

CEMENTITIOUS BARRIERS PARTNERSHIP FY2013 END-YEAR REPORT

CBP-TR-2014-001, Rev. 0

CEMENTITIOUS BARRIERS PARTNERSHIP FY2013 END-YEAR REPORT

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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) / Consortium for Risk Evaluation with Stakeholder Participation (CRESP), 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) is providing research 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

FY2013 End-Year Report

Summary

In FY2013, the Cementitious Barriers Partnership (CBP) demonstrated continued tangible progress toward fulfilling the objective of developing a set of software tools to improve understanding and prediction of the long-term structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. In November 2012, the CBP released “Version 1.0” of the CBP Software Toolbox, a suite of software for simulating reactive transport in cementitious materials and important degradation phenomena. In addition, the CBP completed development of new software for the “Version 2.0” Toolbox to be released in early FY2014 and demonstrated use of the Version 1.0 Toolbox on DOE applications.

The current primary software components in both Versions 1.0 and 2.0 are LeachXS/ORCHESTRA, STADIUM, and a GoldSim interface for probabilistic analysis of selected degradation scenarios as shown in Figure 1. The CBP Software Toolbox Version 1.0 supports analysis of external sulfate attack (including damage mechanics), carbonation, and primary constituent leaching. Version 2.0 includes the additional analysis of chloride attack and dual regime flow and contaminant migration in fractured and non-fractured cementitious material as shown in Figure 2.0.

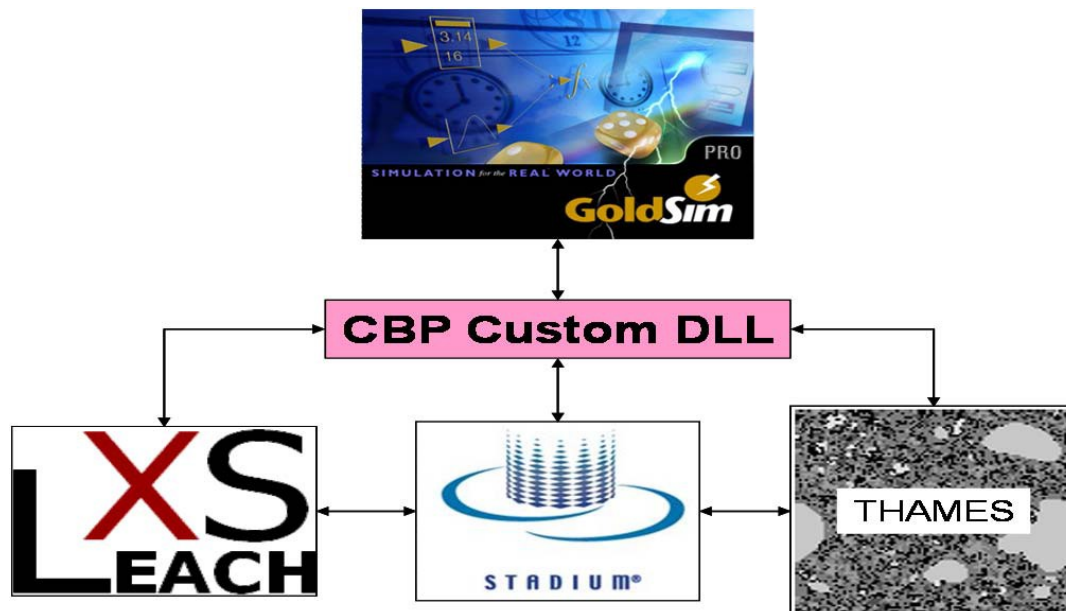


Figure 1. CBP Software Toolbox Software

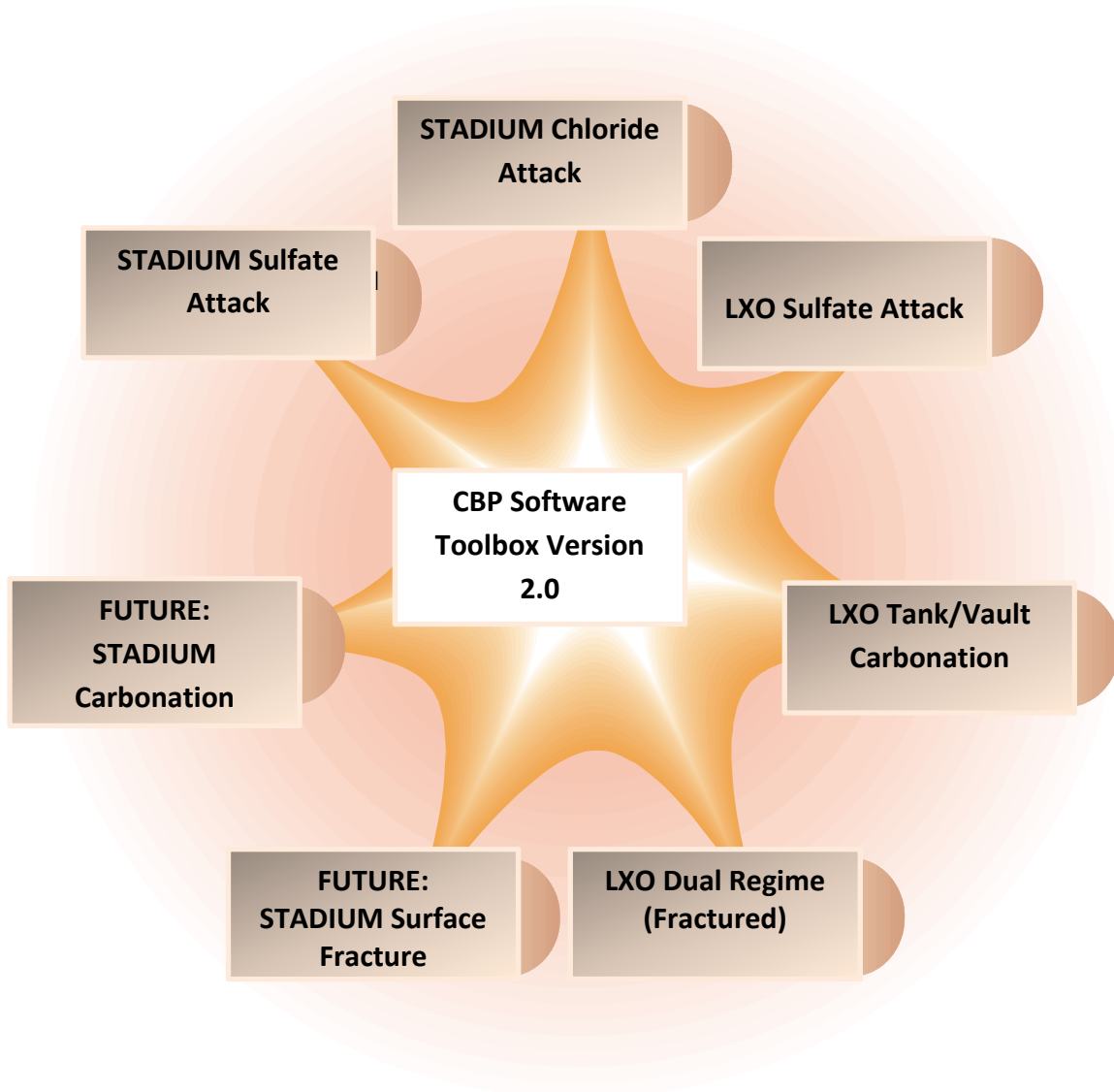


Figure 2. CBP Software Toolbox Software Modules in Version 2.0

The LeachXS component embodies an extensive material property measurements database along with chemical speciation and reactive mass transport simulation cases with emphasis on leaching of major, trace and radionuclide constituents from cementitious materials used in DOE facilities, such as Saltstone (Savannah River) and Cast Stone (Hanford), tank closure grouts, and barrier concretes. STADIUM focuses on the physical and structural service life of materials and components based on chemical speciation and reactive mass transport of major cement constituents and aggressive species (e.g., chloride, sulfate, etc.). THAMES is a planned future CBP Toolbox component focused on simulation of the microstructure of cementitious materials and calculation of resultant hydraulic and constituent mass transfer parameters needed in modeling.

Two CBP software demonstrations were conducted in FY2013, one to support the Saltstone Disposal Facility (SDF) at SRS and the other on a representative Hanford high-level waste tank. The CBP Toolbox

demonstration on the SDF provided analysis on the most probable degradation mechanisms to the cementitious vault enclosure caused by sulfate and carbonation ingress. This analysis was documented and resulted in the issuance of a SDF Performance Assessment Special Analysis by Liquid Waste Operations this fiscal year. The two new software tools supporting chloride attack and dual-regime flow will provide additional degradation tools to better evaluate performance of DOE and commercial cementitious barriers. The CBP SRNL experimental program produced two patent applications and field data that will be used in the development and calibration of CBP software tools being developed in FY2014.

The CBP issued numerous reports and other documentation that accompanied both versions of the CBP Software Toolbox including a User Guide and Installation Guide. These documents, as well as, the presentations from the CBP Software Toolbox Demonstration and User Workshop from FY2012 can be accessed from the CBP webpage at <http://cementbarriers.org/>.

The CBP software and simulation tools varies from other efforts in that all the tools are based upon specific and relevant experimental research of cementitious materials utilized in DOE applications. The CBP FY2013 program involved continuing research to improve and enhance the simulation tools as well as developing new tools that model other key degradation phenomena not addressed in Version 1.0. Also efforts to continue to verify the various simulation tools through laboratory experiments and analysis of field specimens are ongoing and will continue into FY2014 to quantify and reduce the uncertainty associated with performance assessments. This end-year report summarizes FY2013 software development efforts and the various experimental programs that are providing data for calibration and validation of the CBP developed software.

FY2013 CBP Software Demonstrations and Development

CBP Software Demonstrations

The CBP Software Toolbox has produced tangible benefits to the DOE Performance Assessment (PA) community. In FY2013, the CBP Software Toolbox software components were used to produce two major evaluations in support of the Saltstone Disposal Facility (SDF) at Savannah River Site (SRS) and Hanford's High Level Waste (HLW) Tanks. The results of the SDF analysis on sulfate attack and carbonation degradation were used directly to support a DOE Performance Assessment Special Analysis that is scheduled to be issued this fiscal year (DRAFT: SRR-CWDA-2013-00062, Rev.0, *"FY2013 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site"*.) These key analyses are presented in this section, along with, CBP Toolbox enhancements and the developmental efforts of several new software tools.

CBP Software Toolbox Demonstration on the Saltstone Disposal Facility

Documented in: Savannah River National Laboratory Report SRNL-STI-2013-00118, Rev. 0 *"Degradation of Cementitious Materials Associated With Saltstone Disposal Units"* by CBP Partners and Associates: G. P. Flach and F. G. Smith III; March 2013.

The CBP Software Toolbox Version 1.0 was utilized on DOE applications by evaluating the performance of the DOE Savannah River Site (SRS) Saltstone Disposal Facility (SDF) under the most probable degradation mechanisms and consequent release of constituents. The results from this demonstration are being utilized in the modification of the current SDF Performance Assessment (PA) via a special analysis.

The SDF disposes of low-level radioactive salt solution originating from liquid waste storage tanks at the site using cementitious materials. 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 an SDF disposal unit (SDU) represents an additional physical and chemical barrier to radionuclide release to the environment. Together the waste form and the SDU 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 timescales 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, using the CBP Software Toolbox, degradation time scales for each of these three degradation phenomena were estimated for the SDF. The combined effects of multiple phenomena were then considered to determine the most limiting degradation time scale for each cementitious material (i.e., vault and waste form). The CBP Software Toolbox was used to provide estimates of the degradation times using the numerical simulation codes in the Toolbox

(<http://cementbarriers.org>).

CBP Analysis of a USDOE High-Level Waste Tank Closure Scenario using an Upgraded Carbonation Module
Documented in: *"Modeling Carbonation of High-Level Waste Tank Integrity and Closure,"* by CBP Partners and Associates: K. G. Brown, J. Arnold, S. Sarkar, G. P. Flach, H. van der Sloot, J.C.L. Meeussen and D. S. Kosson; NUCPERF 2013.

The CBP is focused on reducing uncertainties in current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency in the assessment process. One important set of US Department of Energy challenges is assessing the integrity and closure of the high-level waste (HLW) tanks that currently store millions of gallons of highly radioactive wastes. Many of these tanks are decades past their design lives, have leaked or been overfilled, and must be emptied and closed to satisfy regulatory agreements. Carbonation-induced corrosion has been identified as a primary degradation and possible failure mechanism for the HLW tanks prior to closure. After closure the impact of carbonation (and concurrent oxidation) may be to increase the release and short-range transport of contaminants of concern.

In Version 2.0 of the Toolbox, the CBP has upgraded the LeachXS™/ORCHESTRA carbonation module originally in Version 1.0 and used it to evaluate a representative HLW tank closure scenario including the potential impacts of carbonation on waste tanks prior to and post closure (see Figure 3.0). CBP software tools, including LeachXS™/ORCHESTRA (LXO), are being used to simulate waste tank carbonation, major constituent leaching, and contaminant releases to evaluate the source term and near-field conditions. The performance of the closed tanks over centuries, if not millennia, must be assessed to evaluate the potential release of residual radionuclides to the environment. Simulations included sensitivity analyses for uncracked concrete to varying input parameters to evaluate sensitivity of the resulting predicted carbonation results. Input parameters included composition, soil-gas CO₂ concentration, concrete saturation, porosity, CO₂ effective diffusivity, mineral set, and thermodynamic parameters. The results indicated that carbonation to pH 9 (from depassivation of embedded steel) requires at least on the order of 700 years and possibly up to 7000 years based on a probabilistic analysis on the modeling.

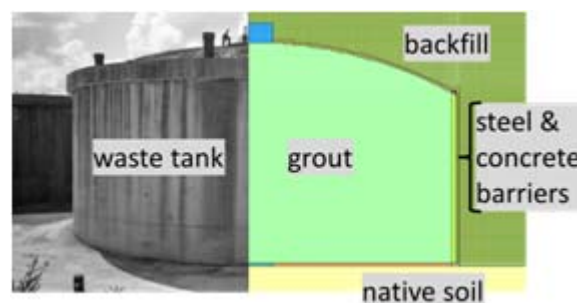


Figure 3. CBP Analysis of a Representative USDOE High-Level Waste Tank

This CBP analysis of a HLW Tank provides an efficient method for assessing effectiveness of current closure grouts and designing of future grouts. Future work will ensure longer simulation times and consideration of gas exchange reactions (e.g. CO₂ and O₂) to provide useful additional information.

CBP Software Development

CBP Dual Regime Module Development

Documented in: “A Dual Regime Reactive Transport Model for Simulation of High Level Waste Tank Closure Scenarios”, by CBP Partners and associates: Sohini Sarkar, David S. Kosson, Hans Meeussen, Hans van der Sloot, Kevin Brown and Andrew C. Garrabrants; Waste Management 2013 -13375.

In FY2013, a reactive transport model was developed as part of the CBP to simulate the release of radionuclides from grout that is both in-tact and fractured and to estimate the evolution of pH. In tank closure, as well as, any cementitious closure facility where grout is used to stabilize radionuclide species, the grout can be assumed to have varying extents of cracking. The partially or completely degraded grouted tank is idealized as a “dual regime” system as shown in Figure 4 comprised of two regimes:

1. A mobile region with cracks and macropores, and
2. An immobile/ stagnant region comprising of the solid matrix with micropores.

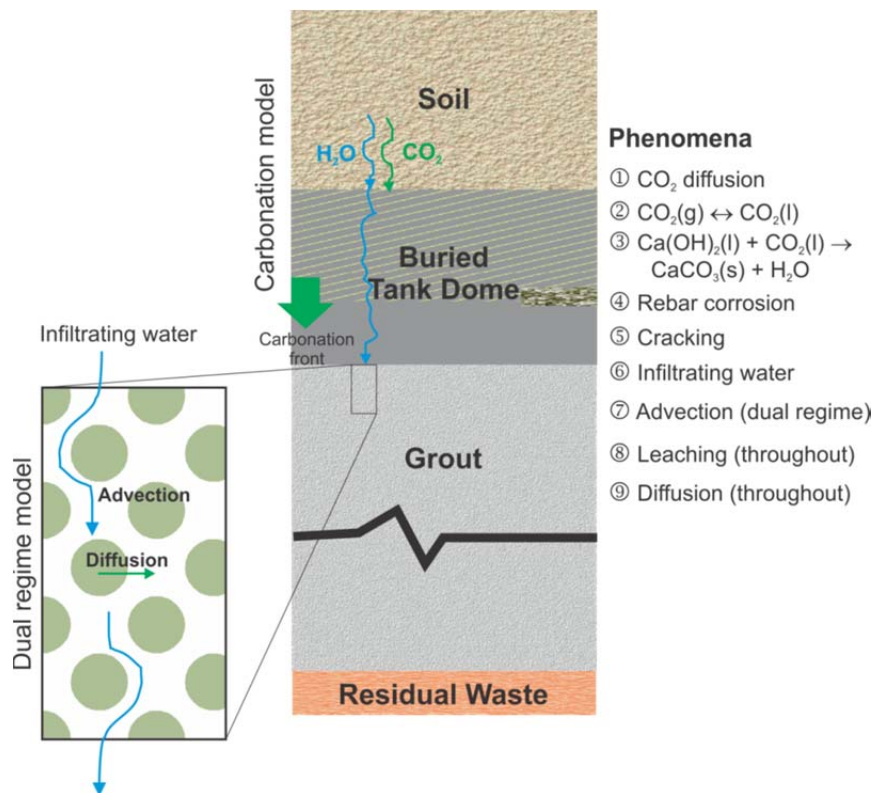


Figure 4. Dual-Regime System

The transport profiles of the species are calculated by incorporating advection of species through the mobile region, diffusion of species through the immobile/stagnant region, and exchange of species between the mobile and immobile regions. A geochemical speciation code in conjunction with the pH dependent test data for a grout material is used to obtain a mineral set that best describes the trends in the test data of the major species (see Figure 5). The dual regime reactive transport model predictions are compared with the release data from an up-flow column percolation test. The coupled model is then used to assess effects of crack state of the structure, rate and composition of the infiltrating water on the pH evolution at the grout-waste interface. The coupled reactive transport model developed in this work can be used as part of the performance assessment process for evaluating potential risks from leaching of a cracked tank containing elements of human health and environmental concern.

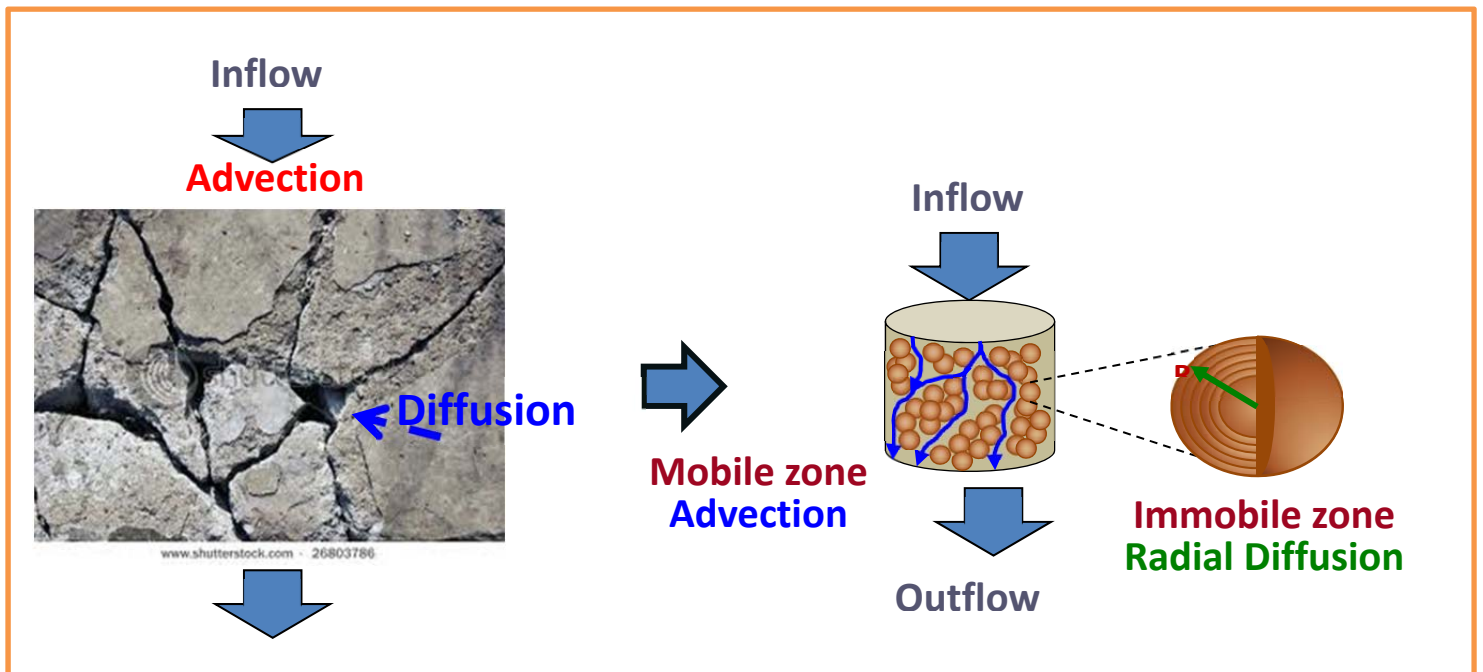


Figure 5. Model Framework of Fractured and Solid Matrix in a Dual Regime System

CBP Chloride Attack Module

The CBP Software Toolbox, Version 2.0, includes a STADIUM chloride attack module to predict chloride ingress and corrosion initiation predictions. STADIUM uses time-step finite element analysis to simulate the progress of harmful ions such as chloride and hydroxide through concrete, by considering the chemical and physical properties of the concrete being analyzed. The STADIUM® Chloride Attack module software simulates the physical and chemical changes in concrete as it reacts with its environment, taking into account concrete variables such as chemical composition, permeability, ion diffusion coefficients, moisture transport coefficients, tortuosity, and many other factors, as well as exposure conditions such as ambient humidity, temperature, and chemical aggression. This added software module provides a method to accurately predict the degradation of cementitious materials exposed to chloride and other harmful ions.

CBP Software Toolbox Enhancements

CBP Software Toolbox Version 2.0 Code Integration Enhancements

Documented in: CBP-TR-2013-03, Rev.0, “*CBP Toolbox Code Integration Enhancements*” by CBP Partner and Associates: F.G. Smith, G.P. Flach, and K.G. Brown; April 2013.

In FY2013, enhancements were made to the CBP Software Toolbox Version 1.0, specifically the code integration functionality aspects of the Toolbox. The most significant enhancements were:

- 1) Improved graphical display of model results – The CBP Toolbox has been modified with improved methods for displaying results including two and three-dimensional plotting capabilities as shown in Figure 6.

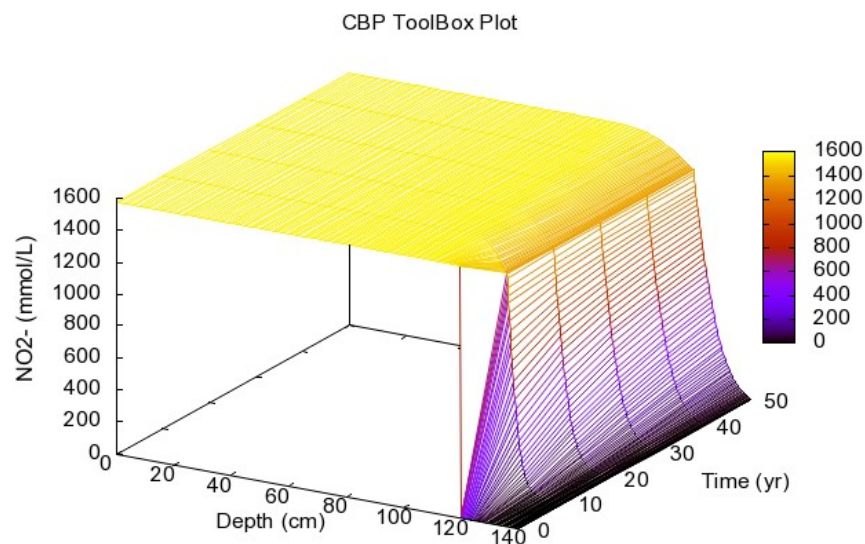


Figure 6. Three-dimensional surface plot of nitrate concentration from a 2-layer model

- 2) Improved error analysis and reporting – In previous years, the CBP developed a custom Dynamic Link Library (DLL) to enable data communication between the Toolbox software components, allowing comparative analysis. Recently, error messages have been enhanced to more clearly explain problems encountered during execution of the DLL instruction files. The additional information will allow the User to quickly identify the problem and take corrective actions.
- 3) Increase in the default maximum model mesh size from 301 to 501 nodes – Modifications to increase the mesh size provides a finer resolution necessary to operate the multi-layers within the STADIUM model. The finer resolution will improve the distinctions between the layers.
- 4) The ability to designate the LeachXS™/ORCHESTRA (LXO) simulation time frames through the GoldSim interface – The original version of the CBP Software Toolbox did not allow the User to change the degradation simulation time of the cementitious barrier. Now the Goldsim User Interface (GUI) has been modified for LXO so that the User can determine the time frames desired or dictated by the performance assessment.

FY2013 CBP Experimental Programs

CBP experimental efforts to date have focused on external sulfate attack, carbonation, and primary constituent leaching phenomena. In FY2013, the experimental program focus at SRNL includes:

- Measurement of the progress of the oxidation front which impacts the retention of redox sensitive radionuclides such as Tc-99,
- Development of methods to measure hydraulic and transport properties of fractured materials, and
- Determination of the initial mineral phases of saltstone cementitious materials (Mineral assemblage has been determined to significantly impact the modeling results).

Measurement of the Oxidation Front Progress and Reduction Capacity of Cementitious Waste Forms

Documented in: CBP-TR-2013-02, Rev. 0, *"Effect Of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms"* by CBP Partners and Associates: P. M. Almond, D. B. Stefanko, and C. A. Langton; 2013.

The rate of oxidation is important to the long-term performance of waste forms that contain redox sensitive contaminants (i.e., solubilities are a function of the oxidation state) such as technetium. The rate of oxidation front advancement into a monolith and the effect of oxygen ingress on redox sensitive contaminants are needed to:

- 1) Develop the conceptual model for performance predictions,
- 2) Provide data to parameterize fate and transport models, and
- 3) Validate computational codes.

Several U.S. DOE sites use waste forms and concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as technetium and chromium. These waste forms and containment structures are typically deployed in near surface unsaturated oxidizing environments. Consequently, the effect of exposure to air (oxygen) and water containing dissolved oxygen during production, during the period of institutional control, and over the long term period of performance is important for predicting the speciation and mobility of the redox sensitive radioactive contaminants.

Technetium in salt solution is reduced to Tc(IV) by reacting with ingredients in the waste form to precipitate a low solubility sulfide compound. Upon exposure to oxygen, the compounds containing Tc(IV) oxidize to form pertechnetate ion (TcO_4^-) which is very soluble. Consequently, the rate of Tc oxidation front advancement into a monolith and the Tc leaching profile as a function of depth from an exposed surface are important to waste form performance and ground water concentration predictions. Depth discrete sampling of materials exposed to realistic conditions in combination with short term leaching of crushed samples has potential for advancing the understanding of factors influencing performance and will support conceptual model development.

In FY2013, an experimental program for measuring contaminant oxidation rate based on leaching of select contaminants of concern has been conducted and documented in CBP-TR-2013-002. In addition, the relationship between reduction capacity and contaminant oxidation is addressed. Chromate was used as a non-radioactive surrogate for technetium in simulated waste form samples. Depth discrete subsamples were cut from material exposed to SRS “field conditions”. The subsamples were prepared and analyzed for both reduction capacity and chromium leachability.



Figure 7. Slag-based waste form spiked with 1000 ppm of Chromium and exposed to SRS “field conditions.”

The objective of this study was to provide information for developing a conceptual model for redox-controlled contaminant release from cementitious waste forms. Results from field-cured samples indicate that the depth at which leachable chromium was detected advanced further into the sample exposed for 302 days compared to the sample exposed to air for 118 days (at least 50 mm compared to at least 20 mm) as shown in Figure 8. The carbonation front was also estimated to have advanced to at least 28 mm in 302 days based on visual observation of gas evolution during acid addition during the reduction capacity measurements. These results indicate that depth discrete sampling of materials exposed to realistic conditions in combination with short term leaching of crushed samples has potential for advancing the understanding of factors influencing performance and will support conceptual model development.

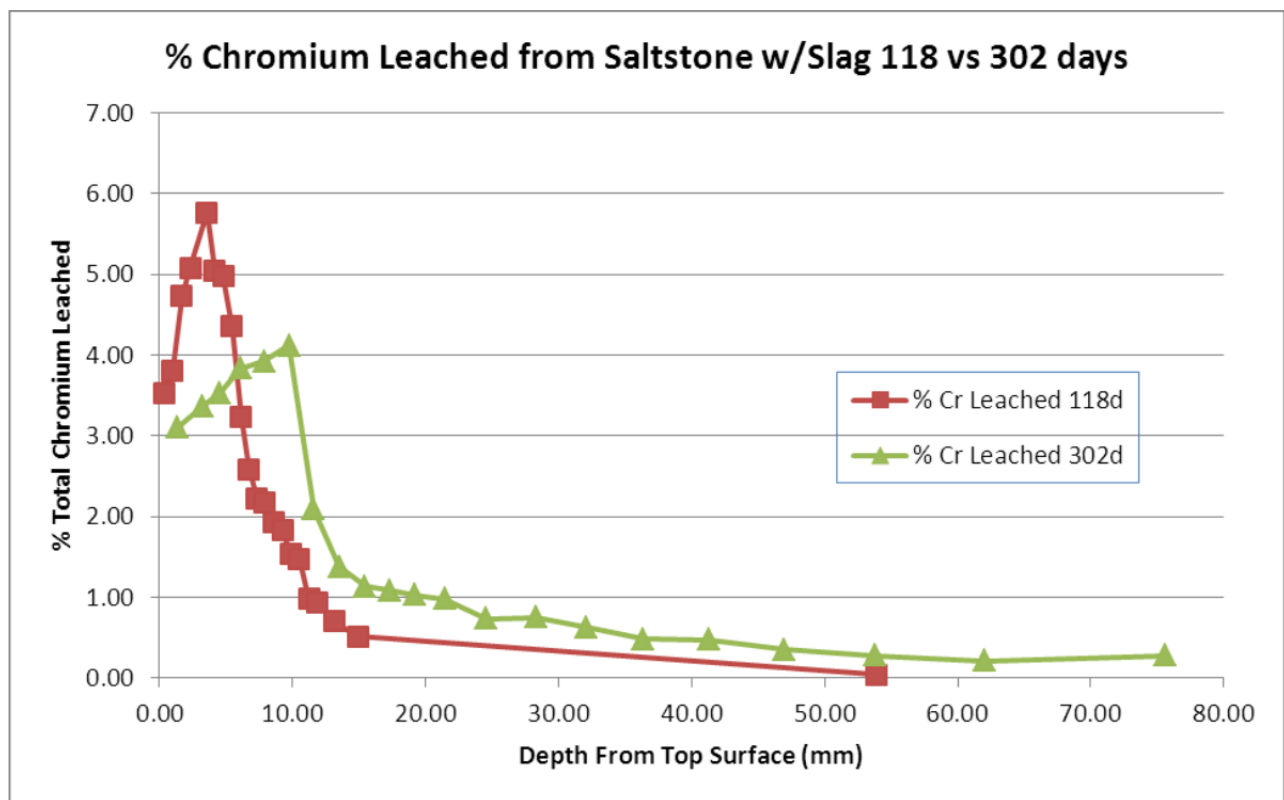


Figure 8. Comparison of leachable chromium versus sample depth for 118 and 302 day aged samples.

Method Development for Measuring Transport Properties in Fractured Materials

Documented in: Savannah River National Laboratory Report SRNL-STI-2013-00522 and SRNL-L3200-2012-00029, Rev. 0 "Fractured Media Update," by CBP Associates: J.L. Kohn, K.L. Dixon, R.L. Nichols; October 2012.

The hydraulic properties, primarily unsaturated hydraulic conductivity/permeability, of damaged (fractured) saltstone and concrete have not been measured. Plausible, but unvalidated, theoretical model constructs for unsaturated hydraulic conductivity of fractured porous media are currently used in Performance Assessment (PA) modeling for cracked saltstone and concrete. The Nuclear Regulatory Commission (NRC) has expressed concern about the lack of model support for these assumed moisture characteristic curves data.

The objective of this task was to advance PA model support by developing an experimental method for determining the hydraulic conductivity of fractured cementitious materials (see Figure 9) under unsaturated conditions, and to demonstrate the technique on fractured saltstone samples.

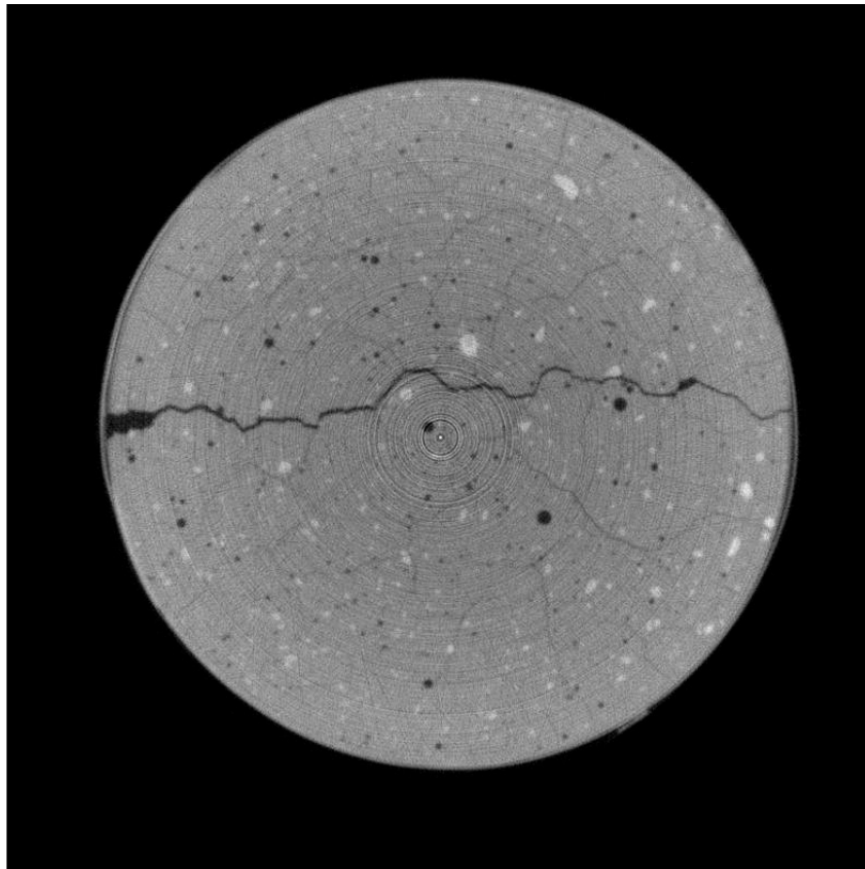


Figure 9. Transverse slice of cementitious material showing microfracture network heterogeneity and large scale porosity as represented by black speck features.

Preliminary method development previously conducted by Kohn et al. identified transient outflow extraction as the most promising method for characterizing the unsaturated properties of fractured porous media (see Figure 10). While the research conducted by Kohn et al. focused on fractured media analogs such as stacked glass slides, the current task focused directly on fractured saltstone. The overall results of this study indicate that the outflow extraction method is suitable for measuring the hydraulic properties of micro-fractured porous media. The resulting cumulative outflow data can be analyzed using the computer code Hydrus-1D to generate the van Genuchten curve fitting parameters that adequately describe fracture drainage. The resulting characteristic curves are consistent with blended characteristic curves that combine the behaviors of low pressure drainage associated with fracture flow with high pressure drainage from the bulk saltstone matrix.



Figure 10. Transient Outflow Extraction Test Set-Up with Outflow Extractor, Fraction Collector, Peristaltic Pump, and High Precision Digital Balance.

CBP Cementitious Material Mineral Phase Characterization

While extensive information is available on the solid phases and microstructure of ordinary Portland cement matrixes, only limited analogous information is available for the ternary mix designs (e.g., Portland cement with fly ash and granulated blast furnace slag). X-ray Diffraction (XRD) and neutron diffraction evaluations are underway of the representative CBP grout wasteform formulation to directly identify and characterize major mineral phases.

CBP Papers and Abstracts

The CBP Partners submitted many abstracts and papers in the Waste Management Symposia 2013 on various aspects of CBP research and modeling as described in this section.

- a. *"The Cementitious Barriers Partnership (CBP) Software Toolbox Capabilities in Assessing the Degradation of Cementitious Barriers", Waste Management 2013 -13487*

The CBP Software Toolbox is and will continue to produce tangible benefits to the working DOE Performance Assessment (PA) community. A review of prior DOE PAs has provided a list of potential opportunities for improving cementitious barrier performance predictions through the use of the CBP software tools. These opportunities include:

- 1) Impact of atmospheric exposure to concrete and grout before closure, such as accelerated slag and Tc-99 oxidation,
- 2) Prediction of changes in Kd/mobility as a function of time that result from changing pH and redox conditions,
- 3) Concrete degradation from rebar corrosion due to carbonation,
- 4) Early-age cracking from drying and/or thermal shrinkage and
- 5) Degradation due to sulfate attack.

The CBP has already had opportunity to provide near-term, tangible support to ongoing DOE-EM PAs such as the Savannah River Saltstone Disposal Facility (SDF) by providing a sulfate attack analysis that predicts the extent and damage that sulfate ingress will have on the concrete vaults over extended time (i.e., > 1000 years). This analysis is one of the many technical opportunities in cementitious barrier performance that can be addressed by the DOE-EM sponsored CBP software tools. Modification of the existing tools can provide a plethora of opportunities to bring defense in depth in prediction of the performance of cementitious barriers over time.

b. "CBP Phase I Code Integration", Waste Management 2013 - Paper 11446

The CBP simulation tools are being used to evaluate and predict the behavior of cementitious barriers used in near surface engineered waste disposal systems including wasteforms, containment structures, entombments, and environmental remediation. These cementitious materials are exposed to dynamic environmental conditions that cause changes in material properties via (i) aging, (ii) chloride attack, (iii) sulfate attack, (iv) carbonation, (v) oxidation, and (vi) primary constituent leaching. A set of state-of-the-art software tools has been selected as a starting point to capture these important aging and degradation phenomena.

Integration of existing software developed by the CBP partner organizations was determined to be the quickest method of meeting the CBP goal of providing a computational tool that improves the prediction of the long-term behavior of cementitious materials. The CBP partner codes selected for the Phase I integration effort were:

- LeachXS™/ORCHESTRA developed by the Energy Research Centre of the Netherlands (ECN) and
- STADIUM® developed by SIMCO Technologies, Inc.

These partner codes were selected based on their maturity and ability to address the problems outlined above. The GoldSim Monte Carlo simulation program was chosen as the code integration platform. GoldSim (current Version 10.5) is a Windows based graphical object-oriented computer program that provides a flexible environment for model development. GoldSim is capable of performing deterministic and probabilistic simulations and of modeling radioactive decay and constituent transport.

As part of the CBP project, a general Dynamic Link Library (DLL) interface was developed to link GoldSim with external codes. The DLL uses a list of code inputs provided by GoldSim to create an input file for the external application, runs the external code, and returns a list of outputs (read from files created by the external application) back to GoldSim. In this way GoldSim provides: 1) a unified user interface to the applications, 2) the capability of coupling selected codes in a synergistic manner, and 3) the capability of performing probabilistic uncertainty analysis with the codes. GoldSim is made available by the GoldSim Technology Group as a free "Player" version that allows running but not editing GoldSim models. The player version makes the software readily available to a wider community of users that would wish to use the CBP application but do not have a license for GoldSim.

c. *"Cementitious Barriers Partnership (CBP): Training and Release of CBP Toolbox Software, Version 1.0", Waste Management 2013 - 13480*

CBP software tools were made available to selected DOE Office of Environmental Management and other users for training and evaluation based on a set of important degradation scenarios, including sulfate ingress/attack and carbonation of cementitious materials. The tools that were presented at two-day training workshops held at NIST, Savannah River, and Hanford included LeachXS™/ORCHESTRA, STADIUM®, new U.S. Environmental Protection Agency leaching test methods based on the Leaching Environmental Assessment Framework (LEAF), and a CBP-developed GoldSim Dashboard Interface. Collectively these components form the CBP Software Toolbox. The CBP Dashboard uses a custom Dynamic-link library developed by CBP to couple to the LeachXS™/ORCHESTRA and STADIUM® codes to simulate reactive transport and degradation in cementitious materials for selected performance assessment scenarios. The first day of the workshop introduced participants to the software components via presentation materials, and the second day included hands-on tutorial exercises followed by discussions of enhancements desired by participants. Tools were revised based on feedback obtained during the workshops; the resulting improved CBP Software Toolbox, including evaluation versions of STADIUM® and LeachXS™/ORCHESTRA, has been made available to workshop and selected other participants for further assessment.

d. *"Cementitious Barriers Partnership (CBP): Using the CBP Software Toolbox to Simulate Sulfate Attack and Carbonation of Concrete Structures", Waste Management 2013 - 13481*

The CBP project has developed a set of integrated modeling tools and leaching test methods to help improve understanding and prediction of the long-term hydraulic and chemical performance of cementitious materials used in nuclear applications. Although each of the CBP tools has demonstrated utility as a standalone product, coupling the models over relevant spatial and temporal solution domains should provide more accurate predictions of cementitious materials behavior over relevant periods of performance. The LeachXS™/ORCHESTRA and STADIUM® models were first linked to the GoldSim Monte Carlo simulator to better characterize model uncertainties and as a means to coupling the models. Two important degradation scenarios were selected for initial demonstration: sulfate ingress / attack and carbonation of cementitious materials. When sufficient sulfate is present in the pore

solution external to a concrete barrier, sulfate can diffuse into the concrete, react with the concrete solid phases, and cause cracking that significantly changes the transport and structural properties of the concrete. The penetration of gaseous carbon dioxide within partially saturated concrete usually initiates a series of carbonation reactions with both dissolved ions and the hydrated cement paste. The carbonation process itself does not have a negative effect, per se, on the paste physical properties and can even result in reduced porosity and can help form a protective layer at the surface of concrete. However, carbonation has been shown to increase leaching of some constituents and can potentially have a detrimental effect on reinforced concrete structures by destroying the passive layer around embedded steel (e.g. rebar) and accelerating corrosion, which are important processes related to high-level waste tank integrity and closure evaluations. The use of the CBP Software Toolbox to simulate these important degradation phenomena for both concrete vaults and high-level waste tanks are demonstrated in this paper.

e. *"A Dual Regime Reactive Transport Model for Simulation of High Level Waste Tank Closure Scenarios", Waste Management 2013 -13375*

A numerical simulation framework is presented in this paper for estimating evolution of pH and release of major species from grout within high-level waste tanks after closure. This model was developed as part of the Cementitious Barriers Partnership. The reactive transport model consists of two parts – (1) transport of species, and (2) chemical reactions. The closure grout can be assumed to have varying extents of cracking and composition for performance assessment purposes. The partially or completely degraded grouted tank is idealized as a dual regime system comprising of a mobile region with cracks and macropores, and an immobile/stagnant region comprising of the solid matrix with micropores. The transport profiles of the species are calculated by incorporating advection of species through the mobile region, diffusion of species through the immobile/stagnant region, and exchange of species between the mobile and immobile regions. A geochemical speciation code in conjunction with the pH dependent test data for a grout material is used to obtain a mineral set that best describes the trends in the test data of the major species. The dual regime reactive transport model predictions are compared with the release data from an up-flow column percolation test. The coupled model is then used to assess effects of crack state of the structure, rate and composition of the infiltrating water on the pH evolution at the grout-waste interface. The coupled reactive transport model developed in this work can be used as part of the performance assessment process for evaluating potential risks from leaching of a cracked tank containing elements of human health and environmental concern.

Additional References:

Journal Articles

Sarkar, S, Mahadevan, S, Meeussen, JCL, van der Sloot, HA & Kosson, DS 2012, *Sensitivity Analysis of Damage in Cement Materials under Sulfate Attack and Calcium Leaching*, Journal of Materials in Civil Engineering, vol. 24, no. 4, pp. 430-440.

Sarkar, S, Kosson, DS, Mahadevan, S, Meeussen, JCL, van der Sloot, H, Arnold, JR & Brown, KG 2012, *Bayesian calibration of thermodynamic parameters for geochemical speciation modeling of cementitious materials*, Cement and Concrete Research, vol. 42, pp. 889-902.

van der Sloot, HA & Kosson, DS 2012, *Use of characterisation leaching tests and associated modelling tools in assessing the hazardous nature of wastes*, Journal of Hazardous Materials, Vols. 207-208, pp. 36-43.

Arnold, J, Kosson, DS, Brown, KG, Garrabrants, AC, Meeussen, JCL & van der Sloot, HA 2013, *Characterization and modeling of major constituent equilibrium chemistry of a blended cement mortar*, EPJ Web of Conferences, vol. 56, 01004.

Brown, KG, Arnold, JR, Sarkar, S, Flach, G, van der Sloot, HA, Meeussen, JCL, & Kosson, DS 2013, *Modeling Carbonation of High-Level Waste Tank Integrity and Closure*, EPJ Web of Conferences, vol. 56, 05003.

Arnold, J, Kosson, DS, Garrabrants, AC, Meeussen, JCL & van der Sloot, HA 2013, *Solution of the nonlinear Poisson–Boltzmann equation: Application to ionic diffusion in cementitious materials*, Cement and Concrete Research, Vol. 44, pp. 8-17.

Reports and Articles by Task

Brown, KG, Flach, GP & Smith III, FG 2013, *GoldSim Interface for the CBP Software Toolbox, Version 2.0 User Guide*, Cementitious Barriers Partnership, Nashville, TN and Aiken, SC, CBP-TR-2013-004-1, Rev. 0.

Brown, KG, Flach, GP & Smith III, FG 2013, *CBP Software Toolbox, Version 2.0 Installation Guide*, Cementitious Barriers Partnership, Nashville, TN and Aiken, SC, CBP-TR-2013-004-2, Rev. A (DRAFT).

Conferences and Proceedings (e.g., Waste Management, RILEM)

Arnold, J, Kosson, DS, Brown, KG, Garrabrants, AC, Meeussen, JCL, van der Sloot, HA 2012, *Characterization and modeling of major constituent release from a blended cement mortar exposed to accelerated aging conditions*, NUCPERF 2012, Cadarache, France.

Brown, KG 2012, *Modeling Carbonation of High-Level Waste Tank Integrity and Closure*, NUCPERF 2012, Cadarache, France.

Kosson, DS 2012, *An Overview of the Cementitious Barriers Partnership Results and Available Tools*, NUCPERF 2012, Cadarache, France.

Brown, KG, Kosson, D, Garrabrants, A, Sarkar, S, Flach, G, Langton, C, Smith III, F, Burns, H, van der Sloot, H, Meeussen, JCL, Samson, E, Mallick, P, Suttora, L, Esh, D, Fuhrmann, M & Philip, J 2013, *Cementitious Barriers Partnership (CBP): Training and Release of CBP Toolbox Software, Version 1.0 – 13480*, WM'2013, WMSymposia, Phoenix, Arizona.

Brown, KG, Kosson, D, Garrabrants, A, Sarkar, S, Flach, G, Langton, C, Smith III, F, Burns, H, van der Sloot, H, Meeussen, JCL, Samson, E, Mallick, P, Suttora, L, Esh, D, Fuhrmann, M & Philip, J 2013, *Cementitious Barriers Partnership (CBP): Using the CBP Software Toolbox to Simulate Sulfate Attack and Carbonation of Concrete Structures – 13481*, WM'2013, WMSymposia, Phoenix, Arizona.

Flach, GP, Burns, HH, Langton, C, Smith III, FG, Brown, KG, Kosson, D, Garrabrants, A, Sarkar, S, van der Sloot, H, Meeussen, JCL, Garboczi, E, Bullard, JW, Stutzman, PE, Samson, E, Mallick, P, Suttora, L, Esh, D, Fuhrmann, M & Philip, J 2013, *The Cementitious Barriers Partnership (CBP) Software Toolbox Capabilities in Assessing the Degradation of Cementitious Barriers – 13487*, WM'2013, WMSymposia, Phoenix, Arizona.

Sarkar, S, Kosson, DS, Meeussen, JCL, van der Sloot, HA, Brown, KG, & Garrabrants, A 2013, *A Dual Regime Reactive Transport Model for Simulation of High Level Waste Tank Closure Scenarios – 13375*, WM'2013, WMSymposia, Phoenix, Arizona.

