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# **CEMENTITIOUS BARRIERS PARTNERSHIP FY2015 END-YEAR REPORT**

**CBP-TR-2015-014, Rev. 0**

## **CEMENTITIOUS BARRIERS PARTNERSHIP FY2015 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 CRADA partners are the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) (funded by the 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 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 2015 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 status report highlights the CBP 2015 Software and Experimental Program efforts and accomplishments that support DOE 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 2015, the CBP developed a beta release of the CBP Software Toolbox – “Version 3.0”, which includes new STADIUM carbonation and damage models, a new SRNL module for estimating hydraulic properties and flow in fractured and intact cementitious materials, and a new LeachXS/ORCHESTRA (LXO) oxidation module. In addition, the STADIUM sulfate attack and chloride models have been improved as well as the LXO modules for sulfate attack, carbonation, constituent leaching, and percolation with radial diffusion (for leaching and transport in cracked cementitious materials). These STADIUM and LXO models are applicable to and can be used by both DOE and the Nuclear Regulatory Commission (NRC) end-users for service life prediction and long-term leaching evaluations of radioactive waste containment structures across the DOE complex.

In 2015, the Cementitious Barriers Partnership 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. To reflect this progress, CBP partners authored numerous reports presented at WM2015 which include:

- *The Cementitious Barriers Partnership Experimental Programs and Software Advancing DOE’s Waste Disposal/Tank Closure Efforts – 15436*: Heather Burns, Greg Flach, Frank Smith, Christine Langton, Savannah River National Laboratory (SRNL), Savannah River Site (SRS), Aiken, SC; Kevin Brown, David Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; Eric Samson, SIMCO Technologies, Inc.; Pramod Mallick, US DOE.
- *Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the Multistep Outflow Method - 15461*: Greg Flach, Ken Dixon, and Ralph Nichols, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

- Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack – 15477: J. L. Branch, K. G. Brown, and D. S. Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; J. R. Arnold, NIST, 100 Bureau Drive, Stop 1070, Gaithersburg, MD; and H. A. van der Sloot, Hans van der Sloot Consultancy, Langedijk, The Netherlands.
- X-Ray Diffraction of Slag-based Sodium Salt Waste Forms – 15513: C. A. Langton and D. M. Missimer, Savannah River National Laboratory, Savannah River Site, Aiken, SC.
- Tc Oxidation in Slag-Based Sodium Salt Waste forms Exposed to Water and Moist Hanford Soil – 15514: C. A. Langton, Savannah River National Laboratory, Savannah River Site, Aiken, SC.
- Demonstrating Integration of CBP and ASCEM Simulation Tools – 15627: Pramod Mallick, Justin Marble, Patricia Lee, US DOE; Greg Flach, Heather Burns, Roger Seitz, Savannah River National Laboratory, Savannah River Site, Aiken, SC; Paul Dixon, Los Alamos National Laboratory.

#### FY2015 CBP Experimental Studies Overview

In 2015, the CBP experimental programs are continuing to have a significant impact on the DOE Complex by providing specific data unique to DOE sodium salt wastes at both Hanford and SRS that are not available in the literature. These programs are designed to produce significant data shedding light on the performance of the cementitious materials selected for disposal of DOE salt waste forms at SRS. Experimental programs on technetium (Tc) mobility, cement phase characterization of damaged cementitious materials, and concrete performance after exposure to aggressive solutions and gasses (i.e., oxygen and carbon dioxide) are anticipated to have a significant impact to improve the understanding of the performance DOE cementitious barriers. The experimental studies listed below are summarized in this report.

- I. Tc Mobility – Measurement of Oxidation and Carbonation Fronts in Cementitious Materials
- II. Test Beds – Exposure Studies
  - Durability of DOE Cementitious Material under Aggressive Solutions
  - Transport Properties Measurement
  - Effect of Damage on Transport Properties of Concrete
- III. Characterization of Damaged CBP Cementitious Material Phases
- IV. Method Development for Cementitious Fractured Materials – Measurement of Hydraulic Conductivity



FY2015 New CBP Software Overview

In 2015, the CBP plans to release its new Software Toolbox - Version 3.0, a software package providing new concrete degradation models that assist in service life predictions for cementitious structures and waste forms. The experimentally-supported Software Toolbox will include new and improved software modules used to predict degradation depths and damage due to sulfate attack, chloride attack, and carbonation for DOE cementitious waste structures. The CBP provides enhanced software QA testing and documentation to assist DOE users in qualifying the use of the software.



**Fig. 1. CBP Software Toolbox, Version 3.0 Capabilities**

- SRNL
  - FloXcel Fractured Property and Flow Data Base
  - Gnuforplot – Integrated Plotting Software for the CBP Software Toolbox

- SIMCO Technologies, Inc. (SIMCO)
  - Sulfate attack model that predicts time-evolution of concrete transport properties,
  - Carbonation model that predicts time-evolution of pH in concrete,
  - Calculation of chemical species fluxes at domain boundaries, to connect with external far-field reactive transport models.
  
- Vanderbilt University
  - Carbonation and Oxidation Module – New Functionality to Treat REDOX-Sensitive Constituents (Tc) in combination with Carbonation – Carbonation and Oxidation now in a Single Module
  - Minor Refinements to Sulfate Attack and Percolation with Radial Diffusion Modules

### **CBP Software Quality Assurance**

CBP Software has been used in recent performance assessment analysis for DOE cement barriers and end-users have communicated the need for improved software QA documentation that more readily helps them meet their site QA requirements. CBP Partners have responded to this request by producing more comprehensive software QA documentation that the anticipated users can more easily satisfy their site-specific QA requirements. . The intent of this effort is that end-users can be confident in the quality of the CBP software and easily leverage CBP documentation to satisfy their site-specific software QA implementation procedures, verify the validity of their local installation, and readily identify software configurations associated with chronological events (e.g., releases, workshops).

## **I. FY2015 CBP EXPERIMENTAL STUDIES**

The CBP provides great value to the DOE complex through the development of the experimentally-based simulation tools that model important degradation mechanisms much needed for technical support of the DOE facility PAs. The experimental programs, in addition to providing data for parameterization, 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 critical need in the DOE Complex.

In FY2015, CBP experimental efforts have focused on the following DOE areas of interest:

- Technetium (Tc) Mobility,
- Test Bed Exposure Studies of DOE cementitious barrier materials under various exposure conditions and measurement of the resultant properties.
- Characterization of exposed and damaged DOE cementitious materials to understand and identify aging and degradation mechanisms (sulfate attack, carbonation, oxidation) including measurement of key transport properties (hydraulic conductivity) in cementitious materials (method development).

The significance and deliverables as well as status for these efforts are shown in Table 1.

**Table 1: CBP Experimental Program and Significance**

Experimental Program	Significance	Report
<b>A. Tc Mobility Studies</b>	1. <u>Tc Mobility Studies In Different Exposure Conditions</u> (“ <i>Technetium Oxidation in Slag-based Sodium Salt Waste Forms Exposed to Water and Moist Hanford Soil</i> ”) - SRNL testing has shown Tc mobility is most influenced by exposure to oxygen. Testing includes exposing DOE salt-based waste forms to various conditions in water & Hanford soils to better understand the impact to Tc mobility.	Conference WM2015 - 15514 &  CBP-TR-2014-005
	2. <u>Tc Mobility: Oxidation Rate Measurement Development</u> (“ <i>Method Development For Studying Oxidation of Porous Cementitious Materials</i> ”) - This work includes development of a method to measure the oxygen diffusion rate through cementitious material.	CBP-TR-2015-011
<b>B. Test Bed Exposure Studies</b>	1. <u>“OPC Paste Samples (i.e., Cementitious Materials) Exposed to Aggressive Solutions”</u> - Phase I experimental results showed that damage does not occur in high pH solutions in the presence of sulfate.	CBP-TR-2015-001
	3. <u>“SCM Paste Samples (i.e., DOE Cementitious Barrier Materials) Exposed to Aggressive Solutions (Phase II)”</u> - Phase II results show damage to some of the samples exposed to sulfate, nitrate and hydroxides in high pH	CBP-TR-2015-007
	4. <u>“Cementitious Barriers Partnership Concrete Mixture Characterization”</u> - Measurement of porosity, diffusion coefficient and permeability of Vault 1/4 and Vault 2 concrete mixes, over a two-year period. Measurement of statistical distribution of properties.	CBP-TR-2015-008
	5. <u>“Transport Properties of Damaged Materials”</u> – Measurement of porosity/diffusion coefficients of damaged concrete samples, compared to undamaged ones, for meaningful data for modeling effort.	CBP-TR-2015-002
	6. <u>Damage of DOE Concrete Exposed To Wasteform Material</u> (“ <i>CBP (Task 12) Experimental Study of the Concrete/Saltstone Two-layer System</i> ”) - Laboratory concrete samples placed in contact with Saltstone for 2 years. Characterization performed in FY15.	CBP-TR-2015-015 (DRAFT)
<b>C. Studies on Fractured/ In-Tact Cementitious</b>	1. <u>“X-Ray Diffraction of (DOE) Slag-based Sodium Salt Waste Forms”</u> – FY2015 report on characterization of sodium based salt waste forms has been issued. Results will be incorporated into CBP models to significantly impact the results.	Conference WM2015 - 15513 & CBP-TR-2014-004

Materials		
	<p>2. <u>Characterization of CBP Damaged DOE Cementitious Barrier Materials</u> – In FY2015, SRNL continued characterization work on damaged CBP cementitious materials (SDU 2 analogue) from SIMCO testing under aggressive solutions (Figure 3). SRNL has been utilizing XRD and SEM to characterize the phases and understand the mineral assemblage and to better determine the mechanism that initiated the degradation. A report is scheduled for release in December 2015.</p>	<p>In progress</p>
	<p>3. <u>“Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the Multistep Outflow Method”</u> – Methods exist for intact cementitious materials but not fractured. SRNL is developing a method to measure hydraulic conductivity in fractured materials. Considered “cutting edge” technology for fractured materials.</p>	<p>SRNL–STI-2014-00618 &amp; Conference WM2015 - 15461</p>
	<p>4. <u>“Reactive Transport Modeling and Characterization of Concrete Materials with Fly ash Replacement under Carbonation Attack”</u> - Characterize changes in cement microstructure and speciation resulting from carbonation using SEM-EDS and pH dependence testing; results were then used in reactive transport modeling to predict material performance under carbonation attack.</p>	<p>Conference WM2015 - 15477</p>
	<p>5. <u>Characterization and Reactive-Transport Modeling of the Changes in the Chemical Speciation and Microstructure of Cementitious Materials as a Result of Carbonation</u> - Evaluated selected (non-radioactive) Cast Stone samples using EPA Methods 1313 and 1315. This information being evaluated using LeachXS/ORCHESTRA to develop a “source-term” model for Cast Stone to support Hanford Low Activity and Secondary Waste including chemical speciation, redox, adsorption, uncertainty.</p>	<p>Conference IWWG-307 ARB 2015</p>

**A. Technetium (Tc) Mobility Studies**

**1. Tc Mobility Studies in Different Exposure Conditions**

*“Technetium Oxidation in Slag-based Sodium Salt Waste Forms Exposed to Water and Moist Hanford Soil”, C.A. Langton, Savannah River National Laboratory, Savannah River Site, Aiken, S.C., WM2015-15514 and CBP-TR-2014-005*

Several U.S. DOE sites use or plan to use waste forms and/or concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as  $Tc(VII)O_4^-$  and  $Cr(VI)O_4^{2-}$ . 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 and stable contaminants. An understanding of factors that affect the oxidation state of redox sensitive contaminants stabilized in cementitious waste forms is required to improve waste forms and engineered barriers for shallow land disposal. In addition, the parameters and relationships for the 1) rate of bulk matrix oxidation and 2) potential for and efficiency of re-reduction of soluble Tc in cured un-oxidized portions of waste forms are required for predicting long-term performance.

The rate of oxidation is important to the long-term performance of reducing salt waste forms because the solubility of some contaminants, e.g., technetium, is a function of oxidation state.  $\text{TcO}_4^-$  in the salt solution is reduced to Tc(IV) and has been shown to react with ingredients in the waste form to precipitate low solubility sulfide and/or oxide phases. Upon exposure to oxygen, the compounds containing Tc(IV) oxidize to the pertechnetate ion,  $\text{Tc(VII)O}_4^-$ , which is highly soluble in water and aqueous solutions. Consequently, the rate of technetium oxidation front advancement into a monolith and the technetium leaching profile as a function of depth from an exposed surface are important to waste form performance and ground water concentration predictions. 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.

A method for measuring contaminant oxidation fronts for redox sensitive contaminants in cementitious waste forms containing GGBFS was recently developed at the Savannah River National Laboratory (SRNL). This method is based upon leaching depth-discrete subsamples obtained as a function of distance from an exposed surface. Leaching is performed in a zero head space container using deionized, de-aerated water to minimize oxidation during the leaching process. Leaching time was  $48 \pm 4$  hours.

The objectives of this study were to: utilize depth-discrete sampling and zero head space leaching to explore the effect of exposing cured waste forms to moist soil and DI water in a 1-D experimental configuration. More specifically, the effect of these exposure conditions on Tc leachability as a function of distance from the exposed surface was determined.

## 2. Tc Mobility: Oxidation Rate Measurement Development

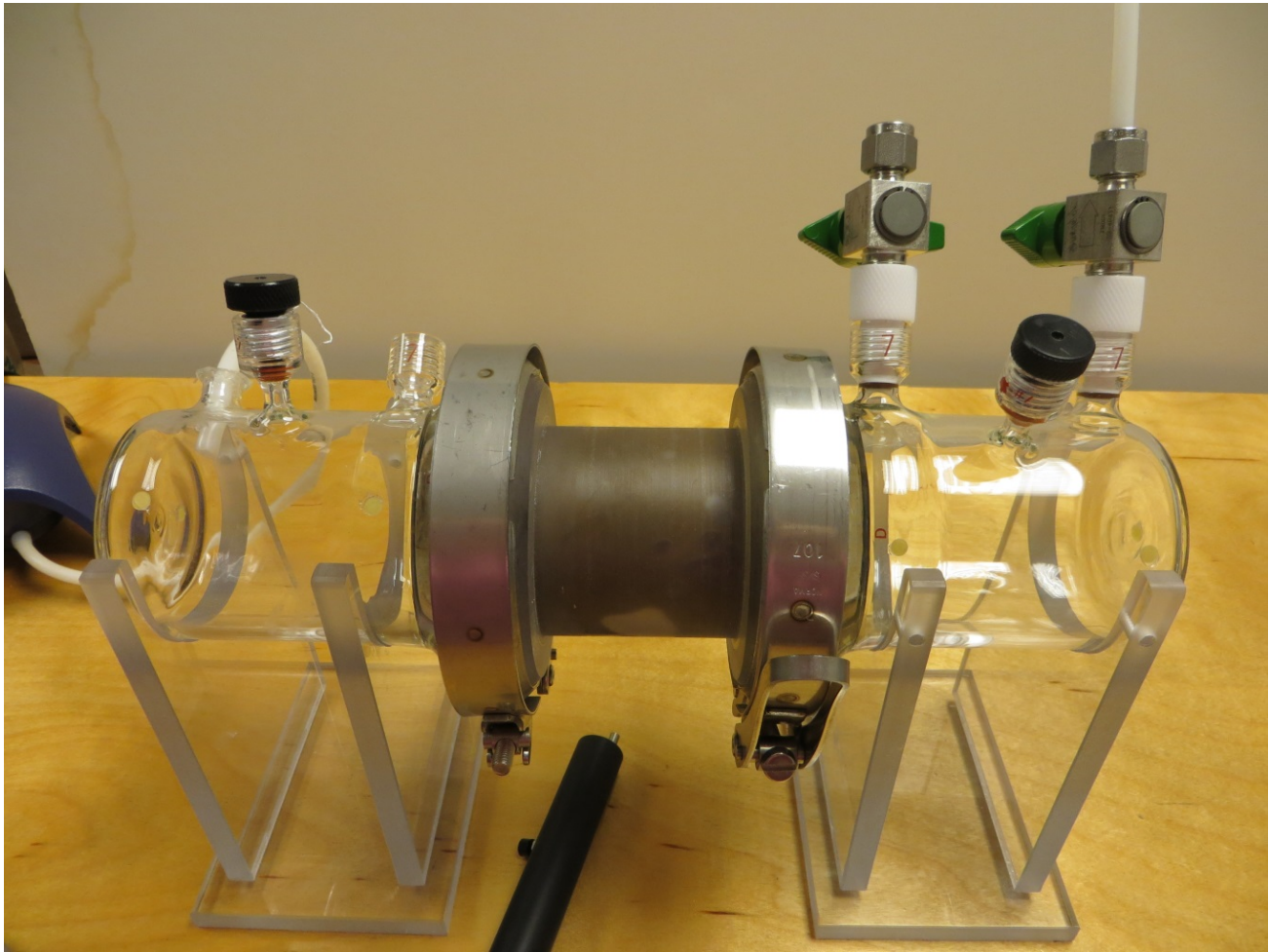
*"Method Development For Studying Oxidation of Porous Cementitious Materials," W.P. Kubiilus and C.A. Langton, Savannah River National Laboratory, Savannah River Site, Aiken, S.C, CBP-TR-2015-011*

This experimental work involved studying the diffusion of oxygen through porous cementitious media. Several U.S. DOE sites use or plan to use cementitious wastefoms and/or concrete containment structures for radioactive waste disposal that are required to have a chemically reducing environment, in order to immobilize technetium (Tc), which is highly soluble under oxidizing conditions, but inert in reducing conditions. These wastefoms

and containment structures are typically located in the vadose zone and backfilled and covered with soil, which contains air and aerated infiltrating pore water. Consequently, it is important to understand the long term effects on concrete wastefoms of exposure to air (oxygen) and water containing dissolved oxygen, in order to predict the speciation and mobility of technetium and other redox-sensitive constituents.

A diffusion cell apparatus was constructed to accommodate 2 and 3-inch diameter test cylinders of cementitious material, with each end connected to a glass cell as shown in Figure 2. The input cell is in contact with one end of the cementitious cylinder, and may contain air, pure oxygen, or other gas mixtures. It simulates the soil pore gas with which a concrete wasteform will be in contact. The measurement cell is in contact with the other end of the cylinder and filled with an inert gas different from the diffusing gas; gas which has diffused through the cylinder can be sampled from it at various times. Both cells have sample ports adaptable to analytical instruments such as a gas chromatograph or mass spectrometer. However, for this study, oxygen concentrations were measured non-destructively with an OxySense® 5250I analyzer and OxyDot® fluorescent oxygen sensors, placed inside the measurement cell.

Preliminary results of diffusion cell experiments indicate that the apparatus, configured for quasi-steady state measurements, is suitable for estimating rates of oxygen and other gases diffusion through cylinders of cementitious materials. However, oxygen leakage from outside air is occurring in the apparatus. Planned future work will reconfigure the experimental setup to counter the effect of leakage. Also, experimental results indicate that future work be performed on cementitious samples of less than one inch in length.



**Fig. 2. Gaseous Diffusion Cell with a cementitious sample**

## **B. Test Bed Exposure Studies**

### **1. Cementitious Materials Exposed to Aggressive Solutions**

*"OPC Paste Samples Exposed to Aggressive Solutions", E. Samson, SIMCO Technologies, Inc., Quebec, Canada, CBP-TR-2015-001*

The SIMCO Technologies, Inc. (SIMCO) experimental work aimed at supporting the assessment of long-term durability of concrete barriers containing sulfate-bearing salt wastefoms, 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. 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.

2. DOE Cementitious Barrier Materials Exposed to Aggressive Solutions

*"SCM Paste Samples Exposed to Aggressive Solution (Phase II)", E. Samson, SIMCO Technologies, Inc., Quebec, Canada, CBP-TR-2015-007*

SIMCO conducted additional experimental studies with contact solutions that examine limit cases useful for understanding the interaction between waste form pore solutions and the new SDU units (i.e., SDU 2) in Phase II. 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 used at SRS in storage structures. 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  $\text{SO}_4^{2-}$  (14,400 ppm) were present. The solutions included different pH conditions and different sodium content.

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 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 Vault 2 paste analog (Figure 3). 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 GGBFS led to the presence unreacted silica. It is hypothesized 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 explain the poor behavior of mix PV2 in presence of NaOH.





**Fig 3. Vault 2 analog paste samples after 8 months in aggressive solution**

3. CBP Concrete Mixture Characterization

*"Cementitious Barriers Partnership Concrete Mixture Characterization", E. Samson, SIMCO Technologies, Inc., Quebec, Canada, CBP-TR-2015-008*

The mixtures were designed at the Savannah River National Laboratory and are identified as follow:

- Vault 1/4 concrete: w/b ratio of 0.38, prepared with ASTM Type I/II cement and slag;
- Vault 2 concrete: w/b ratio of 0.38, prepared with ASTM Type V cement, slag, fly ash, and silica fume.

Both mixtures were prepared with approximately 425 kg of binder. All raw materials were shipped to SIMCO Technologies' laboratory, where the batches were prepared and the samples tested.

The testing protocol mostly focused on determining the transport properties of the mixtures. It was based on test methods developed by SIMCO. The same tests are incorporated in the protocol developed by the US Department of Defense and described in the Unified Facilities Guide Specifications (UFGS – 03 31 29) for new marine concrete construction, issued in August 2012. The tests yield parameters that can directly be incorporated in STADIUM®, a reactive transport model dedicated to the prediction of chemical alteration sustained by cement-based materials in aggressive environments. STADIUM® is a proprietary code developed by SIMCO and is part of the CBP Toolbox. The following transport properties were evaluated:

- Volume of permeable voids (porosity), in accordance with the ASTM C642 standard procedure: Standard Test Method for Density, Absorption and Voids in Hardened Concrete,
- Diffusion coefficients, on the basis of migration test results, which is a modified version of the ASTM C1202 procedure: Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration,
- Water permeability, on the basis of drying test results, in accordance with ASTM C1792: Measurement of Mass Loss Versus Time for One-Dimensional Drying of Saturated Concretes.

Tests were performed after different curing durations. In order to obtain data on the statistical distribution of transport properties, the measurements after 2 years of curing were performed on 10+ samples.

Overall, both mixtures exhibited very low tortuosities and permeabilities, a direct consequence of their low water-to-binder ratio and the use of supplementary cementitious materials. The data generated on 2-year old samples showed that porosity, tortuosity and permeability follow a normal distribution.

#### 4. Transport Properties of Damaged Materials

*"Transport Properties of Damaged Materials", E. Samson, SIMCO Technologies, Inc., Quebec, Canada, CBP-TR-2015-002*

The objective of this experimental study was to provide experimental data relating damage in cementitious materials to changes in transport properties, which can eventually be used to support predictive model development.

In order to get results within a reasonable timeframe and to induce as much as possible uniform damage level in materials, concrete samples were exposed to freezing and thawing (F/T) cycles. The methodology consisted in exposing samples to F/T cycles and monitoring damage level with ultrasonic pulse velocity measurements. Upon reaching pre-selected damage levels, samples were tested to evaluate changes in transport properties.

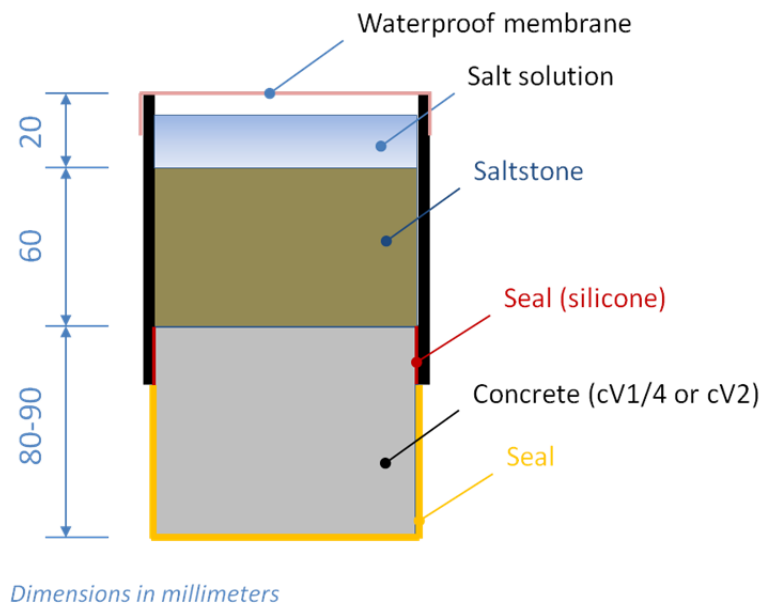
Material selection for the study was motivated by the need to get results rapidly, in order to assess the relevance of the methodology. Consequently, samples already available at SIMCO from past studies were used. They consisted in three different concrete mixtures cured for five years in wet conditions. The mixtures had water-to-cement ratios of 0.5, 0.65 and 0.75 and were prepared with ASTM Type I cement only.

The results showed that porosity is not a good indicator for damage caused by the formation of microcracks. Some materials exhibited little variations in porosity even for high damage levels. On the other hand, significant variations in tortuosity were measured in all materials. This implies that damage caused by internal pressure do not necessarily create additional pore space in the microstructure but likely create new thin pathways between existing pore space for species to travel.

5. Damage of DOE Concrete Exposed to Wasteform Material

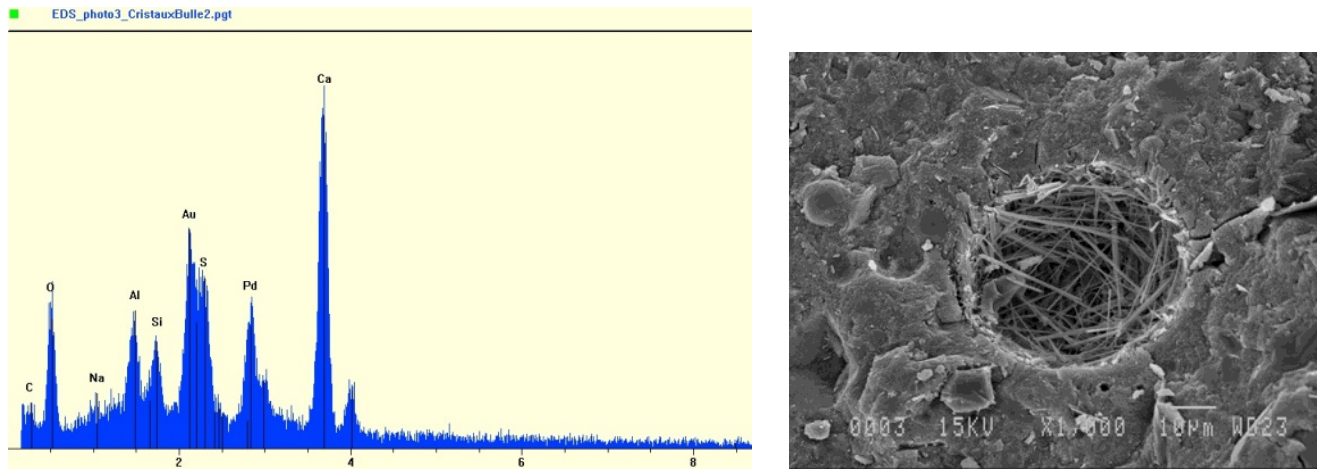
*“CBP (Task 12) Experimental Study of the Concrete/Saltstone Two-layer System”, E. Samson, SIMCO Technologies, Inc., Quebec, Canada, CBP-TR-2015-015 (DRAFT)*

The objective of this experimental study was to provide data from an actual Saltstone/concrete system, prepared in the lab maintained in a controlled environment. Saltstone slurry was cast over Vault 1/4 and Vault 2 concrete samples. The experimental program included full characterization of the slurry transport properties. The concrete mixtures were characterized in a previous stage of the ongoing experimental program performed at SIMCO. The setup is illustrated on Figure 4.



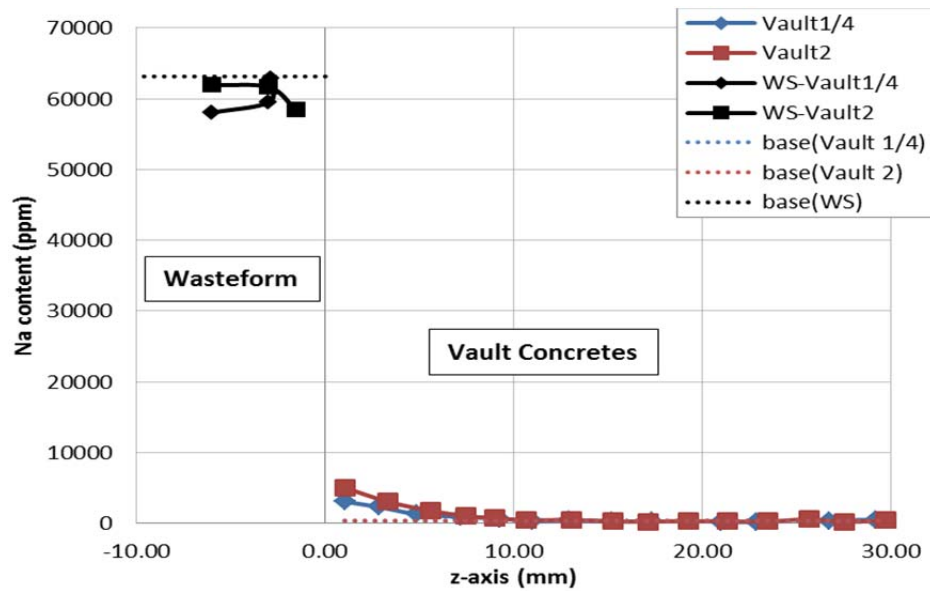
**Fig. 4. Setup for the Saltstone/concrete study**

The experiment started in 2013. The 2-year duration was reached in the first half of FY2015. At the time of preparing the mid-year report for FY15, the analysis was still ongoing. Early results showed that the presence of sulfate in the wasteform led to the formation of ettringite in the concrete substrate (Figure 5). However, ettringite presence was limited to the first mm in the substrate.



**Fig. 5. Presence of ettringite in the concrete layer beneath the wasteform**

After two years, the saltstone/concrete 2-layer systems were cleaned of the external sealant and separated. The objective of the tests was to measure the extent of species contamination in the concrete layer. Successive layers were milled with a grinding bit from the surface of the concrete sample corresponding to the exposed surface. The nominal thickness of each layer was 2 mm, and grinding was performed over 30 mm. A few layers were also milled in the saltstone, to provide comparison with results in concrete. Powder from each layer was analyzed to measure the content in sulfur, nitrogen and sodium. The case of sodium is illustrated on Figure 6.



**Fig. 6. Sodium content at the Saltstone/concrete interface**

The results indicated limited sulfur transfer from the slurry to the concrete. Concrete did not show significant damage. SEM observations confirmed visual observations and only showed minor microcracks in the concrete mixes.

## C. Characterization Studies on Fractured and In-Tact Cementitious Materials

### 1. X-Ray Diffraction of DOE Slag-based Sodium Salt Waste Forms

*"X-Ray Diffraction of (DOE) Slag-based Sodium Salt Waste Forms", C.A. Langton, Savannah River National Laboratory, Savannah River Site, Aiken, S.C., WM2015-15513 and CBP-TR-2014-004*

Cementitious materials are used to solidify and stabilize aqueous based radioactive waste containing sodium salts. The types and proportions of cementitious ingredients used to treat aqueous radioactive waste streams containing sodium salts depend on the performance objectives for the waste forms and the compositions of the waste streams. Matrix phases can stabilize certain contaminants (co-precipitation, substitution, ion exchange, and / or sorption), influence processing properties, and are responsible for physical properties and durability of the cured waste forms. Consequently, characterization of the matrix (binder) mineralogy (chemical compositions and crystalline / non crystalline structures) is important for predicting contaminant leaching and evolution of the materials as a function of time and changing conditions.

At the present time, the matrices of these cementitious waste forms are not well characterized because a large portion of the matrix is made up of phases that have poorly ordered structures and form solid solutions involving cation and anion substitutions. In addition, the matrix consists of micrometer and sub-micrometer particles inter grown to the extent that individual particles are difficult to characterize using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

SRNL conducted an experimental program characterizing a series of DOE sodium salt-based waste forms using x-ray diffraction last year. 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.

A report has been published in FY2015 on the results of the mineral phase characterization of DOE salt-based waste forms. The objective of this report was to characterize the phase assemblages in the Cementitious Barriers Partnership reference case sodium salt waste form [Langton, 2009]. 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 matrix mineralogy, 3) understand and predict anion and cation leaching behavior of contaminants of concern, and 4) predict performance of the waste forms and 5) identify appropriate phase solubility and thermodynamic data. Characterization of the mineralogy is also important for understanding the buffering effects that the waste form has on infiltrating water / leachates.

2. Characterization of CBP Damaged DOE Cementitious Barrier Materials

*In- Progress*

In FY2015, SRNL continued characterization work on CBP materials, specifically, damaged CBP cementitious materials from SIMCO testing under aggressive solutions (Figure 7). The samples were Saltstone Disposal Unit 2 binders which had been exposed to two solutions: 1)  $\text{NaSO}_4 + \text{Na}(\text{OH})$  and 2)  $\text{NaSO}_4 + \text{Na}(\text{OH}) + \text{NaNO}_3$ . These solutions were prepared to investigate the effect of salts and pore solution chemistry on vault concrete. In particular they were designed to evaluate the potential for sulfate attack, alkali silica reaction and/or soluble salt attack. Sample characterization at SRNL is in progress. SRNL has been utilizing XRD and SEM to characterize the phases and understand the mineral assemblage and to better determine the mechanism that initiated the degradation. A report is scheduled for release in December 2015.



**Fig. 7. CBP Cementitious Barrier Sample exposed to .15 M  $\text{Na}_2\text{SO}_4$ , 0.5M  $\text{NaOH}$ , and 3.0 M  $\text{NaNO}_3$  for approximately 1 year**

3. Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the Multistep Outflow Method

*“Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the Multistep Outflow Method”*, G. P. Flach, K. L. Dixon, F. G. Smith III and R. L. Nichols, *Savannah River National Laboratory, Savannah River Site, Aiken, S.C.*, SRNL-STI-2014-00618, Rev. 0, April 2015

In FY2015, SRNL continued the CBP experimental program on the method development for measuring hydraulic conductivity in fractured cementitious materials which is a key transport property used in DOE performance assessments. 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 published a report in FY2015 describing the experimental program on the *outflow extraction method* apparatus and procedure (Figure 8), adapted for use with fractured media to measure the unsaturated hydraulic conductivity. The report documents results of the measurement of three micro-fractured grout specimens (Figure 9) through inverse modeling with HYDRUS-1D. The estimated hydraulic curves generally conform to expectations and appear to be reproducible based on repeat testing and similar results being achieved for similar fracture networks. These observations suggest that the *outflow extraction method* is a viable technique for characterizing the unsaturated hydraulic conductivity of micro-fractured cementitious materials. However, further testing is needed to provide rigorous method validation to confirm this tentative conclusion. With respect to PA applications, comparisons of the unsaturated conductivity for the micro-fractured grout samples suggests that soils may serve as conservative surrogates for damaged cementitious materials, assuming that higher conductivity at higher tension heads is conservative for facility performance.



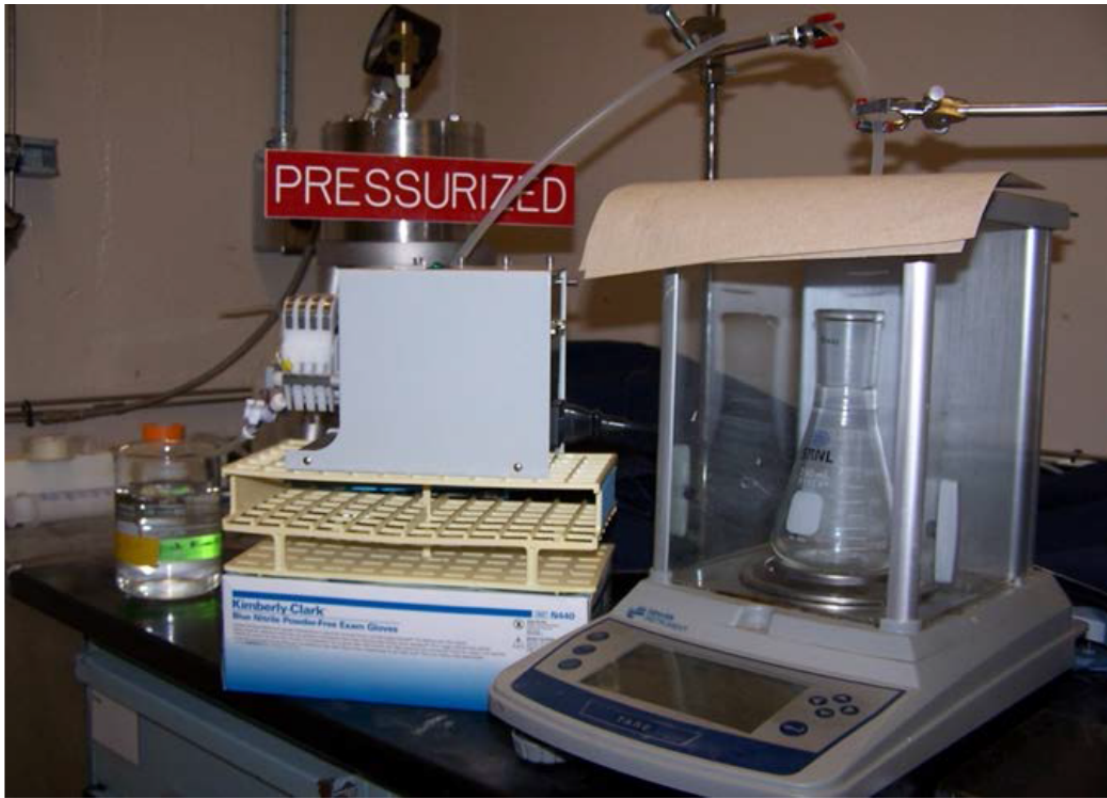


Fig. 8. Experimental apparatus for outflow extraction method

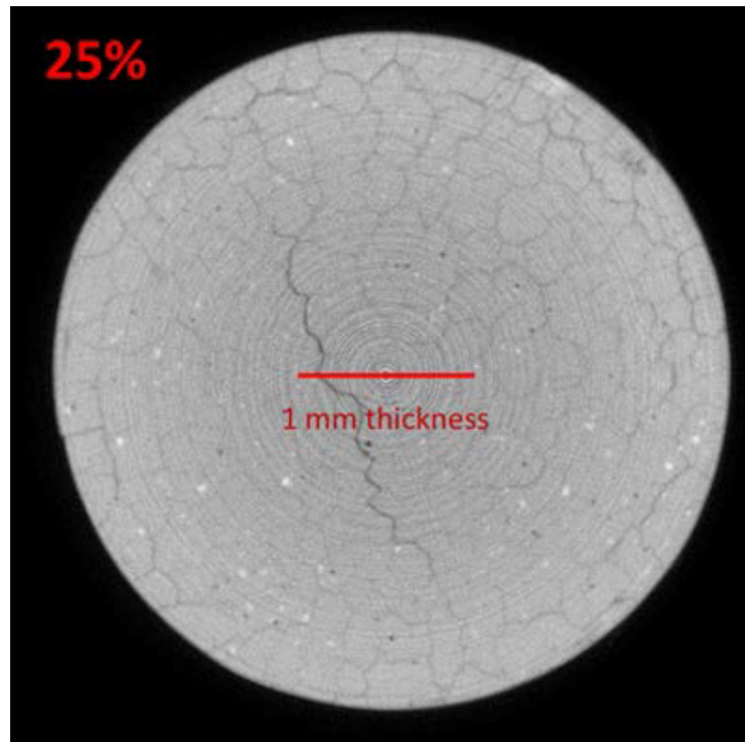


Fig. 9. Radiography image showing fracture network in TR437 at 25% depth from the top surface



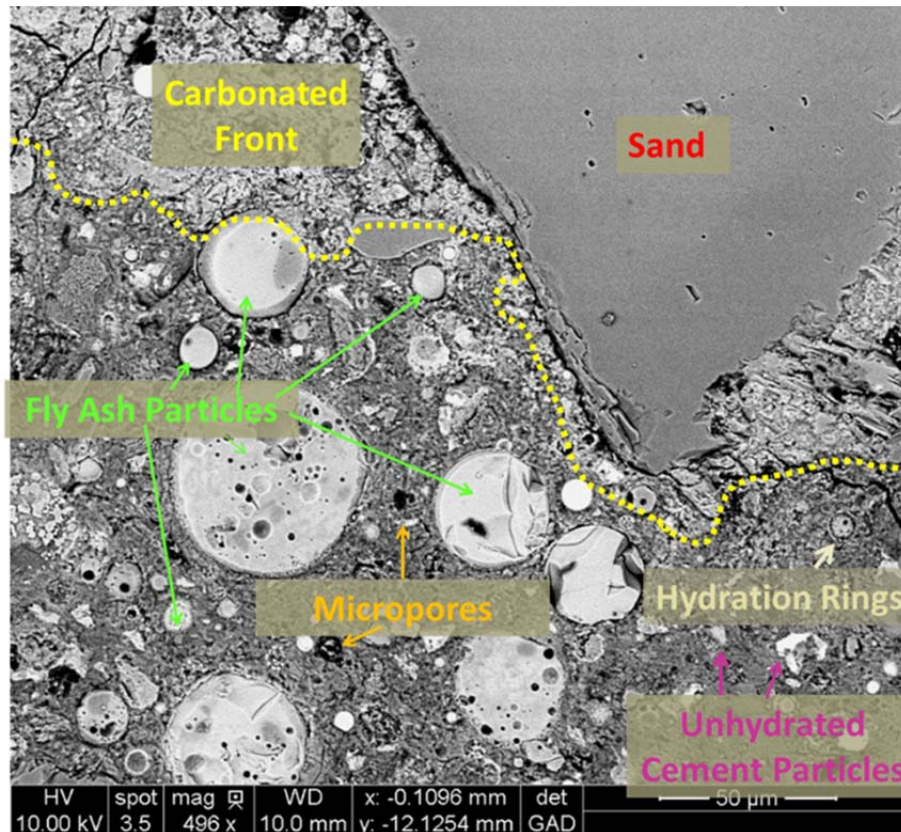
4. Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack

*“Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack”*, Branch, JL, Brown, KG, Arnold, JR, van der Sloot, JA & Kosson, DS; WM2015-15477, Phoenix, Az.

Carbonation has been identified as a key degradation method for cementitious materials that are used to immobilize and serve as barriers for hazardous waste, contaminated soil, and nuclear waste. Carbonation can lower the alkalinity of the reinforced cementitious material, which can lead to depassivation of the steel reinforcement and ultimately cracking. 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 are 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.



Fig. 10. Exp. approach to understanding impact of carbonation/oxidation on rad. leaching



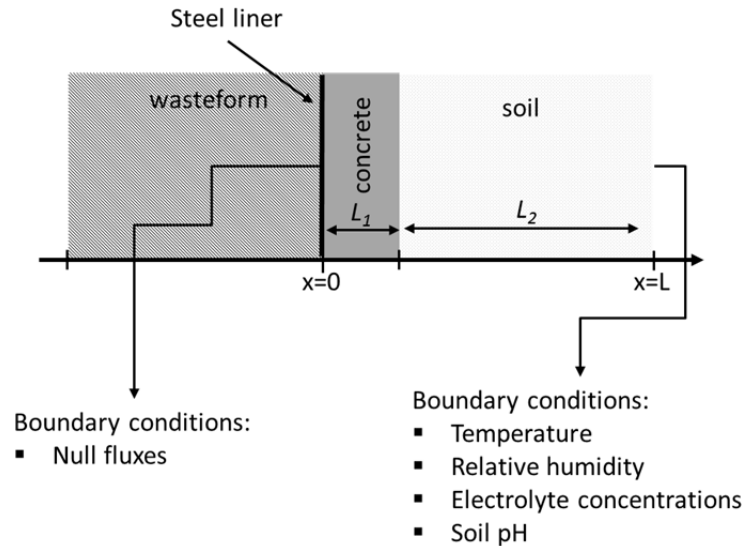
**Fig. 11. Backscatter SEM image illustrating the changes in concrete mortar microstructure in response to carbonation ingress**

5. Characterization and Reactive-Transport Modeling of the Changes in the Chemical Speciation and Microstructure of Cementitious Materials as a Result of Carbonation  
*"Characterization and Reactive-Transport Modeling of the Changes in the Chemical Speciation and Microstructure of Cementitious Materials as a Result of Carbonation-307"*, Branch, JL, Kosson, DS, Brown, KG, Van Der Sloot, HA, & Garrabrants, A ; IWWG-307, ARB 2015, Shanghai, China.

Vanderbilt University evaluated selected (non-radioactive) Cast Stone samples using EPA Methods 1313 and 1315. The resultant data is being evaluated using LeachXS/ORCHESTRA to develop a "source-term" model for Cast Stone to support Hanford Low Activity and Secondary Waste including chemical speciation, redox, adsorption, uncertainty.

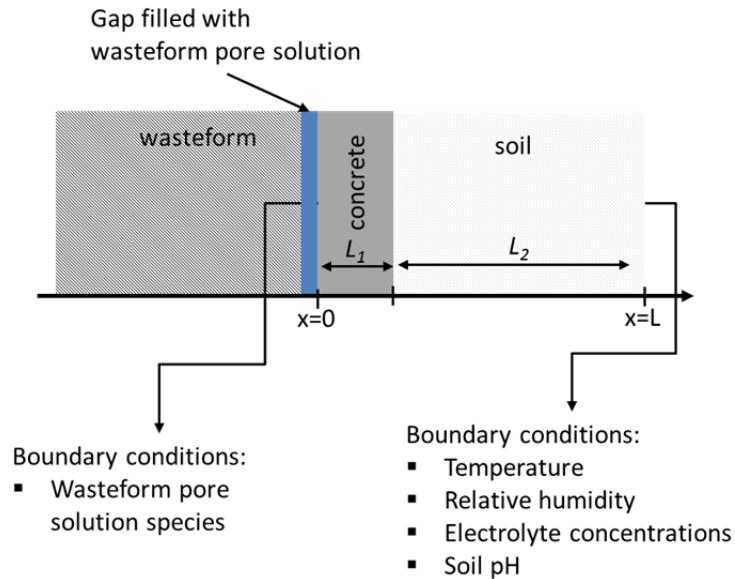


- ii. Steel liner/Concrete/Soil case (Figure 13): this test case is similar to the previous one except a steel liner prevents exchange between the wasteform and the concrete barrier. The simulation will show how this specific configuration affects the degradation rate at the concrete/soil interface.



**Fig. 13. Test Case 2: Steel Liner/Concrete/Soil**

- iii. Wasteform pore solution/Concrete/Soil case (Figure 14): this test case assumes that a gap exists between the wasteform and the concrete barrier. The gap is constantly replenished with pore solution.



**Fig. 14. Test Case 3: Wasteform Pore Solution/Concrete/Soil**

## 2. STADIUM Individual Software Packages

- i. Sulfate Attack Damage Model: In parallel with the experimental program, SIMCO continued the development of the damage model to be coupled with the sulfate ingress model. The model is based on the alteration of the pore size distribution following the local formation or dissolution of minerals in concrete exposed to aggressive environments.
  - o This approach needed the development of a new calculation module to predict the composition of mineral phases in hydrated cement pastes, in presence of supplementary cementitious materials such as fly ash or ground granulated blast furnace slag. Compared to the previous methodology developed by SIMCO, the new module improved the prediction of iron-based hydrates and now accounts for magnesium in cement and admixtures.
  - o A prototype model was completed in the first-half of FY2015. The implementation of the model in the STADIUM platform will be completed in the second-half of 2015.
- ii. Chloride Model: a chloride ingress model was already included in STADIUM when the CBP project started. The model was improved recently, in part because of the improvements to the mineral phase calculation module, as described previously. The new model better accounts for the impact of iron-based AFm phases on chloride binding in concrete. This improves the reliability of the prediction of corrosion initiation of steel rebars in concrete mixes exposed to chloride-laden environments.
- iii. Carbonation Module: the impact of the presence of carbonates in groundwater on concrete can be accounted for in STADIUM. Species and minerals were added to STADIUM chemical database. The model predicts for instance the formation of calcite and carbonate-AFm phases upon carbonate ingress, along with the corresponding pH drop in the material and dissolution of portlandite resulting from the formation of calcite. These functionalities will be fully integrated in the STADIUM software platform in the second-half of FY2015.

## B. FY2015 CBP LeachXS/ORCHESTRA (LXO) Software

1. Carbonation and Oxidation Module: Certain redox-sensitive species (e.g., Tc-99) drive predicted long-term risks for waste disposal at major DOE Sites, including both Hanford and Savannah River. For example, Tc-99 becomes mobile in the environment when oxidized and thus understanding the movement of oxygen and the redox behavior of important, redox-sensitive constituents in cementitious wasteforms and other materials is a major focus. A source-term model including chemical speciation and redox effects has

been developed for cementitious materials to describe both Saltstone (SRS) and Cast Stone (Hanford). Because oxygen and carbon dioxide will both be entering the cementitious material via the gas phase, the unsaturated model for carbonation has been extended to include oxygen ingress and oxidation reactions for Cast Stone and the existing vault materials currently in the CBP Toolbox. Thus coupled carbonation and oxidation reactions can be evaluated. An integrated experimental program is on-going to evaluate these coupled impacts to parameterize, calibrate, and validate the reactive transport models being developed.

2. Existing Modules: Minor improvements have been made to the existing LXO modules for parameterization and to improve their performance under probabilistic scenarios.

C. FY2015 SRNL Software: FloXcel - Fractured Property and Flow Data Base

*“Development and Demonstration of Material Properties Database and Software for the Simulation of Flow Properties in Cementitious Materials,” F.G. Smith and G.P. Flach, Savannah River National Laboratory, March 2015; SRNL-STI-2015-00190, Rev. 0*

SRNL recognized the need of a materials property database of transport properties for both fractured and in-tact cementitious materials in addition to a tool for simulating the flow properties through degraded cementitious materials. Software development began in FY2014 and was completed in FY2015 for the development of this new software module designated as FloXcel. FloXcel 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 becomes available. In summary, the software module, now included in the CBP Toolbox, Version 3.0, 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.

### III. CBP Software QA Documentation

CBP Software has been used in recent performance assessment analysis for DOE cement barriers and end-users have communicated the need for improved software QA testing documentation that more readily helps them meet their site QA requirements. The CBP Partners have responded to this request by producing more comprehensive software QA documentation that the anticipated users can more easily satisfy their site-specific QA requirements. The intent of this effort is that end-users can be confident in the quality of the CBP software and easily leverage CBP documentation to satisfy their site-specific software QA implementation procedures, verify the validity of their local installation, and readily identify software configurations associated with chronological events (e.g., releases, workshops).

#### A. STADIUM Software

The STADIUM QA report includes the following:

1. Description of the reactive transport model
2. Description of input parameters
3. Test cases used for model verification and implementation
4. Test cases used to validate the model (comparison with experimental data)
5. Description of output parameters

#### B. LeachXS/ORCHESTRA (LXO) Software

The LXO Software QA documentation includes 3 separate reports including the following:

1. LeachXS Quality Assurance Documentation  
(*"LeachXS QA Documentation,"* P. Seignette, ECN, Petten, The Netherlands, September 2015)
2. Verification and Validation Report for LXO Virtual Materials  
(*"Verification and Validation Report for LXO Virtual Materials,"* September 2015)
3. ORCHESTRA Software Quality Assurance Documentation  
(*"ORCHESTRA Software Quality Assurance (SQA) Documentation,"* J.C.L. Meeussen, NRG, Petten, The Netherlands and K.G. Brown, Vanderbilt University, Nashville, TN.

#### C. SRNL Software

The SRNL Software QA documentation includes 4 separate reports including the following:

1. Software Quality Assurance Plan for MESH2D  
(G-SQP-G-00015, *"Software Quality Assurance Plan for MESH2D,"* G.P. Flach and F.G. Smith, III, Savannah River National Laboratory, Sept. 2015)
2. Software Quality Assurance Plan for DIExternalCode

- (G-SQP-G-00016, “Software Quality Assurance Plan for DIIExternalCode”, G.P. Flach and F.G. Smith, III, Savannah River National Laboratory, Sept. 2015)
3. Software Quality Assurance Plan for FloXcel  
(G-SQP-G-00017, “Software Quality Assurance Plan for FloXcel”, F.G. Smith, III and G.P. Flach, Savannah River National Laboratory, Sept. 2015)
  4. Software Quality Assurance Plan: CBP Toolbox GoldSim Dashboard Graphical User Interface  
(G-SQP-G-00018, “Software Quality Assurance Plan: CBP Toolbox GoldSim Dashboard Graphical User Interface”, F.G. Smith, III, and G.P. Flach, Savannah River National Laboratory, Sept. 2015)

## CBP WM2015 REPORT ABSTRACTS

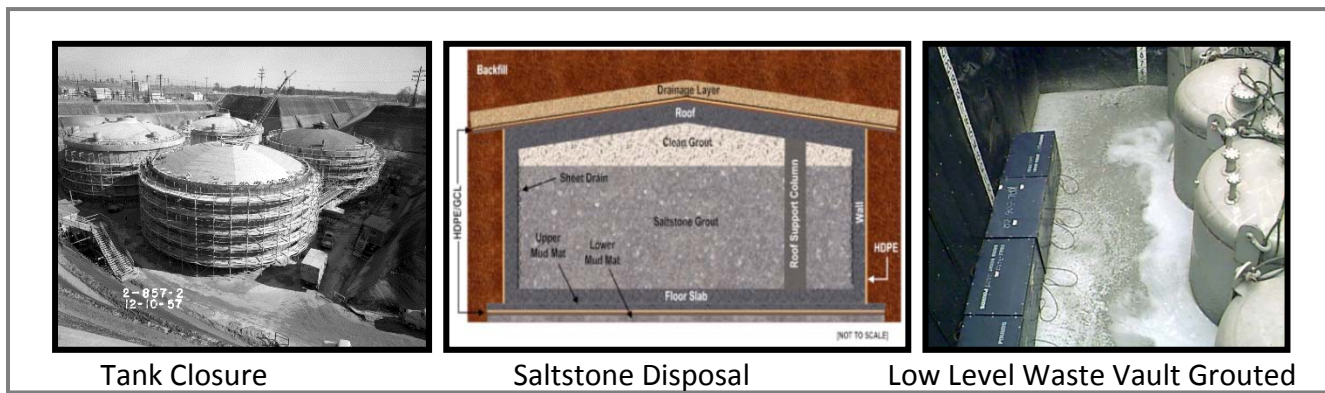
**The Cementitious Barriers Partnership Experimental Programs and Software Advancing DOE’s Waste Disposal/Tank Closure Efforts – 15436:** Heather Burns, Greg Flach, Frank Smith, Christine Langton, Savannah River National Laboratory (SRNL), Savannah River Site (SRS), Aiken, SC; Kevin Brown, David Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; Eric Samson, SIMCO Technologies, Inc.; Pramod Mallick, US DOE.

The U.S. Department of Energy Environmental Management (DOE-EM) Office of Tank Waste Management sponsored 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. DOE needs in this area include the following to support progress in final treatment and disposal of legacy waste and closure of High-Level Waste (HLW) tanks in the DOE complex:

- Long-term performance predictions and
- Flow sheet development and flow sheet enhancements
- Conceptual designs for new disposal facilities

The DOE-EM Cementitious Barriers Partnership is producing software and experimental programs resulting in new methods and data needed for end-users involved with environmental cleanup and waste disposal. Both the modeling tools and the experimental data have already benefited the 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 2014, the CBP Partnership 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 includes constituent leaching. 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 15) including:





**Fig. 15. Various DOE Cementitious Barriers in Waste Management**

- Future SRS Saltstone and HLW tank performance assessments and special analyses
- Hanford site HLW tank closure projects and other projects in which cementitious barriers are required
- 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 Hanford and SRS which are not readily available in the literature. Two recent experimental programs on cementitious phase characterization and on technetium (Tc) mobility have provided significant conclusions as summarized below:

- Recent 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 addition, recent experimental studies related to technetium 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.

**Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the Multistep Outflow Method – 15461** Greg Flach, Ken Dixon, and Ralph Nichols, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

The multistep outflow method is routinely used to characterize the unsaturated hydraulic conductivity of soils. The technique involves placing a soil sample in a pressure plate apparatus, subjecting the sample to multiple gas pressures in discrete steps through time, and measuring the transient volume of pore fluid extracted. Unsaturated hydraulic property values are estimated through inverse modeling of the experimental conditions. In this study the multistep outflow concept was applied to micro-cracked cementitious materials to assess the efficacy of the technique for these materials. The cementitious materials tested were salt-waste simulant grout samples artificially damaged through oven-drying.

Compared to typical soils, fractured media exhibit higher saturated conductivity and lower air-entry pressure, and the volume of fluid extractable from fractures is much lower than soil porosity. To accommodate these material differences the standard test apparatus was modified to incorporate a higher conductivity ceramic pressure plate, a high-precision digital balance for logging outflow mass, a low volume (diameter) effluent line, multiple inline high-precision gas regulators, and a high-precision low-range pressure gauge. Testing to date indicates that the modified apparatus can provide a viable means to measure the unsaturated hydraulic properties of micro-fractured cementitious materials. However the accuracy/uniqueness of inverse modeling is limited by the inherent characteristics of fractured media: high saturated conductivity, low air-entry pressure, and strong non-linearities. Hydraulic property results in the form of van Genuchten / Mualem curves are presented for three fractured grout specimens.

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, as implemented in the present study, provides a suitable method for estimating these material properties.

**Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack – 15477:** J. L. Branch, K. G. Brown, and D. S. Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; J. R. Arnold, NIST, 100 Bureau Drive, Stop 1070, Gaithersburg, MD; and H. A. van der Sloot, Hans van der Sloot Consultancy, Langedijk, The Netherlands.

There currently lacks sufficient knowledge to accurately characterize structural, hydraulic, and chemical performance of cementitious materials that are required to contain and shield nuclear

waste for thousands of years. There are a number of degradation methods that can affect the integrity of these materials over this time frame including carbonation which lowers the alkalinity of the material and can induce cracking in materials with steel reinforcement. The rate and extent of carbonation in these materials is impacted by the addition of fly ash and its composition which can vary depending on the fly ash source. To characterize the carbonation reaction, the 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). Microconcretes were prepared with no fly ash (control case) and with fly ash of various calcium compositions. The progression of the carbonation front was observed in the backscattered electron images by the formation of calcium carbonate and depth was confirmed with a phenolphthalein pH indicator test. The migration and deposition of chemical species were observed in carbonated regions from EDS data and were explained based on the changes in material alkalinity and solubility determined from EPA Method 1313 (Liquid-solid partitioning (LSP) as a function of eluate pH). The changes in mass transport properties from carbonation were observed using EPA Method 1315 (Mass transfer rates in monolithic and compacted granular materials using semi-dynamic tank leaching procedures). The carbonation reaction in each material was simulated using LeachXS/ORCHESTRA, a reactive transport modeling tool, which provided further evidence of localized deposition and migration of chemical species due to changes in speciation and solubility.

**X-Ray Diffraction of Slag-based Sodium Salt Waste Forms – 15513** C. A. Langton and D. M. Missimer, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

Cementitious materials are used to solidify and stabilize aqueous based radioactive waste containing sodium salts. The types and proportions of cementitious ingredients used to treat aqueous radioactive waste streams containing sodium salts depend on the performance objectives for the waste forms and the compositions of the waste streams. This paper documents sample preparation and x-ray diffraction results for a series of materials made with water or highly alkaline sodium salt simulated waste water and cementitious binders. The objective of this study was 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.

In summary, mixtures of Type II portland cement, Grade 100 ground granulated blast furnace slag (GGBFS) and carbon burn-out (CBO) Class F Fly ash which were hydrated with water contained hydrated phase assemblages typical of those reported in the literature. The calcium silicate hydrate phase assemblage in samples hydrated with the alkaline 4.4 M sodium salt simulated waste solution was found to be a function of the  $(\text{CaO} + \text{MgO}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$  ratio of the samples characterized. No significant differences were detected in samples cured 2 months and 14 months in sealed containers at ambient indoor temperatures.

Slag and a blend of slag and cement hydrated with caustic 4.4 M Na salt solution resulted in the most crystalline matrix. In addition to poorly ordered C-S-H, these samples contained fairly well ordered C-S-H I (a precursor of 14Å tobermorite) and 11 Å Al-substituted tobermorite. These crystalline C-S-H phases did not form or were present in only trace amounts in slag blends containing about 45 to 62 mass percent fly ash. These slag-Class F fly ash blends had a higher silica plus alumina content relative to lime and magnesia than the blends that produced C-S-H I and Al-substituted tobermorite. The calcium silicate binder in the 10:45:45 mixture of cement : slag : fly ash was made up of poorly ordered C-S-H. The sample cured for 14 months may contain a small amount of the more crystalline calcium silicate hydrate phases.

Layered double hydroxides in the hydrotalcite (magnesium-aluminum carbonate hydroxide) and hydrocalumite / AFm phases (calcium aluminum hydroxide) were present in mixtures containing slag. The specific phase(s) were not identified because these phases form solid solutions and have a considerable amount of overlap in their x-ray patterns. Sodium nitrate was the only sodium salt phase identified in x-ray diffraction patterns of the samples hydrated with salt solution. Drying during x-ray diffraction sample preparation may have resulted in precipitation of the sodium nitrate or it may have been present in the samples prior to x-ray sample preparation. Sodium sulfate, aluminate, and carbonate may have been incorporated in the structures of the layered double hydroxide (AFm) type phases. These mixed metal layered double hydroxides make up an important fraction of the matrix in the slag containing blends hydrated with caustic salt solution. They are among the few oxide-based phases that exhibit substantial, permanent anion exchange capacity [Kirkpatrick, et al. 1999, Plamer, et al., 2009, and Zhang and Reardon, 2003]. They also contribute to the structural properties of cementitious matrices [Taylor, 1997].

#### **Tc Oxidation in Slag-Based Sodium Salt Waste forms Exposed to Water and Moist Hanford Soil – 15514** C. A. Langton, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

Several U.S. DOE sites use or plan to use waste forms and/or concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as  $\text{Tc(VII)O}_4^-$  and  $\text{Cr(VI)O}_4^{2-}$ . 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 and stable contaminants.

Both the SRS and Hanford waste streams contain soluble technetium which may require stabilization to meet disposal requirements. Technetium stabilization is a difficult problem because: 1) Tc is soluble and very mobile in the oxidized form typical of near surface environments, and 2) Tc-99 is a long-lived isotope with a half-life of  $2.1\text{E}+05$  years which places demanding requirements on the engineered barriers and environment to meet current regulatory disposal requirements.

A depth-discrete sampling and leaching method approach for measuring contaminant oxidation rate (effective contaminant specific oxidation rate) was used in this study. The method was modified by coating all sides of a cylindrical sample with an impermeable epoxy and cutting a fresh surface 2 to 2.5 cm from the original top surface eliminates sample inhomogeneity as the result of settling as a reason from observed results and provides 1-D soluble ion transport and gas transport information.

Soluble Tc was leached from all of the depth-discrete subsamples from both Tc2-9 and Tc2-10 which strongly suggests that oxygen was present in the entire length of both samples. About 24 mass percent of the Tc in the original sample, was leached (soluble) from subsamples between 0.8 and 46 mm below the exposed surface of Tc2-9 (exposed to Hanford sediment). The same percent (24%) was leached from the subsamples between 0.8 and 11 mm below the exposed surface of Tc2-10 (exposed to DI water). This suggests that the rate of oxygen migration into the sample exposed to soil was faster than the rate of migration into the sample exposed to water which is consistent with the more rapid transport of ions through a gas phase as compared to a liquid phase. It is assumed that moisture in the Hanford sediment was not sufficient to completely block the surface pores with respect to gas transport across the soil-waste form boundary. Based on nitrate leaching results for the depth-discrete subsamples, regions depleted in nitrates were identified from the top surfaces to 9.5 and 3 mm into samples Tc2-9 (exposed to moist Hanford sediment) and Tc2-10 (DI water). Low mass fractions of nitrate were leached from these depth-discrete samples compared to samples further from the exposed surface presumably because a significant portion of the nitrate had already migrated into the soil or water, respectively. Depth-discrete subsample leaching results for Na can be interpreted in the same way over the same regions in the two samples tested.

In conclusion, leaching monolithic porous cementitious waste forms in water appears to be conservative for non-redox sensitive contaminants. However, leaching data obtained under saturated exposure conditions do not appear to be conservative for redox sensitive contaminants which are easily oxidized. Leaching crushed samples in water still seems to be a conservative approach to estimating the concentrations of soluble contaminants in a waste form.

**Demonstrating Integration of CBP and ASCEM Simulation Tools – 15627:** Pramod Mallick, Justin Marble, Patricia Lee, US DOE; Greg Flach, Heather Burns, Roger Seitz, Savannah River National Laboratory, Savannah River Site, Aiken, SC; Paul Dixon, Los Alamos National Laboratory.

DOE-EM is supporting two crosscutting projects to develop software and conduct targeted experiments to enhance performance and risk assessment capabilities: the Cementitious Barriers Partnership (CBP) and the Advanced Simulation Capability for Environmental Management (ASCeM). The CBP is a smaller-scale project of coordinated software development and experimentation focused on cementitious materials. ASCeM is a larger-scale project aimed at developing next-generation, science-based, reactive flow and transport simulation capabilities and supporting modeling toolsets within a high-performance computing framework to address DOE-EM's waste management and environmental cleanup challenges. Complementary integration of CBP and ASCeM software toolsets has been demonstrated through a joint simulation of radionuclide release and transport in a representative tank closure scenario. Specialized CBP capabilities for simulating

reactive transport in cementitious materials were utilized in a near-field simulation of radionuclide leaching from the engineered system. The high-performance computing (HPC) capabilities of the ASCEM Amanzi simulator were utilized to simulate far-field flow and transport in the natural environment outside the closed tank. The ASCEM flow simulation provided boundary conditions to the CBP near-field model, which in turn provided radionuclide source terms to the ASCEM far-field transport simulation. The joint demonstration illustrates how the two crosscutting projects can be used in a complementary manner to enhance DOE performance and risk assessment.

### **CBP IWWG-ARB 2015 (SHANGHAI, CHINA) REPORT ABSTRACT**

**Characterization and reactive-transport modeling of the changes in the chemical speciation and microstructure of cementitious materials as a result of carbonation-307:** Branch, JL, Kosson, DS, Brown, KG, Van Der Sloot, HA, & Garrabrants, A, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN.

Carbonation has been identified as a key degradation method for cementitious materials that are used to immobilize and serve as barriers for hazardous waste, contaminated soil, and nuclear waste. To better predict material performance under carbonation attack, an equilibrium leaching as function of pH test was used to measure the release of key constituents from a variety of cementitious materials that had been carbonated. These results were used in a reactive-transport modeling tool (LeachXS/ORCHESTRA) to simulate the carbonation reaction. Specifically, the impact of material composition including the addition of fly ash and the impact of carbonation exposure time was assessed. Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) was used to connect the changes observed from the pH dependence test to the microstructural changes and chemical speciation. Results from the pH dependence tests indicate the carbonation reaction neutralized the alkalinity of the cementitious materials. For carbonated materials, the solubility increased for some constituents, including arsenic, but the solubility decreased for other constituents, including calcium at the natural pH. Redistribution of calcium was observed with a deposition of calcium in the carbonated region and a corresponding decalcification in the non-carbonated region. Reactive-transport modeling results from all materials supported the experimental characterization of these materials including the redistribution of calcium and other constituents in the material.

### **ACKNOWLEDGEMENTS**

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