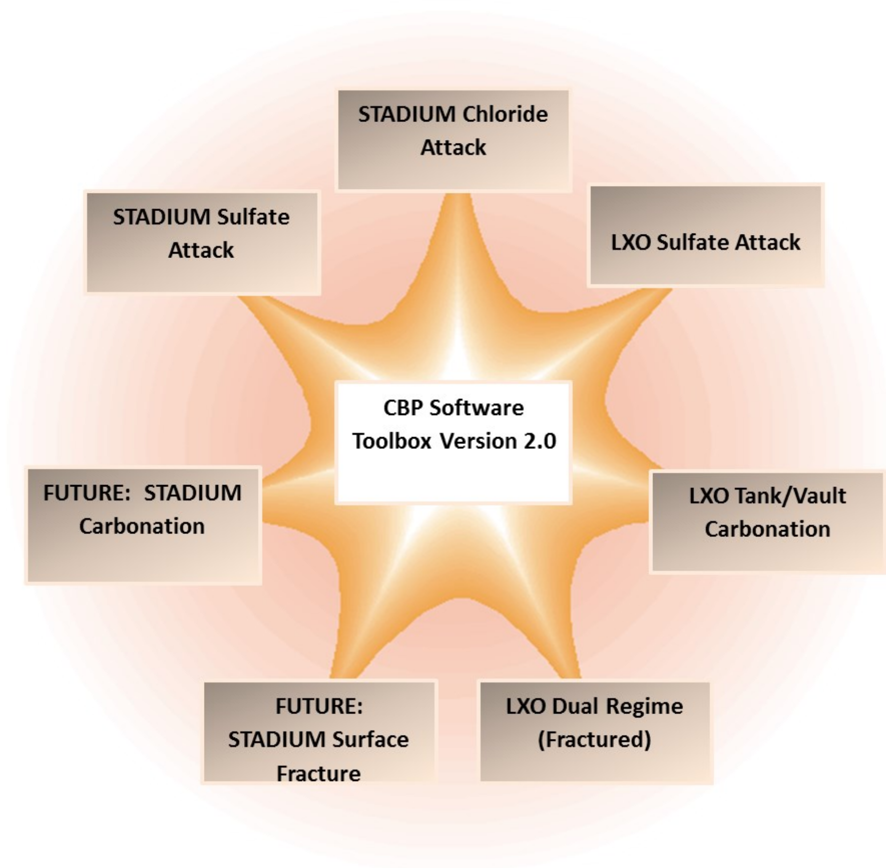


Figure 4: CBP Software Simulating Cementitious Degradation & Leaching Mechanisms

The integrated software package has also been upgraded with new plotting capabilities and many other features that increase the “user-friendliness” of the package. Experimental work has been generated to provide data to validate the models to improve the credibility of the analysis and reduce the uncertainty. Tools selected for and developed under this program have been used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems for periods of performance up to or longer than 100 years for operating facilities and longer than 1000 years for waste disposal. The CBP Software Toolbox is and will continue to produce tangible benefits to the working DOE performance assessment community.

The CBP is currently working on experimental programs and developing simulation tools based upon these programs to model other degradation mechanisms that include damage mechanics which estimate damage based upon contaminant ingress. Previously, performance assessments have assumed complete damage relative to ingress but these tools will predict the degree of damage based upon experimental results which will reduce unrealistic conservatism in the PA. Other degradation mechanisms of cementitious materials that the CBP will be developing include alkali silica reactions and acidic soil attack. For all these mechanisms, experimental programs are designed and software constructed from the experimental results. Figure 5 shows the timeline of CBP development plans.

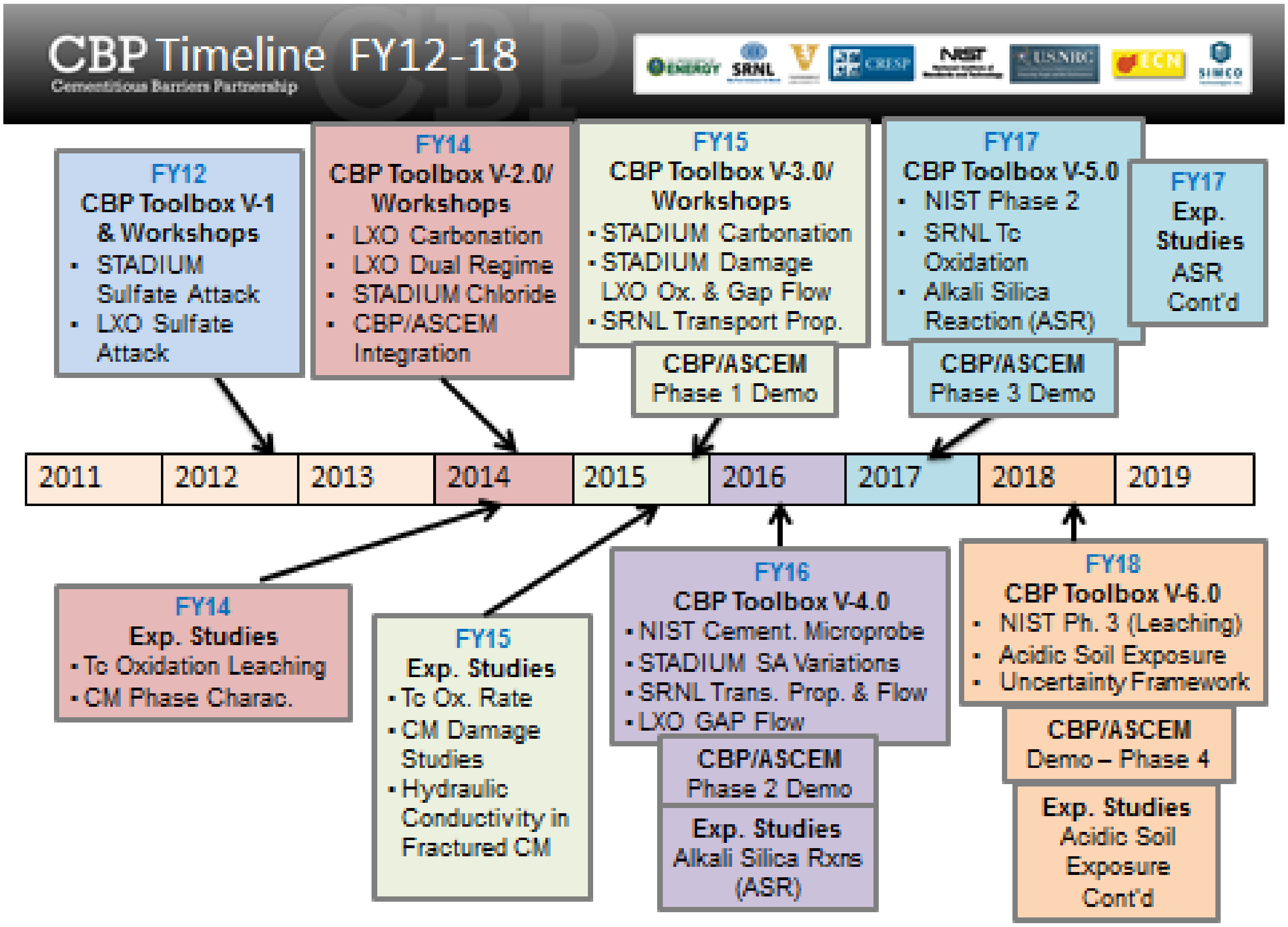


Figure 5: CBP Experimental and Modeling Integrated Timeline

2014 CBP SOFTWARE DEMONSTRATIONS, WORKSHOPS AND DEVELOPMENT

The CBP has made significant contributions to the DOE complex with the Software Toolbox – Version 2.0 released in 2014. These contributions are discussed in this section and include:

- DOE–sponsored user workshops showcasing the CBP products,
- Site-specific demonstration of the CBP software, and
- Preparation for an integrated demonstration using both CBP & ASCEM software.

DOE emerging issues identified through the recommendations and needs from the workshop attendees have been incorporated into the CBP future program plan. In the site-specific demonstration, two CBP software modules were used to assess sulfate attack on various cementitious barriers and provide model-model validation. Specifically, these tools were used to evaluate the degradation of DOE cementitious barriers and salt-based waste forms at SRS.

CBP Workshop Showcasing Software & Experimental Programs that Address DOE Emerging Issues

The CBP hosted workshops at Hanford, NIST, and SRNL in late summer through fall in 2014 to showcase the new CBP Software Toolbox – Version 2.0 and to identify and address DOE emerging issues related to cementitious barriers. In these workshops, new capabilities of the CBP Software Toolbox were presented, including user-interface improvements, an enhanced carbonation module and sulfate attack module, and the addition of a chloride attack and a dual regime transport module for fractured and in-tact systems. Specific applications and simulation needs of participants were discussed at the workshops so that future CBP experimental programs and software tools could be designed to support the current needs of the DOE Tank Waste Management Programs. In response, CBP partners are planning enhancements to the existing software modules to provide continued support for DOE site operational and post-closure scenarios. Examples of some of these enhancements include equipping the STADIUM external sulfate attack modules to include many layered composite barriers and to mimic various degrees of saturation based on exposure conditions that vary between arid and tropical environments. The CBP will be developing the future program to include the near- and long-term development work to support these user needs as shown in Table 1.

Table 1: DOE Emerging Issues and How the CBP is Addressing These Issues

DOE Emerging Issues *(Identified in 2014 CBP Workshops)*	**How CBP is Addressing DOE Emergent Issues**
Bulk Chemistry Variations & Impact to Cementitious Material (CM) Phases (Impact to Modeling Results)	**SRNL FY14 Experimental Program** Has provided initial work on CM phases. Future work will increase understanding.
Need Damage Model & Impact to Hydraulic Conductivity	**SIMCO STADIUM Damage Module** Planned Release *(FY15)*
Need CBP Software Tools on Additional Degradation Mechanisms (Oxidation, Alkali-Silica Reactions (ASR))	**CBP Program on Alkali-Silica Reactions** **Vanderbilt Oxidation Module** *(FY15)* and impact to DOE cementitious barriers *(FY16)*
Need DOE Compliant QA Documentation of CBP Software	**CBP Program to Develop QA Guidelines** And documentation that complies with DOE Site standards *(FY15)*
Need Realistic Predictions of Damaged CM Properties	**SIMCO STADIUM Damage Module Release/ NIST THAMES Software** to simulate time-evolution of CM Prop. *(FY15-17)* **Vanderbilt Carbonation Program** to characterize changes in microstructure and speciation resulting from carbonation *(FY15)*
Need Protection of Tc in Waste Form from Oxidation	**SRNL FY15 Experimental Program** Method development to measure oxidation rate
Need CBP Sulfate Attack Software to simulate High Sulfate Concentrations in Waste.	**SIMCO STADIUM Software Demo. Case** with high (30,000 - 50,000 ppm) sulfate concentration *(FY15/16)*
Is Liner Needed in New SRS Disposal Units for Cost Savings?	**SIMCO STADIUM Software Demo. Case** with and without liner *(FY15/16)*
CBP Software needs to reflect various material layers of disposal units	**SIMCO STADIUM Software Demo. Case** *(FY15)* **Vanderbilt LeachXs/ORCHESTRA Demo.** *(FY15-16)* to include multiple layers for existing models
Need to simulate less saturated conditions at Hanford soils vs 100% saturated at SRS	**SIMCO STADIUM Software Demo. Case** to conduct simulations with varying saturation levels.
Need Time-Evolution of Cementitious Materials (CM) and Transport Properties	**NIST THAMES Software** Designed to simulate Changes in CM/ Properties

CBP/ASCEM Integrated Software Demonstration

CBP and Advanced Simulation Capability for Environmental Management (ASCEM) software capabilities are to be leveraged in a joint simulation of radionuclide release from a hypothetical closed waste tank. Specialized CBP capabilities for simulating reactive transport in cementitious materials were utilized in a near-field simulation of radionuclide leaching from the engineered system (i.e., the waste tank). The high-performance computing (HPC) capabilities of the ASCEM Amanzi simulator will be utilized to simulate far-field flow and transport. Figure 6 provides a view of how the two crosscutting projects can be used in a complementary manner to enhance the DOE-EM PA and risk assessment. The ASCEM flow simulation provides boundary conditions to the CBP near-field model, which in turn provides radionuclide source terms to the ASCEM far-field transport simulation. The purpose of the joint analysis is to demonstrate specialized CBP capabilities for simulating reactive transport in cementitious materials, and ASCEM reactive transport capabilities (cement/waste form leachate impacted in far-field soil), and guide ASCEM and CBP development of interfaces to external codes and information.

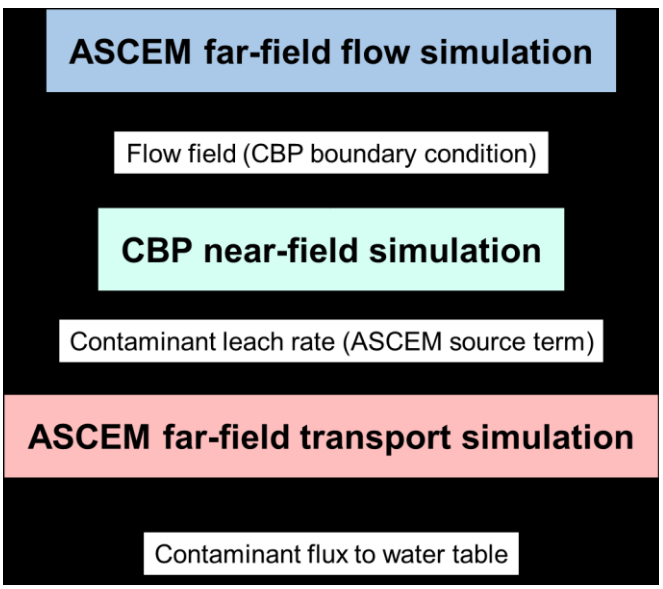


Figure 6: CBP / ASCEM Integrated Software Coupling

CBP Software Used to Evaluate DOE Cementitious Barriers

Documented in: Savannah River National Laboratory Report SRNL-STI-2013-00118, Rev.2 *"Degradation of Cementitious Materials Associated With Saltstone Disposal Units"* by CBP Partners and Associates: G. P. Flach and F. G. Smith III; September 2014.

Two CBP models were used to assess sulfate attack on SRS cementitious barriers and salt-based waste forms. One model is a version of the STADIUM code developed by SIMCO which models the transport of chemical ions and water through porous materials and reactions between the chemical and mineral species. The model solves a set of coupled differential equations describing one dimensional transport processes while simultaneously evaluating local diffusion coefficients and equilibrium chemical and mineral compositions in the materials. STADIUM can model systems with one (concrete), two (concrete and saltstone) or three (concrete, saltstone and soil) layers of materials. One current limitation of STADIUM modeling is that structural changes and damage to the concrete have no direct impact on the diffusion and transport properties. In the CBP Software Toolbox, Version 3.0 to be released in FY2015, the STADIUM software will include a damage model to assess the structural changes.

The other model included in the CBP Toolbox is a sulfate attack module based on LeachXS/Orchestra (LXO) developed at the ECN and Vanderbilt University with CRESP funding. Similar to STADIUM, LXO calculates transport rates of species through porous media and chemical equilibria between local chemical and mineral phases. However, the LXO sulfate attack module also performs a damage calculation and modifies transport properties where damage is predicted. LXO can also model trace species chemistry and transport. LXO models the material as a network of interconnected cells within which chemical equilibrium is maintained while transport of chemical species between cells occurs by diffusion and convection.

The saltstone facilities at the DOE Savannah River Site (SRS) stabilize and dispose of low-level radioactive salt solution originating from liquid waste storage tanks at the site. The Saltstone Production Facility (SPF) receives treated salt solution and mixes the aqueous waste with dry cement, blast furnace slag, and fly ash to form a grout slurry which is mechanically pumped into concrete disposal cells that compose the Saltstone Disposal Facility (SDF). The solidified grout is termed "saltstone". Cementitious materials play a prominent role in the design and long-term performance of the SDF. The saltstone grout exhibits low permeability and diffusivity, and thus represents a physical barrier to waste release. The waste form is also reducing, which creates a chemical barrier to waste release for certain key radionuclides, notably Tc-99. Similarly, the concrete shell of a saltstone disposal unit (SDU) represents an additional physical and chemical barrier to radionuclide release to the environment. Together the waste form and the SDU concrete wall compose a robust containment structure at the time of facility closure. However, the physical and chemical state of cementitious materials will evolve over time through a variety of phenomena, leading to degraded barrier performance over Performance Assessment (PA) timescales of thousands to tens of thousands of years. Previous studies of cementitious material degradation in the context of low-level waste disposal have identified sulfate attack, carbonation influenced steel corrosion, and decalcification (primary constituent leaching) as the primary chemical degradation phenomena of most relevance to SRS exposure conditions.

In this study, degradation time scales for each of these three degradation phenomena were estimated for saltstone and concrete associated with each SDU type. The combined effects of multiple phenomena were then considered to determine the most limiting degradation time scale for each cementitious material. Degradation times were estimated using a combination of analytic solutions from literature and numerical simulation codes provided through the CBP Software Toolbox. The modeling study found that degradation of these concrete barriers generally occurs from combined sulfate attack and corrosion of embedded steel following carbonation. Saltstone is projected to degrade very slowly by decalcification, with complete degradation occurring in excess of 200,000 years for any SDU type.

From the analyses described in the preceding sections, the LXO model was found to predict faster concrete degradation from sulfate attack than was seen in the STADIUM simulations, in part because the model modifies transport properties based on predicted damage. LXO incorporates mineral availabilities that are generally less than 100%, which leads to faster depletion of solid reactants. STADIUM and LXO also assume different initial chemical compositions, which affects the results. Therefore, lacking long term experimental data to confirm either model, the more conservative LXO results were recommended for estimating concrete degradation from sulfate attack.

For the SDU 2 design with a clean cap fill, the roof, wall, and floor components are projected to become fully degraded under Nominal conditions at 3855, 922, and 1413 years, respectively. For SDU 4 the roof and floor are estimated to be fully degraded under Nominal conditions after 1106 and 1404 years, respectively; the wall is assumed to be fully degraded at time zero in the most recent PA simulations. Degradation of these concrete barriers generally occurs from combined sulfate attack and corrosion of embedded steel following carbonation. Saltstone is projected to degrade very slowly by decalcification, with complete degradation occurring in excess of 200,000 years for any SDU type. For the SDU 6 design, the roof and floor components are projected to fully degrade by 1413 years while the tapered wall fully degrades at 815 years for the thinnest section and 1822 years for the thickest section.

Development of a Material Properties Database and Software Tool for Simulation of Flow Properties Through Degraded Cementitious Materials

Work performed by the Savannah River National Laboratory (SRNL) in fiscal year 2014 to develop a new Cementitious Barriers Project (CBP) software module designated as FLOExcel. FLOExcel incorporates a uniform database and flow simulator to capture experimental data and simulate transport flow through both fractured and intact cementitious materials. The software module includes hydraulic parameters for both fractured and intact cementitious materials in the database and a standalone GoldSim framework to manipulate the data. The database will be updated with new data as it comes available. The software module will later be integrated into the new release of the CBP Toolbox, Version 3.0. A report will be published in FY2015 describing the development of the FLOExcel package that includes:

1) A uniform database to capture CBP data for cementitious materials including their hydraulic properties.

2) A Software and GoldSim User Interface to calculate hydraulic flow properties of degraded and fractured cementitious materials.

2014 CBP EXPERIMENTAL PROGRAMS AND IMPACT

The CBP provides great value to the DOE complex through the development of the experimentally-based simulation tools that model pertinent degradation mechanisms much needed for technical support of the DOE facility PAs. The experimental programs, in addition to providing data for calibration and validation of the CBP software tools, provide support directly to future DOE facility flowsheets and design. Applying understanding through experimental efforts to simulation tools and facility design is a necessary need in the DOE complex.

CBP experimental efforts to date have focused on external sulfate attack, carbonation, and primary constituent leaching phenomena. In 2014, the experimental program focus at SRNL and SIMCO and its significance is shown in Table 2.

Table 2: CBP Experimental Program and Significance

CBP Partner	Experimental Program	Significance
SRNL	**Tc Mobility in Various Environments**	Tc mobility initial experimental works suggests that conventional leaching protocols may not be conservative for direct disposal of Tc containing waste forms in vadose zone environments.
	Determination of Mineral Phases in Salt-Based Waste Forms	Mineral assemblage has been determined to significantly impact the modeling results.
	Method Development for Transport Properties of Fractured Cementitious Materials (CM)	Methods exist for in-tact cementitious materials but not fractured. Considered "cutting edge" of technology to provide for fractured materials.
SIMCO	**Exposure of Cementitious Materials to Corrosive Solutions (Phase I)**	Phase I experimental results showed that damage does not occur in high pH solutions in the presence of sulfate. Good quality mixtures could thus prove durable over the long term and act as an effective barrier to prevent radionuclides from reaching the environment.
	Exposure of DOE Cementitious Materials to Corrosive Solutions (Phase II)	Preliminary Phase II results shows the same results as Phase I for the SDU 1/4 concrete, however, SDU 2 concrete shows damage.
Vanderbilt University	**Microstructure Evaluation of Cementitious Material undergoing Carbonation**	Characterize changes in the microstructure and chemical speciation from carbonation in cementitious materials as a function of material alkalinity and exposure conditions to evaluate the carbonation front, transport of gases, and reaction chemistry.

SRNL Tc Oxidation and Mobility Studies in DOE Salt Waste Forms

In FY2014, SRNL completed an experimental program on oxidation of DOE cementitious materials, specifically, slag-based salt waste forms that are representative of both SRS and future Hanford waste. Both the SRS and Hanford waste streams contain soluble redox sensitive technetium (Tc) which requires stabilization to meet disposal requirements and poses great challenges to performance predictions of cementitious barriers used in stabilizing Tc due its high solubility and mobility. SRNL has developed a new method known as the "Depth-Discrete Sampling and Leaching Method" that provides a way to determine the oxidation state of Tc, and in turn, provides much needed data for modeling Tc releases to the environment.

In the oxidation studies, slag-based salt waste form samples were exposed to both Hanford sediments and deionized (DI) water. Soluble Tc was leached from all of the depth-discrete subsamples which strongly suggests that oxygen was present in the entire length of both samples. The results also reveal that the oxidation rate of the sample exposed to soil was faster than that of the sample exposed to water. This conclusion is consistent with the more rapid transport of ions through a gas phase as compared to a liquid phase. This conclusion has the potential to challenge current leaching protocols of redox sensitive contaminants in water. A report was issued in FY2014 describing the SRNL Tc oxidation and mobility studies in DOE salt waste forms. In the report is Figure 7 graphically showing the results of Tc leaching (in green) from two samples exposed for 154 days: Tc2-9 exposed to Hanford sediment with 4.5 % moisture (as received condition) and Tc2-10 exposed to DI water. After exposure for 154 days, the depth-discrete subsamples were cut, crushed and leached in deaerated, DI water.

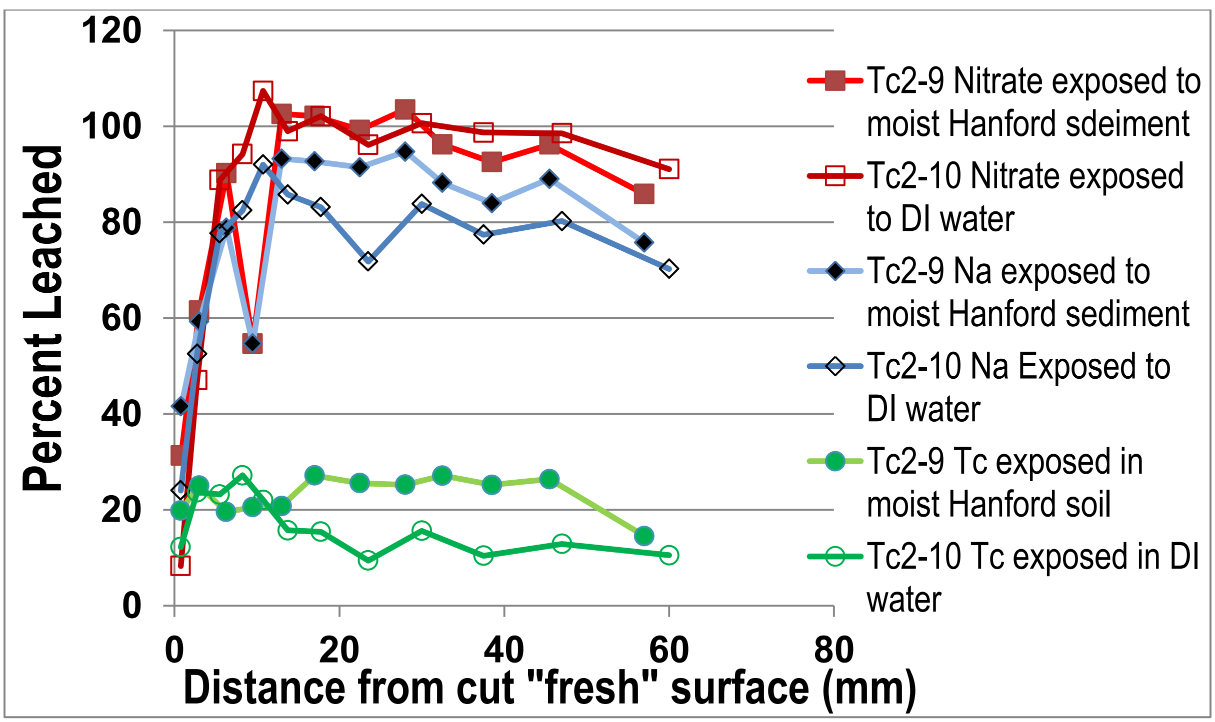


Figure 7. Percent Tc-99 leached from depth-discrete subsamples as a function of distance from fresh surfaces exposed to unsaturated Hanford sediment and DI water.

The Tc fraction leached from Tc2-9 (exposed to Hanford sediment) increased to 0.25 to 0.27 and dropped to the lowest value measured in that sample, 0.145, possibly identifying the oxidation front resulting from exposure in soil. The Tc-99 mass fraction leached from Tc2-10 (exposed to DI water) dropped to 0.09 to 0.16 between 12 and 65 mm below the exposed surface. The leveling off of the leachable Tc below 12 mm may indicate the location of the oxidation front resulting from oxygen supplied to the fresh cut surface by the DI water.

SRNL Characterization of Mineral Phases in DOE Salt-Based Waste Forms

SRNL conducted an experimental program in FY2014 characterizing a series of DOE sodium salt-based waste forms using x-ray diffraction. Characterization of the matrix mineralogy is important for predicting contaminant leaching and evolution of the materials as a function of time and changing conditions. The objective of this study was to provide initial phase characterization for the cementitious salt waste form. This information can be used to: 1) generate a base line for the evolution of the waste form as a function of time and conditions, 2) design new binders based on mineralogy of the binder, 3) understand and predict anion and cation leaching behavior of contaminants of concern, and 4) predict performance of the waste forms for which phase solubility and thermodynamic data are available. Characterization of the mineralogy is also important for understanding the buffering effects that the waste form has on infiltrating water / leachates. A report will be published in FY2015 on the results of the mineral phase characterization of DOE salt-based waste forms.

SRNL Hydraulic Conductivity Method Development in Fractured Cementitious Materials

Another SRNL CBP experimental program included the method development of measuring important transport properties in fractured cementitious materials. Specifically, the scope was to develop a method to measure one of the most important thermodynamic properties in modeling, the hydraulic conductivity of fractured material. DOE Performance Assessments often involve cementitious barriers and/or waste forms that are predicted or assumed to degrade over time due to various mechanisms such as carbonation-influenced reinforcing steel corrosion, external sulfate attack, differential settlement, and seismic activity. Physical degradation typically takes the form of small-scale cracking / fracturing, and the affected materials reside in unsaturated hydrogeologic zones. In these cases, unsaturated hydraulic properties are needed for fractured cementitious materials to simulate moisture movement and contaminant transport within and around the facility. The outflow extraction method has been developed to provide a suitable method for estimating these material properties. SRNL will publish a report in FY2015 on the method development of hydraulic conductivity in fractured cementitious materials.

SIMCO Exposure of DOE Barriers to Aggressive Solutions Experimental Study (Phase I and II)

The SIMCO Technologies, Inc. (SIMCO) experimental work aimed at supporting the assessment of long-term durability of concrete barriers containing sulfate-bearing salt wasteforms, present at both SRS and Hanford. SIMCO had conducted a two phase study with surprising results in the second phase study. Phase I experimental results showed that damage does not occur in high pH solutions in the presence of sulfate. SIMCO conducted additional experimental studies with contact solutions that mimic more closely waste form pore solutions and the new SDU units (i.e., SDU 2) in Phase II. Preliminary Phase II results showed the same results as Phase I for the SDU 1/4 concrete, however, SDU 2 concrete showed damage.

The first experimental study (Phase I) showed that sulfate damage does occur in neutral environments, however, in high pH solutions such as is characteristic of DOE salt wastes, no signs of damage was observed in any of the paste mixtures. The deleterious mineral phases associated with sulfate exposure did not form in the high pH environment. A possible explanation for this is the absence of gypsum formation at high pH. SIMCO concluded that, although these results need further confirmation, they indicate that the high sulfate content found in the wasteform pore solution will not necessarily lead to severe damage to concrete typical of that used in SRS Saltstone Disposal Units 1/4. Good quality mixtures could thus prove durable over the long term and act as an effective barrier to prevent radionuclides from reaching the environment. However, additional experiments with contact solutions that mimic more closely wasteform pore solution and the impact to the new SDU units concrete were needed in future studies. This conclusion led to the Phase II experimental study.

In the Phase II experimental study, the scope was extended to hydrated cement pastes incorporating supplementary cementitious materials (SCM) such as fly ash and ground granulated blast furnace slag (GGBFS) that is characteristic of DOE cementitious barrier materials. Two paste mixes were equivalent to Vault 1/4 and SDU 2 concrete mixes uses at SRS in storage structures. The experimental program aimed at testing aggressive contact solutions that more closely mimic the chemical composition of saltstone pore solution. Five different solutions, some of which incorporated high levels of carbonate and nitrate, were placed in contact with four different hydrated cement paste mixes. In all solutions, 150 mmol/L of SO_4^{2-} (14, 400 ppm) were present. The solutions included different pH conditions and different sodium content. Two additional paste mixes, cast at the same water-to-cement ratio and using the same cements but without SCMs, were also tested.

Globally, results were in line with the previous study and confirmed that high-pH may limit the formation of some deleterious phases like gypsum. In this case, ettringite may form but is not necessarily associated with damage. However, the high concentration of sodium in the SDU 2 may be associated with the formation of an AFm-like mineral called U-phase.

The most significant evidences of damage were all associated with the SDU 2 paste analog. This material proved very sensitive to high-pH. All measurement techniques used to monitor and evaluate damage to samples indicated significant alterations to this mix when immersed in contact solutions containing sodium hydroxide. It was hypothesized that the low cement content, combined with high silica content coming from silica fume, fly ash and slag led to the presence unreacted silica. It is possible that the pozzolanic reaction of these SCMs could not be activated due to the low alkali content, a direct consequence of low cement content. In this scenario, the material end up having a lot of silica available to react upon contact with sodium hydroxide, possibly forming a gel that may be similar to the gel formed in alkali-silica reactions. This scenario needs further experimental confirmation but it may well explain the poor behavior of mix SDU 2 in presence of NaOH. SIMCO will publish reports in FY2015 detailing the experimental programs and the results.

Vanderbilt University Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack

There are various degradation methods that can affect the integrity of these materials over this time frame including carbonation which lowers the alkalinity of the material that can lead to cracking in materials with steel reinforcement. The rate and extent of carbonation in these materials can be impacted by the addition of fly ash and the fly ash source. To characterize the carbonation reaction, changes in the microstructure and elemental distribution as a function of extent of carbonation and fly ash type were evaluated using scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS). The migration and deposition of chemical species were observed in carbonated regions from EDS data, which are attributed to changes in alkalinity and solubility as determined from EPA Method 1313 (Liquid-solid partitioning (LSP) as a function of eluate pH). Changes in mass transport properties resulting from carbonation were observed using EPA Method 1315 (Mass transfer rates in monolithic and compacted granular materials using semi-dynamic tank leaching procedures). Carbonation reactions in each material were simulated using LeachXS/ORCHESTRA, a reactive transport modeling tool, to provide further evidence of localized deposition and migration of chemical species due to changes in speciation and solubility.

CONCLUSIONS

The CBP partnership provides competence, continuity, and credibility to the DOE need to use engineered barriers in near surface disposal facilities and to advance progress in final treatment and disposal of legacy waste and closure of HLW tanks in the DOE complex. Therefore, the CBP will continue to focus efforts in:

- Oxidation of redox sensitive contaminants, specifically, technetium (Note: Tc is of significant concern because it is long-lived and highly mobile in the environment.)
- Alkali silica reaction degradation predictions for DOE cementitious containment structures
- Alkali silica module applied to Nuclear Power Plant concrete (required for service life prediction)
- Verification and validation of all models to DOE standards of quality assurance
- Multiple mechanism model (i.e., synergistic impact of dual and triple mechanisms impacting the degradation of structures)
- Analysis (experiments/modeling) of additional mechanisms that impact DOE cementitious containment(e.g., acidic soil exposure)
- Analysis (experiments/modeling) of the change in microstructure and transport properties as the cementitious material degrades

The CBP Software Toolbox has been used to provide important technical insights to the DOE PA process regarding sulfate attack on the DOE Saltstone Disposal Facility and carbonation on a typical high-level waste tank. Current development efforts in the areas of carbonation, transport in fractured and intact media, and chloride attack have resulted in the second release of the Toolbox. Recognizing that physical damage to cementitious materials typically occurs in the form of cracking, ongoing CBP development efforts are also focused on predicting damage through fracture mechanics considerations, determining the hydraulic and transport properties of fractured materials, and implementing corresponding Toolbox simulation capabilities.

ACKNOWLEDGEMENTS

The Cementitious Barriers Partnership is sponsored by the U.S. DOE Office of Tank Waste Management in collaboration with the U. S. NRC and administered through Savannah River National Laboratory Cooperative Research and Development Agreement (CRADA) No. CR-08-001.

U.S. DEPARTMENT OF ENERGY

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