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Review of Cementitious Materials Development and Applications That Have Supported DOE-EM Missions:

Waste Treatment, Conditioning, Containment Structures, Tank Closures, Facility Decommissioning, Environmental Restoration, and Structural Assessments

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EXECUTIVE SUMMARY

The Department of Energy (DOE) is tasked with managing the legacy defense wastes that resulted from nuclear materials production and nuclear arms development. Nuclear-waste management encompasses generation, processing (treatment and packaging), storage, transport, and disposal. To date, there are over 100 million gallons of liquid radioactive and chemical mixed wastes within the Department of Energy complex as well as solid waste, debris, and environmental restoration media that require disposal. DOE has been able to meet the challenges involved in dispositioning this waste using unique technical approaches and application-specific data required due to the nature of the constituents to be managed (e.g., long-lived radionuclides and highly mobile radionuclides in the near surface environments). Cementitious materials have played a prominent role historically in the successful disposition of these wastes, in the reduction of risk to the public, and in the closure of decommissioned tanks and facilities across the DOE complex.

This document explores these applications and provides a review of how cementitious materials have been used across the DOE complex. The various approaches, formulations, processing techniques and disposal paths are discussed along with the requirements that drove the various cementitious systems and techniques used. Specifically, focus is provided regarding how/where cementitious materials are used for the following applications:

- High-Level Waste
- Tank Legacy Decontaminated Liquid Salt Waste
- Liquid Secondary Waste associated with Legacy Tank Waste
- Aqueous and Sludge Wastes
- Solid Particulate Waste
- Solid Debris Waste
- Tank and Ancillary System Closure
- In-Situ Decommissioning (i.e., decommissioned reactors)

Also included in this report is a brief review of the performance of the cementitious materials used in tank closures and disposal of radioactive wastes in near-surface disposal facilities. The purpose is to enable better understanding of the risk significance of engineered barrier performance to demonstrating compliance of DOE disposal actions with regulatory performance. The use of cement-based materials for the long periods involved in radioactive waste disposal is outside the general operating envelope for industrial applications, and the ability of these materials to maintain the low permeability and other properties necessary to retain radionuclides for the long time periods – up to and greater than 100 years – required for nuclear waste disposal is uncertain. Significant research has been conducted at the national laboratories and by multi-agency organizations such as the Cementitious Barriers Partnership (CBP) on long-term performance of cementitious barriers and waste forms. A brief review of the efforts deployed to improve the understanding of the long-term performance of cementitious barriers is warranted.

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LIST OF ABBREVIATIONS

AEC	Atomic Energy Commission
ALARA	As Low as Reasonably Achievable
ARP	Actinide Removal Process
BDAT	Best Demonstrated Available Technology
BONUS	Boiling Nuclear Superheater
BSRI	Bechtel Savannah River, Inc.
CBG	Concrete, Binders, and Grout
CBP	Cementitious Barriers Partnership
CEA	Commission for Atomic and Alternative Energies
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CIF	Consolidated Incineration Facility
CLSM	Controlled Low-Strength Material
CSS	Cement Solidification System
CSSX	Caustic Side Solvent Extraction
CST	Crystalline Silicotitanate
DDA	Deliquification, Dissolution, and Adjustment
DFLAW	Direct Feed Low-Activity Waste
DMF	Dry Material Facility
DOE	Department of Energy
EASC	Emergency Avoidance Solidification Campaign
EBR-II	Experimental Breeder Reactor II
EM	Environmental Management
ENTOMB	Entombment
EPA	Environmental Protection Agency
ERDF	Environmental Restoration Disposal Facility
ETF	Effluent Treatment Facility
EU	European Union
FBSR	Fluidized Bed Steam Reforming
FMF	Fuel Manufacturing Facility
FUETAP	Formed Under Elevated Temperatures and Pressures
GAAT	Gunite and Associated Tanks
GDF	Grout Disposal Facility
HEPA	High-Efficiency Purified Air
HFIR	High Flux Isotope Reactor
HLW	High-Level Waste
HRWR	High-Range Water Reducer
HWCTR	Heavy Water Component Test Reactor
IAEA	International Atomic Energy Agency
IDF	Integrated Disposal Facility
INL	Idaho National Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
ISD	In-Situ Decommissioning
LANL	Los Alamos National Laboratory

LAW	Low-Activity Waste
LFL	Lower Flammability Limit
LLHH	Long, Large, and/or Heavy Hazardous
LLLWC	Liquid Low-Level Waste Concentrate
LLW	Low-Level Waste
LSW	Liquid Secondary Waste
LSWG	Liquid Secondary Waste Grout
LUC	Land Use Control
MCU	Modular Caustic Side Solvent Extraction Unit
MNA	Monitored Natural Attenuation
MVSTs	Melton Valley Storage Tanks
MW	Mixed Waste
NNSS	Nevada Nuclear Security Site
NRC	Nuclear Regulatory Commission
NUWCEM	Cement-base Materials for Nuclear Waste
OHF	Old Hydrofracture Facility
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reservation
OU	Operable Unit
PSW	Phosphate/Sulfate Waste
PUREX	Plutonium-Uranium Extraction
RCRA	Resource Conservation and Recovery Act
REDOX	Reduction-Oxidation
S/S	Solidification/Stabilization
SBW	Sodium-Bearing Waste
SCDHEC	South Carolina Department of Health and Environment Control
SDU	Saltstone Disposal Units
SFEN	French Nuclear Energy
SLAW	Supplemental Low-Activity Waste
SNF	Spent Nuclear Fuel
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
SSW	Solid Secondary Waste
SWDF	Solid Waste Disposal Facility
SWPF	Salt Waste Processing Facility
SWSA	Solid Waste Storage Area
TARA	Test Area for Remedial Actions
TD	Technology Development
TFF	Tank Farm Facility
TGE	Transportable Grout Equipment
THOREX	Thorium Extraction
TRU	Transuranic
WAG	Waste Area Grouping

WESF	Waste Encapsulation and Storage Facility
WIPP	Waste Isolation Pilot Plant
WTP	Waste Treatment Plant
WVDP	West Valley Demonstration Project

1.0 Introduction

Cementitious materials are used for treatment and conditioning of radioactive waste and debris, for containment of or waste and waste forms, and for radioactive facility and tank closures in the US Department of Energy (DOE) Complex. Cementitious materials are also a key component in geologic repository and sealed source borehole disposal designs and sealing systems. Nuclear reactor facilities, isotope separation facilities, transportation casks, used fuel dry storage casks, and most other structures associated with nuclear operations are constructed of concrete or contain concrete components.

Radioactive waste form technology has evolved as (1) the need to treat and dispose of new and unique waste streams has arisen, (2) environmental regulations have been promulgated, and (3) DOE orders have been issued and addressed. Flowable, zero-bleed grout and concrete technology was developed at the Savannah River Site (SRS) to support nuclear facility and radioactive waste tank closures (both final and interim). Special concrete formulations and admixtures were formulated to provide long-term environmental protection, address As Low as Reasonably Achievable (ALARA) objectives for closure workers, and meet cost and schedule expectation. Several types of engineered barriers have been designed to provide long-term isolation of waste and waste forms from the environment.

Condition assessments of existing DOE concrete facilities, both operating and excess, is a current need that is expected to increase as these facilities age. Such assessments require knowledge of reinforced concrete as a material and as elements in structures and the effects of the unique radioactive and chemical environments associated with many of the structures. To address this need and to a similar need for waste forms, the DOE Environmental Management Technology Development (EM-TD) office funded an 8-year project, Cementitious Barriers Partnership (CBP) Project, which developed characterization methods and parameters to identify degradation mechanisms and calculate diffusion-based progression of degradation. An annotated summary of CBP publications is provided in Attachment 1. A recent application of data generated in the CBP was an assessment of degradation of various elements in the SRS Saltstone Disposal Units and the impact on hydraulic properties as a function of exposure conditions and time.[1]

In addition to the US DOE TD, other nuclear countries are currently investing in designing low temperature cement-based waste forms and improving understanding of long-term performance of cement-based materials for Safety Case evaluations. In October 2018, the French Commission for Atomic and Alternative Energies (CEA), and the French Nuclear Energy (SFEN) hosted the 3rd International Symposium on Cement-base Materials for Nuclear Waste (NUWCEM). One hundred sixty-two (162) attendees from 17 countries gave 97 oral presentations and posters. CEA researcher are managing a large research effort which includes about 30 graduate students and post doc researchers working on cementitious materials for radioactive waste disposal. Their current focus includes scale up demonstrations and specialty cement materials such as low-pH cement matrices for reactive metal wastes and debris and acidic wastes and cellular matrices for organic liquid encapsulation. CEA is also participating in long-term compatibility studies between cement materials, waste packages, and geologic media in deep geological conditions.[2]

The European Union (EU) has also invested in cementitious material technology development and performance understanding and prediction.[3] The HORIZON 2020 EURATOM Collaborative Project, *Cement-based materials, properties, evolution, barrier functions (Cebama),* was established to support implementation of geological disposal of nuclear waste by improving the knowledge base for the Safety Case. Cement-based materials were identified as being highly relevant in this context, being used as waste forms, liners and structural components or sealing materials in different types of host rocks and disposal concepts.

This 4-year project, 2015 to 2019, is coordinated by the Karlsruher Institute for Technology (Germany) and is being implemented by a consortium of 27 partners consisting of large Research Institutions, Universities, and subject matter experts from nine EURATOM Signatory States, Japan, and Switzerland. Current total funding is 5.95 million Euros. National waste management organizations contribute to the project by participation in the End-User Group, co-funding beneficiaries, and providing for knowledge and information transfer.

Specific objectives of Cebama are (1) experimental studies of interface processes between cement-based materials and host rocks or bentonite, and assessing the specific impact on transport properties, (2) quantifying radionuclide retention under high pH cement conditions, and (3) developing comprehensive modeling approaches. Modeling will support interpretation of results and prediction of the long-term evolution of key transport characteristics such as porosity, permeability and diffusion parameters especially in the interface between cement-based materials and the engineered and natural barriers. Further objectives cover dissemination of results to scientific and non-scientific stakeholders as well as training and education of young professionals for carrying over the expertise into future implementation programs.

This report provides examples of applications of cement-based materials for radioactive waste treatment, conditioning, engineered containment barriers, and decommissioning in the US DOE complex. It also includes examples of recent concrete structure condition assessments. The information is summarized in the following general categories which include both radioactive and mixed waste and debris.

- High-Level Waste
- Tank Legacy Decontaminated Liquid Salt Waste
- Liquid Secondary Waste associated with Legacy Tank Waste
- Aqueous and Sludge Wastes
- Solid Particulate Waste
- Solid Debris
- Tank and Ancillary System Closure
- In-Situ Decommissioning (i.e., decommissioned reactors)

Technology, engineering, and programmatic support that is needed for successful deployment of cement waste forms, closure grouts, engineered concrete barriers, and structural condition assessments are also identified.

2.0 High-Level Waste

Nuclear waste form options for the immobilization of high-level waste (HLW) once included concrete.[4,5] Specifically, the Savannah River Plant evaluated concrete from the FUETAP (formed under elevated temperatures and pressures) process[6] and hot-pressed concrete[7] for HLW disposal. It was determined though that high radioactivity levels and high heat-generating rates (radioactive decay heat) adversely affect the solidification of HLW in concrete.[4] Also, concrete materials are generally porous (concrete is a mixture of hydraulic cement, water, and aggregate), which contributes to possible radiolytic gas production and water vaporization problems. Vitrification in a borosilicate glass is the Best Demonstrated Available Technology (BDAT) waste form for HLW rather than concrete.

3.0 DOE Legacy Tank Waste/Decontaminated Salt Waste

The Savannah River Site (SRS), Hanford Site, and Idaho National Laboratory (INL) processed reactor fuel-target assemblages to recover isotopes for defense needs. Raffinates (liquid portion remaining after solvent extraction) generated by the isotope separation processes were accumulated and stored at the sites. Hanford operated several separations processes (Bismuth phosphate, reduction-oxidation (REDOX) solvent extraction, and plutonium-uranium extraction (PUREX)). SRS operated the PUREX process (with both highly enriched uranium and depleted uranium, which produced very different waste streams). INL operated similar isotope separation processes. These wastes are referred to as DOE tank wastes.

3.1 Savannah River Saltstone

The SRS Saltstone Facility began operation in 1991 to stabilize the decontaminated aqueous salt fraction in a hydrated cementitious matrix. Salt solution and reconstituted salt cake are removed from the HLW tanks, decontaminated with respect to Cs, Sr, and actinides, and the resulting 5-6 M Na salt solution is transferred to the Saltstone Production Facility where it is mixed with preblended cement, slag, and fly ash. To date, over 17 million gallons of saltstone have been produced and disposed in engineered containment structures called Saltstone Disposal Units (SDUs).

A schematic representation of the waste in SRS HLW tanks is shown in Figure 1, and the overall SRS Tank Waste Processing Flowsheet is shown in Figure 2. The nominal composition of decontaminated Low Activity salt solution that is processed in the Saltstone Facility is shown in Table 1.

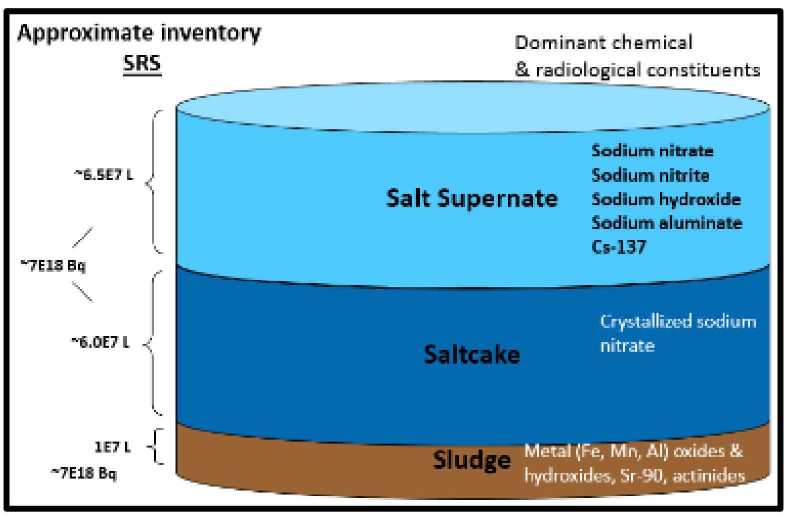

Figure 1. Layers of High-Level Waste Tanks[8]

Table 1. Salt Solution Composition

Nominal Composition			Radioactive Contaminants (nominal)		
Chemical	*mol/L*		*Isotope*	*Bq/mL*	*½ Life (yr)*
Na^+	6		^{90}Sr	74	28.8
NO_3^-	3		^{99}Tc	740	0.2M
OH^-	2		^{129}I	37	16M
NO_2^-	0.5		^{137}Cs	37,000	30.2
CO_3^{2-}	0.2				
SO_4^{2-}	0.1				
pH	> 13				
sp.gr.	≈ 1.23				

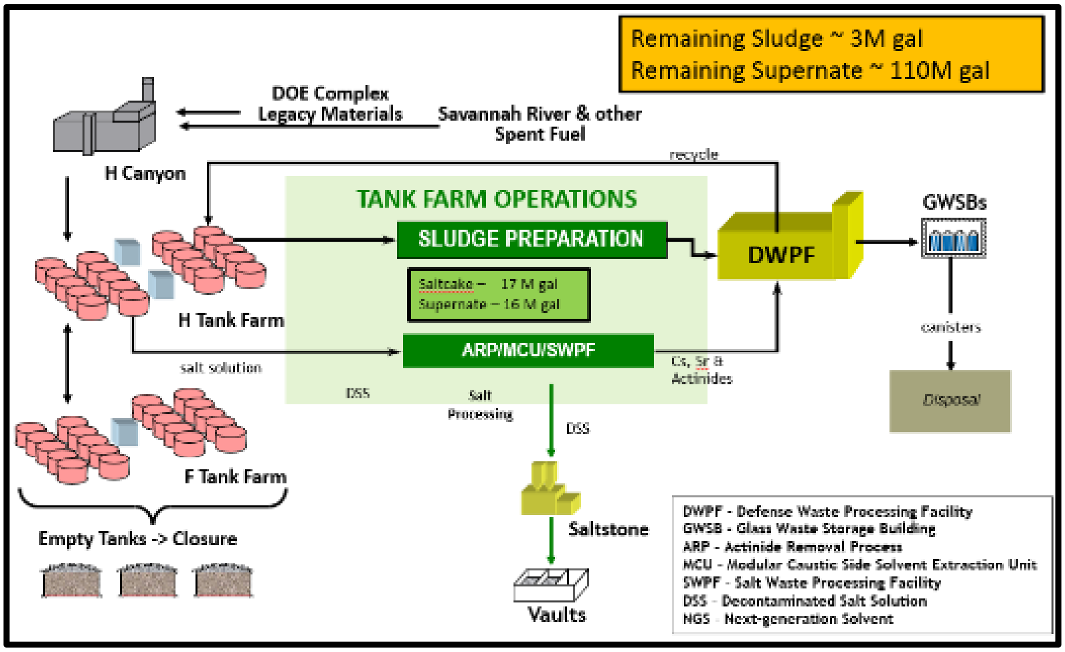

Figure 2. SRS Tank Waste Processing Flowsheet[8]

The Saltstone Disposal Facility Flow Sheet is shown in Figure 3; the Saltstone Production Facility is shown in Figure 4. The nominal composition of the saltstone waste form is provided in Table 2.

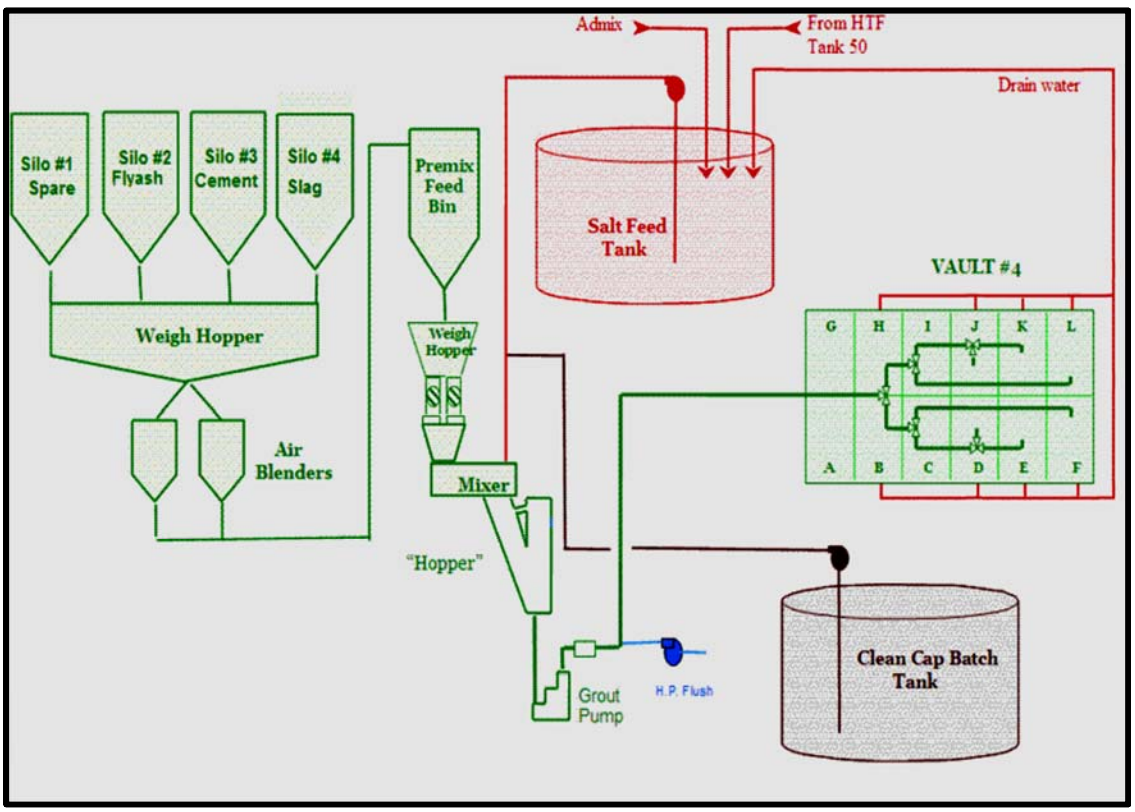

Figure 3. Saltstone Production Facility (SPF) Process Illustration[8]

Table 2. Saltstone Waste Form Composition

Ingredient	Wt. % of Cement Reagent Blend*	SCDHEC Permitted Wt. % Range
Portland Cement, Type I/II	10	0 – 10
Blast Furnace Slag	45	20 – 60
Class F Fly Ash	45	20 – 60
Salt Solution	48	--
Water/Cementitious Materials: 0.58 - 0.6		

* The same blend has been used for all campaigns to date.
SCDHEC – South Carolina Department of Health and Environmental Control

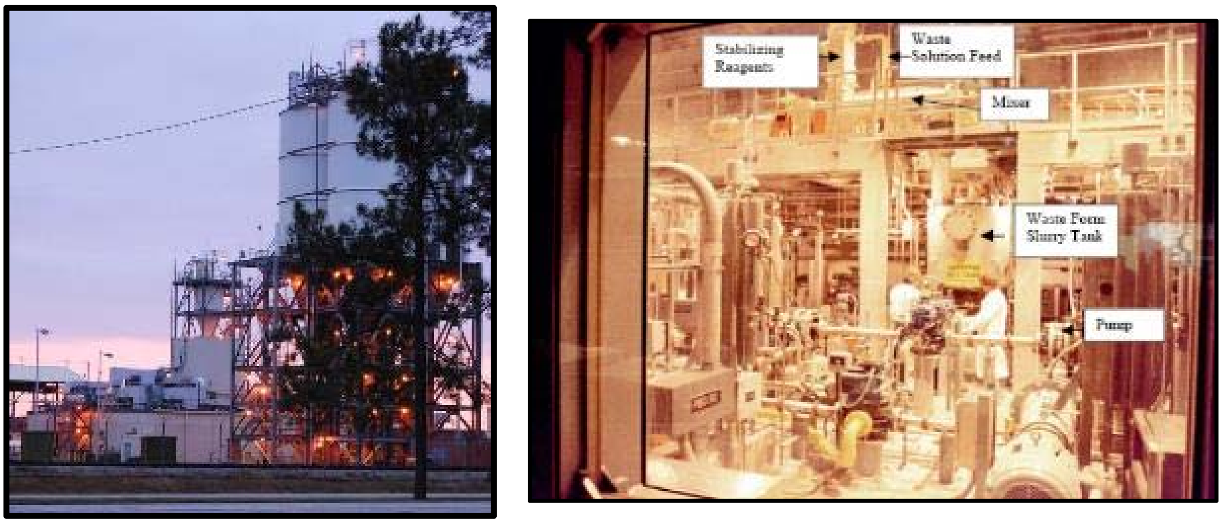

Figure 4. SRS Saltstone Facility (left), Processing Room (right)[8]

Figure 5. Aerial view of Saltstone Disposal Units (SDUs) at SRS[8]

Table 3. SRS Saltstone Processing Campaigns

<table>
<tr><th>Waste Description</th><th>Date of Operation & Waste Volume</th><th>Cementitious Waste Form Matrix</th></tr>
<tr><td>In-Tank Precipitation Demonstration Waste Campaign

Waste water generated during demonstration of sludge washing and removal of Cs, Sr, and actinides from salt solution (tetra phenyl borate, sodium titanate precipitation).

Concentrated salt solution was variable and contained 3-6 M (~32 wt%) dissolved Na salts ($NaNO_3$, $NaNO_2$, Na_2SO_4, $NaAl(OH)_4$, carbonate, oxalate, phosphate, and NaOH with pH ≥ 14).

No further processing once benzene was detected in the process.</td><td>1991-1992

~600,000 gal.</td><td>Saltstone Cement-Based Waste Form<table><tr><td>Portland Cement I/II</td><td>10 wt%</td></tr><tr><td>Blast Furnace Slag</td><td>45 wt%</td></tr><tr><td>Class F Fly Ash</td><td>45 wt%</td></tr><tr><td>Salt Solution</td><td>48 wt%</td></tr></table>Water/Cementitious Materials: 0.58-0.6</td></tr>
<tr><td>Deliquification, Dissolution, and Adjustment (DDA) Campaign

(no Cs, Sr, actinide removal post retrieval from tanks).

Tank 41 dissolved salt solution that has been deliquefied (i.e., extracting the interstitial liquid), dissolved by adding water and pumping out the salt solution, and adjusted for processing at SPF in Tank 41.</td><td>2007-2009

2.8 Mgal.

< 0-5 MCi

600,000 Ci limit including ARP/MCU</td><td>Saltstone

Same as above</td></tr>
<tr><td>Actinide Removal Process (ARP) / Modular Caustic-Side Solvent Extraction Unit (MCU) Decontaminated Tank Salt Waste Campaign

Decontaminated 3-6 M Na salt supernatant resulting from spent nuclear fuel reprocessing for defense purposes commingled with other types of wastes from weapon production and space mission.

Waste decontamination method:
ARP - ^{90}Sr and actinide removal with mono-sodium titanate (MST) and filtration
MCU - Cs removal with modular caustic-side solvent extraction (CSSX) Unit</td><td>2008-2017

7-8 Mgal.

600,000 Ci limit – including DDA</td><td>Saltstone

Same as above</td></tr>
<tr><td>Salt Waste Processing Facility (SWPF) Decontaminated Tank Salt Waste Campaign

SWPF will incorporate both the ARP and CSSX processes in a full-scale shielded facility capable of handling salt with high levels of radioactivity.</td><td>Future Start (TBD)

200,000 Ci limit</td><td>Saltstone

Same as above</td></tr>
</table>

3.2 Hanford Phosphate/Sulfate Waste Grout

Phosphate/Sulfate Waste (PSW) was a low-level liquid generated by activities associated with N Reactor operations at the Hanford Site near Richland, Washington.[9] Grout facilities were designed and constructed to process approximately one million gallons of PSW solution – final transfer to near-surface concrete vaults for solidification and permanent disposal.[10,11] The grout facilities consisted of the Transportable Grout Equipment (TGE) Facility, the 241-AP-102 waste feed pump pit and transfer piping in the 241-AP Tank Farm, the Grout Disposal Facility (vault and portable instrument house), and the Dry Material Facility

(DMF).[11] The vaults at the PSW grout disposal site, located at Hanford's 200-East area, were made of reinforced concrete and lined on the inside with high-density polyethylene – each measured 10.4 m deep, 15.24 m wide, and 38.1 m long.[9]

The PSW grout campaign was initiated August 30, 1988, and processing was halted October 30, 1988 because of deficiencies identified with the surge tank vent system.[10,11] Processing resumed April 13, 1989 (completed first half of the campaign), and again on June 19, 1989 – a total of 1.001 million gallons of waste feed was processed. The cementitious materials and proportions used in the grout treatment process are listed in Table 4.[9,11] The TGE facility mixed the cementitious materials with the liquid waste at a ratio of 7.5 lb/gal, to create a grout slurry.

Table 4. Dry Solids Blend Used for PSW Grout Campaign*

Ingredient	Amount (wt%)
Portland cement, I/II	41
Class F Fly Ash	40
Attapulgite clay	11
Potters clay	8
- Blended at 7.5 lb/gal dry solids to liquid waste	
- Tributyl Phospate was added as an air de-entrainer to minimize foaming, as needed[10]	

* Formulation based on that developed at ORNL for hydrofracture[9]

3.3 Hanford Cast Stone and Liquid Secondary Waste Grouts

As the low-activity waste (LAW) fraction is separated from the high-level waste fraction during waste retrieval from the underground storage tanks at Hanford, the current plan is to immobilize both fractions via vitrification (glass waste form) in preparation for final disposal (Note: DOE must immobilize at least one-third to one-half of the Hanford site LAW by vitrification in glass per an agreement with the State of Washington and the Environmental Protection Agency (EPA)[12]). Liquid tank wastes will be pre-treated at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Once operational, WTP activities will generate liquid secondary waste (LSW) streams from LAW melter off-gas scrubbed effluents and process condensates, which will be solidified in a cementitious grout at the Effluent Treatment Facility (ETF) to meet anticipated waste acceptance criteria for disposal in future Integrated Disposal Facility (IDF).[13,14] Laboratory testing over several years has resulted in many cementitious reagent (ordinary portland cement, blast furnace slag, and Class F fly ash) blends.[15-23] A dry blend similar to saltstone was developed, termed "Cast Stone" (formulation shown in Table 5), in 2005.[17] Other dry-blend proportions have been investigated[17,19,20], as well as water to dry mix proportions.[19,21] The ratio of water to cementitious materials has been tested over the range of 0.4-0.6. Testing with the use of "getters" (materials to lower the mobility of technetium or iodine) has been conducted as well.[15,18] All of this screening testing lead to the selection of Cast Stone as a low-temperature cementitious waste form for stabilization of the ETF-treated wastes.[14]

Table 5. Cast Stone Mix Design

Ingredient	Amount (wt%)
Portland Cement I/II	8
Blast Furnace Slag	47
Class F Fly Ash	45
Technetium getter*	TBD

* Getters are being studied to improve waste form performance.

However, subsequent to the completion of the Cast Stone selection process, additional information about the future liquid wastes to be treated in the ETF indicated that the waste streams to be solidified will be relatively high in sulfate.[14] In this case, the standard Cast Stone formulation with ordinary portland cement, fly ash, and blast furnace slag may not be adequate for solidifying high-sulfate waste streams. Formulations different from the current Cast Stone formulation are referred to as LSW grouts (LSWGs). A testing program was conducted to develop a cementitious waste form for the solidification of high-sulfate wastes after treatment in the ETF – the recommended dry-blend mix included hydrated lime (HL) in place of fly ash (formulation shown in Table 6).[24] The waste simulant was at 30 wt% total solids evaporator condensate.

Table 6. Recommended LSWG Mix Formulation

Ingredient	Amount (wt%)
Portland Cement I/II	36
Blast Furnace Slag	36
Hydrated Lime	28
Technetium getter*	TBD

In the new grout formulation, the HL [$Ca(OH)_2$] is added to initially form ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \bullet 26(H_2O)$] to tie-up sulfate so that ettringite does not form after the cement waste form has set and become a hardened monolith. Late formation of ettringite can lead to undesired swelling and cracking of hardened cementitious waste forms.[25]

In addition, a Supplemental Low-Activity Waste (SLAW) solidification facility is presently planned to provide additional vitrification capacity for Hanford LAW. A variety of SLAW treatment technologies and waste forms are being considered, but DOE does not presently have a preferred alternative regarding supplemental treatment of Hanford LAW. Further studies of potential cost, safety, and environmental performance impacts of the treatment technologies and consequent waste forms may be conducted.

3.4 Idaho National Laboratory (INL)

HLW from processing spent fuels was stored in stainless steel tanks at INL prior to being removed from the tanks and calcined. It is currently being stored as a dry powder in concrete bins at the Idaho site. Approximately 900,000 gallons of an acidic, sodium-bearing waste (SBW) remain as a radioactive liquid and heel solids. The Idaho Nuclear Technology and Engineering Center (INTEC) plans to solidify and stabilize the SBW by fluidized bed steam reforming (FBSR), reclassify the resulting waste form as contact-handled transuranic waste (TRU), and dispose of it at the Waste Isolation Pilot Project (WIPP) at Carlsbad, New Mexico. Construction of the FBSR facility is complete and start-up testing is underway and equipment modifications are occurring to provide successful operations for a radiological environment.

The FBSR facility will produce one of two waste forms: 1) a sodium carbonate-rich powder, or 2) a mineralized aluminosilicate powder. The current plan is to package these powder products in sealed stainless-steel containers for shipment and disposal. If a monolithic waste form is required for disposal, two options are being considered: 1) a geopolymer waste form, or 2) a hydrated cement-based waste form.[26-28]

3.5 Oak Ridge National Laboratory (ORNL)

3.5.1 Hydrofracture Grout

Between 1966 and 1979, Oak Ridge National Laboratory (ORNL) generated waste from various hot cell activities including separation of plutonium from irradiated uranium fuels, production of radiochemical isotopes for medical and research purposes, and other laboratory activities. The waste is referred to as Liquid Low-Level Waste Concentrate (LLLWC). These aqueous solutions and sludges were stored in large underground gunite tanks at ORNL. After tank integrity became a concern in the early 1980s, the waste was retrieved from the tanks, mixed with a blend of cement, fly ash and clay, and then pumped into a shale formation 1000-1200 foot underground on the Oak Ridge Reservation (process known as "hydrofracture).[29] Haliburton, Inc., designed the grout and performed the hydrofracturing and grouting operations. The ingredients and formulations used in the hydrofracture grouts are listed in Table 7.

Table 7. ORNL Hydrofracture Grout Mixes

Liquid waste		***Sludge***	
Ingredient	**Amount (wt%)**	**Ingredient**	**Amount (wt%)**
Portland Cement, I	35.2-44.4	Portland Cement, I	45.5
Class F Fly Ash	33.2-44.1	Class F Fly Ash	45.5
Attapulgite clay	13.2-16.9	Pottery clay (Illite)	9.0
Illite clay	7.1-8.5		
Set retarder	0.04-0.045		
Defoaming agent	As needed		
10.8 lbs. of reagents / 1 gal. of liquid waste			

3.5.2 Emergency Avoidance Solidification Campaign Grout

About 50% of the gunite tanks were emptied by hydrofracture until ^{90}Sr contamination was detected in observation wells. The process was discontinued in 1984. The hydrofracture campaigns disposed of waste containing about 600,000 Ci of radioactivity. The remaining waste in the original gunite tanks was transferred to the Melton Valley Storage Tanks (MVSTs). All ORNL liquid radioactive wastes are now stored in one of eight 50,000-gallon MVSTs at ORNL and two tanks near the evaporator (MSE-194 and MSE 271)[30,31]. Since 1985, the tanks have been at near-capacity and several remediation campaigns have been conducted. In 1988, the Emergency Avoidance Solidification Campaign (EASC) was conducted to increase storage capacity for liquid low-level waste – about 50,000 gallons of supernatant liquid containing ~875 Ci were removed from the MVSTs and treated to produce a nonhazardous grout waste form for on-site disposal (grout formulation shown in Table 8)[32].

Table 8. ORNL EASC Grout Mix

Ingredient	**Amount (wt%)**
Portland Cement	40.4
Blast furnace slag, Grade 120	40.4
Class F Fly Ash	15.4
Celite (moisture absorber)	3.8
10.8 lb. of reagents / 1 gal. of liquid waste	

Grout referred to as "Monoliths"

3.5.3 Melton Valley Storage Tank (MVST) Sludge Grout (proposed)

The remaining waste in the MVSTs is the sludge containing about 5 wt% solids from tank sluicing in 1984. A grout waste form has been selected for solidifying and stabilizing the sludge – the proposed grout formulation (proposed in 2011) is shown in Table 9.[33] The plan is to containerize the resulting grout waste form and dispose of it either on site if possible or at the Nevada National Nuclear Security Site (NNSS), depending on the TRU concentration. The primary radiological contaminants are ^{137}Cs, ^{244}Cm, ^{152}Eu, ^{154}Eu, ^{90}Sr, and actinides (TRU elements). The Resource Conservation and Recovery Act (RCRA) metals are Cd, Cr, Hg, and Pb, and the primary precipitated solids are calcium carbonate and magnesium hydroxides. The start of this grout campaign is currently being determined.

Table 9. Proposed MVST Sludge Grout

Ingredient	Amount (wt%)
Portland cement, I/II	10-35
Blast furnace slag, Grade 120	30-45
Class F Fly Ash	30-45
Sodium metasilicate (Metso Beads)	5-10
Polymer absorbent*	0-1.6
Waste loading (weight ratio): Dry blend 0.65:1 to 1.2:1	

* Waste Lock 770 or NOCHAR A660

3.6 West Valley

From 1966 to 1972, commercial and defense fuels were chopped, dissolved, and processed for PUREX and thorium extraction (THOREX) at the West Valley Site, a commercial spent nuclear fuel reprocessing facility in New York. Fuel reprocessing ended in 1972 for plant modifications, but operations never resumed – changes to increase the plant's capacity and compliance with regulatory standards were deemed too expensive.

In 1980, Congress passed the West Valley Demonstration Project (WVDP) Act[34] as a cooperative effort between the United States Department of Energy and the New York State Energy Research and Development Authority. The WVDP mission was to: 1) Solidify and develop suitable containers for the site's high-level radioactive waste, 2) transport the solidified waste to a federal repository, and 3) dispose of the low-level radioactive and transuranic wastes created during reprocessing operations.

All tank liquid waste was processed through the Supernate Treatment System zeolite process (for ^{137}Cs, ^{90}Sr, and actinide removal), concentrated in the WVDP LLW evaporator, and then blended with cement in the Cement Solidification System (CSS) (Note: the sludge/zeolite went for vitrification).[35] Approximately 20,000 square, 71-gallon drums of solid LLW were produced and stored on-site in the Drum Cell (see Figure 6). All cement-filled drums were removed and transported to the Nevada NNSS for permanent storage (shipments completed in 2007) (see Figure 6).

Figure 6. Square, 71-gallon drums to enter the Drum Cell (left)[36]; Cement-filled drums being prepared for shipment to NNSS (right)[35]

4.0 Low-Level, Mixed, and TRU Wastes

4.1 Solid Low-Level Waste and Mixed Waste

4.1.1 SRS – Ashcrete from the Consolidated Incineration Facility

The Consolidated Incineration Facility (CIF) at SRS was designed to treat low-level radioactive, hazardous, and mixed wastes in both solid and liquid forms.[37] Construction of the CIF began in November 1992 and operations were conducted from 1997 to November 2000. During operation, the CIF generated two residual waste streams: ash formed as a combustion product in the rotary kiln and blowdown liquids from the recirculation of scrubbing and cooling water in the off-gas clean-up system. These two waste streams (ashcrete – made from ash; blowcrete – made from blowdown) were stabilized via the Ashcrete process at CIF by encapsulation in a cement matrix to form a solid monolithic structure in 55-gallon drums (ash was mixed with cement (dry or wet) in drums and drums were tumble-mixed; time to set was typically 28 days).[38-40] The containerized/solidified ashcrete and special case blowcrete forms were buried in shallow unlined trenches in E-Area at SRS.[41]

4.1.2 SRS – Naval Fuels

The 247-F Fuel Manufacturing Facility (FMF) operated from 1985-1989. This facility was to convert uranium stock into a form suitable for naval fuel. It was deemed redundant to other naval fuel pilot plant facilities and shutdown in 1989. Low-level liquid waste from the startup and brief operation of the FMF was converted into “saltcrete.” In 1987, a recommendation was made to change from a cement-only to a cement-fly ash saltcrete mixture.[42] The change would eliminate the excessive heat buildup (>100°C) experienced with the cement-only formulation, as well as improve the waste form (less contaminant release) and lower costs. In total, more than 6,500 drums of saltcrete – waste generated from FMF operations and shutdown – were disposed of in the Z-Area Vaults.[43]

4.1.3 Hanford Secondary Waste

In addition to the LSW that will be generated during future direct-feed low-activity waste (DFLAW) operations and WTP activities at the Hanford Site (see Section 3.3), solid secondary waste (SSW) streams will also be generated. Expected SSW include debris or particulate material – process equipment, contaminated tools and instruments, decontamination wastes, crushed high-efficiency particulate air (HEPA) filters, carbon absorption beds, silver mordenite iodine sorbent beds, and ion-exchange resins/crystalline silicotitanate (CST).[44] The use of Ultra-High-Performance Cementitious Composite (UHPCC) as an encapsulation grout has been investigated for Hanford’s SSW.

Currently, evaporator bottoms from the ETF are being solidified in ammonium sulfate granules and are being sent to the Environmental Restoration Disposal Facility (ERDF). Screening tests have recently been conducted to determine if grout-based waste forms developed for the ETF evaporator bottoms wastes can meet off-site (e.g., WCS, Inc., Texas) and/or on-site Hanford Integrated Disposal Facility (IDF) acceptance criteria.[45]

Further investigation to improve the contaminant and radionuclide (^{99}Tc and ^{129}I) retention of a dry-blend (UHPCC or other) formulation is necessary. Final selection of a cementitious waste form for Hanford’s SSW streams is still under consideration.

4.2 Solid Low-Level and Mixed Debris

4.2.1 Hanford Environmental Restoration Disposal Facility

The fundamental objective of the ERDF (regulated by the EPA under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA)) is to support the timely removal and disposal of contaminants from various locations within the Hanford Site.[46] Under *Resource Conservation and Recovery Act of 1976* and *Washington Administrative Code* land disposal restriction (LDR) treatment requirements, waste that meets the definition of debris can be treated using macroencapsulation. The ERDF accepts waste that is categorized as "long, large, and/or heavy hazardous" (LLHH).

The macroencapsulation method to be used for treatment of the LLHH waste items is performed in an ERDF trench by flood grouting.[46] LLHH waste items to be macroencapsulated are brought to the ERDF from the waste site; driven into the disposal trench; and directly placed on concrete blocks, pads, or inorganic standoffs to elevate the waste debris above the ground, allowing the free flow of grout to completely surround and cover the waste items (all voids and cavities present in the waste debris are also filled). This occurs at a location in the trench that has been prepared for receipt, treatment, and disposal of the item(s). Depending on the overall size/shape of the LLHH waste items, encapsulation is accomplished with single or multiple pours.

Treatment prior to placement within the trench would result in greater risk to human health and the environment.[46] The flood grouting treatment within an ERDF trench is superior to polymer coating macroencapsulation because the waste items will not be moved post-treatment (thus preventing damage to the encapsulating media), and because of the higher ultimate strength of the cured grout. The macroencapsulated (flood grouted) LLHH waste debris is cured for at least 1 week before it is covered with soil. LDR treatment with grout in this manner satisfies 40 CFR 268.45 treatment standards.

4.2.2 SRS Slit Trenches

SRS also disposes of large equipment (e.g., large cesium sources and other low-level radioactive waste) in trenches by using the components-in-grout (or microencapsulation) technique.[47] The technique allows large equipment to be disposed of in trenches, and the waste form is surrounded with grout on all sides (bottom, sides, top) (see Figure 24 as an example). This approach will limit future subsidence and the release of radionuclides. The conceptual design for the SRS slit trenches employs a deeper (11-m or 35-ft deep) and narrower (3-m or 10-ft wide) design than conventional belowground, near-surface radioactive waste disposal facilities to protect the facility from inadvertent human intrusion.

4.3 TRU Waste at Los Alamos National Laboratory

Two cement solidification systems exist at Los Alamos National Laboratory (LANL) – the TA-50 and TA-55 Systems.[48] Both systems treat TRU waste from the evaporator at TA-55, the Plutonium Producing Facility.

4.3.1 TA-50 System

Distillate from the evaporator was sent to the TA-50 facility, where the radionuclides were precipitated and cemented.[48] Each 55-gallon drum was preloaded with 1) a portland cement (282 lb), 2) vermiculite (3 gallons), and 3) sodium silicate (2.5 gallons). Then, 23 gallons of sludge was added. The drum was sealed and then tumbled (two at a time) for mixing. The only issues notified with the TA-50 System were surface moisture appearing on some drums during setting and some drums stored uncovered developed pinhole-sized corrosion holes through the drum walls at the cement surface. No internal liquid was found so the holes were attributed to rainwater gaining entry trough the carbon filter in the lid.

4.3.2 TA-55 System

The TA-55 cementation system at LANL was designed to primarily treat nitric-acid-based evaporator bottoms, along with particulates and water-immiscible organic liquids from TA-55.[48] Envirostone cement, a gypsum-based product containing 20% polymerization agent to increase resistance to leaching, was utilized rather than a portland cement. Envirostone cement had the ability to solidify both acidic and water-immiscible organic wastes in a WIPP-acceptable waste form. Each 55-gallon drum was mixed with a prop mixer.

A large percentage of drums generated free liquid sometime after drum closure, with no reabsorption observed.[48] So much water was produced in some drums that it overflowed out of the carbon filter. Studies were performed to determine the influence of mixing time (extended mixing seemed to eliminate or at least delay the water generation) and the use of other cements (survey of drums produced by the TA-50 portland cement operation detected no liquid).

5.0 HLW Tank Closure

5.1 Savannah River Site

Four types of HLW tanks exist at SRS – Types I, II, III, and IV (see Figure 7).[49]

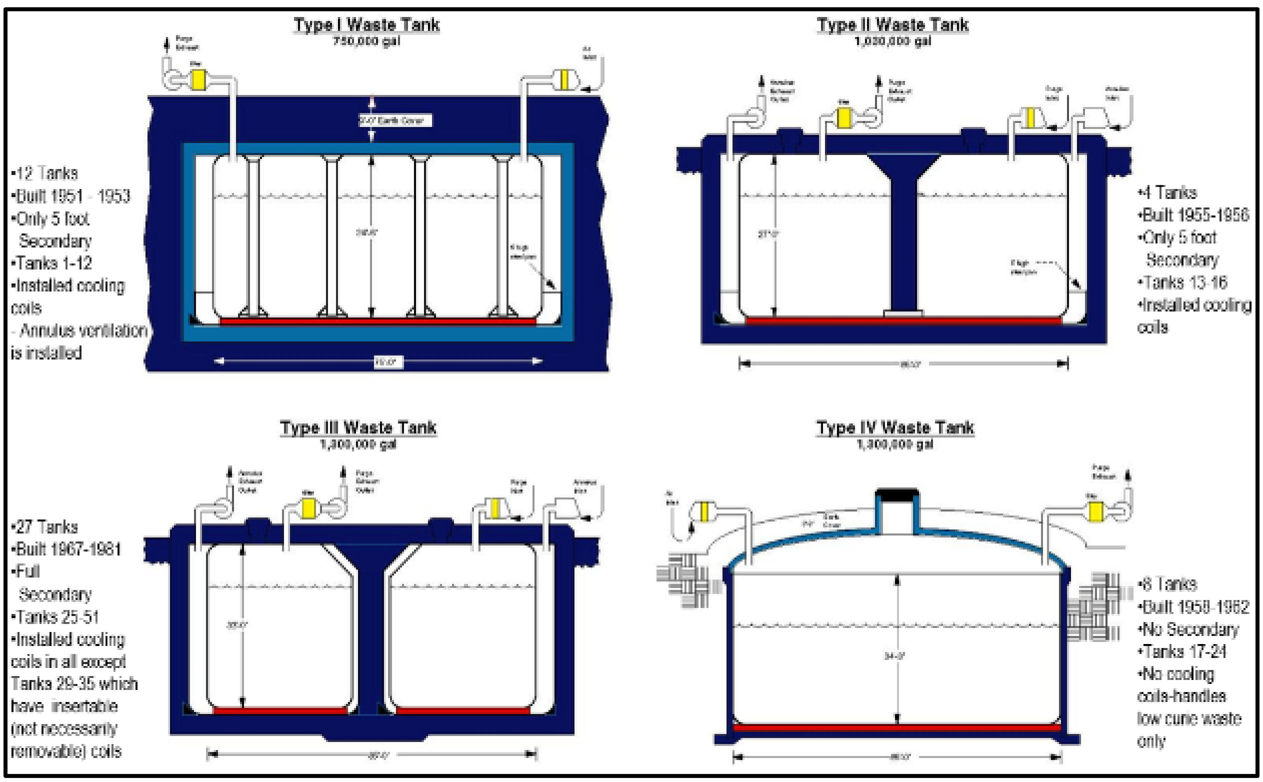

Figure 7. SRS High-Level Waste Tanks[49]

Eight of these tanks have been "closed," or successfully filled with grout. Tanks 17 and 20 in the F-Area Tank Farm were the first two to close (closed in 1997) – both were Type IV (no cooling coils) and were filled with a stabilizing (reducing) grout, a structural (bulk fill) grout, and a capping (strong) grout (see Figure 8 and Table 10). The original concept was to use a high strength reducing grout to encapsulate the residual waste, a Controlled Low-Strength Material (CLSM)[a] for filling the bulk of the tank and a 2000 psi grout as an intruder barrier in the top of the tank.

The original SRS CLSM and 2000 psi grout mixes were modified by SRNL to eliminate bleed water.[50] Initial testing of the Site CLSM and 2000 psi grout indicated that a significant amount of bleed water would be generated in the closed tanks. In early 1997, SRNL and Bechtel Savannah River, Inc. (BSRI) personnel were requested to modify the site CLSM mix and 2000 psi mix to eliminate the need for removing and disposing of radioactively contaminated liquid from the tanks and to improve uniformity of the fill material (reduce settling and stratification). The resulting modified mixes were referred to as SRS zero bleed flowable fill and SRS zero-bleed 2000 psi grout (see Table 10).

In 1998, research was conducted to develop an all-in-one HLW tank fill grout that could be used for both encapsulating the residual waste and bulk fill.[50,51] The driver for this work was the desire to simplify the production requirements for tank fill material. This work resulted in an all-in-one zero bleed reducing fill/grout mix (also provided in Table 10).

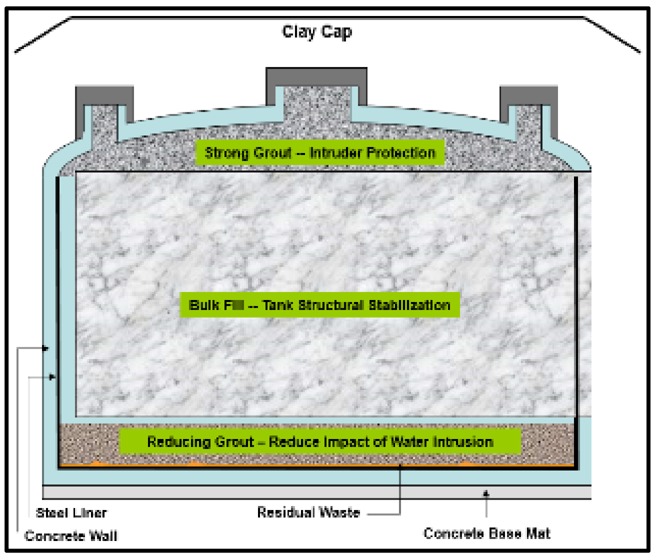

Figure 8. Tank Closure Concept for Type IV HLW Tanks

[a] CLSM is a cementitious, flowable fill that is used as backfill or infill and has soil-like properties. It is self-compacting and consequently does not require mechanical compaction to achieve design density. CLSM typically contains sand, fly ash and less than 100 pounds of hydraulic material per cubic yard of fill.

Hydraulic cementitious material reacts with water to form insoluble hydrated compounds. Portland cement is the best-known hydraulic cement. Slag cement is also hydraulic once it has been activated.

Table 10. SRS Tank Closure Grout Mix Designs from the 1990's[50,52]

Ingredient	SRS Reducing Grout	SRS Zero-Bleed Flowable Fill	SRS Zero-Bleed 2000 psi Grout	All-In-One Zero-Bleed Reducing Fill/Grout**
Portland Cement, Type I/II (lb/yd^3)	1353	150	550	75
Slag Grade 100 (lb/yd^3)	209	---	---	210
Fly Ash, Class F (lb/yd^3)	---	500	---	
Silica Fume (lb/yd^3)	90	---	---	---
Quartz Sand, ASTM C-33 (lb/yd^3)	1625 masonry sand	2300 concrete sand	2285 concrete sand	2300 concrete sand
Water (gal/yd^3)	86.4	63	65	60
HRWR – ADVA® Flow (fl $oz./yd^3$)*	250	90	140	90
Viscosifier – Kelco-crete® (g/yd^3)*	---	275	275	275
Set Retarder (fl $oz./yd^3$)	150	---	---	---
Sodium Thiosulfate (lb/yd^3)	2.1	---	---	2.1 (optional)

* HRWR (ADVA® Flow) and Kelco-crete® were premixed prior to incorporation in the zero-bleed mixes. HRWR – High-Range Water Reducer.

** This mix was developed for future HLW tank closures. The mix proportions can be adjusted to obtain a range of compressive strength suitable for waste encapsulation, bulk fill, and intruder protection.

Unlike Type IV tanks, tanks of Types I, II, III, and IIIA at SRS contain cooling coils (see Figure 7).[53] The ability to successfully fill intact cooling coils with grout depended on developing a grout formulation that satisfied the processing requirements for filling HLW tank cooling coils[54]. The cooling coil grout composition developed and tested is provided in Table 11, along with its physical properties. The MasterFlow® (MF) 816 cable grout was obtained from BASF, Inc. and the grade 100 blast furnace slag from Holcim, Inc. Both the MF 816 and slag are cementitious materials. A unique characteristic of this grout is that it has a fairly long working time such that its physical properties change little over an extended period of time. The rheological properties, both yield stress and plastic viscosity, over a period of 90 minutes of continuous mixing, were essentially constant[53]. This grout also satisfied the piping pressure limit of 150 psig[55] during grout fill, for 1200 linear feet of 2" schedule 40 piping. The condition of flow for this grout is laminar for flow rates up to 200 gallons per minute (gpm), but the actual flow rate will be lower due to the piping pressure limit.

Table 11. Cooling Coil Cable Grout Composition and Physical Properties[54]

Component	Mass fraction
MasterFlow® 816 Cable Grout	0.6767
Blast Furnace Grade 100 Slag	0.0752
Water	0.2481
Density using pycnometer (g/mL)	2.07
Water to Cementitious Mass ratio (W/CM)	0.33
Flow Cone (seconds) at 23°C	20-30

Type I tanks contain 34 vertical cooling coil assemblies (half primary, half auxiliary) and two horizontal cooling coil assemblies (one primary, one auxiliary) (see Table 12)[54]. For the vertical coils, the assemblies contained 180°, 2-foot radius bends. The vertical distance between the top and bottom of the 180°, 2-foot radius bends is 22.5 feet. The horizontal assemblies also had 90° bends to get around the support columns in the tank. The SRS Type I tank linear piping runs vary 2.75 to 65 feet between bends (90° bends connected with 2.75 feet of piping).

Table 12. 2-foot Radius Bend Information for Vertical and Horizontal Cooling Coil Assemblies in SRS Type I Tanks[54]

Vertical Assemblies			
# of Cooling Coil Assemblies		**# of 180°, 2-foot radius bends per assembly**	
12		15	
14		17	
8		19	
Horizontal Assemblies			
Coil Assembly	**# of 2-foot radius bends**		**Total Linear Piping Run (ft)**
	90°	**180°**	
Primary	6	9	700
Auxiliary	10	10	775

Full-scale mockup testing was performed at the Clemson Engineering Technologies Laboratory (CETL) for grouting cooling coil piping. Figure 9 shows part of the vertical cooling coil test setup; Figure 10 shows part of the horizontal cooling coil test setup. Figure 11 and Figure 12 show examples of cross-sectional cuts of grout-filled piping from the vertical and horizontal cooling coil tests performed at CETL, respectively, and the effectiveness of completely filling the piping with grout.

Figure 9. Vertical Cooling Coil Assembly (first floor) – Mockup Testing at CETL[54]

Figure 10. Horizontal Cooling Coil Assembly (top view) – Mockup Testing at CETL[54]

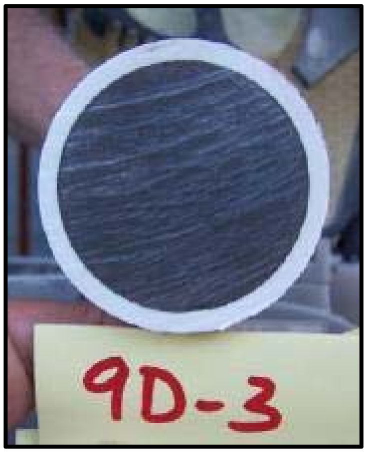

Figure 11. Cross-section of grout-filled piping from vertical tests[56]

Figure 12. Cross-section of grout-filled piping from horizontal tests[57]

The cooling coils were filled with an aqueous solution of chromate and sodium hydroxide, and there was concern that residual liquid of that mixture could adversely impact grout properties (e.g., compressive strength). Tests were conducted with a batched simulant (MF 816 + slag) containing chromate (0.006 M) and sodium hydroxide (0.001 M) at a w/cm ratio of 0.33. Even with a conservatively high amount of chromate and free hydroxide in the cooling coil solution, it was demonstrated that acceptable grout properties will be obtained in the presence of residual chromate and free hydroxide in the water[53].

Utilizing these proven grouts that have been developed, four HLW tanks with cooling coils and four tanks without cooling coils have been closed at SRS (see Table 13).

Table 13. SRS HLW Tank Closures

Tank	Type	Date Closed
20 F	IV	7/28/1997
17 F	IV	12/10/1997
18 F	IV	9/5/2012
19 F	IV	9/5/2012
5 F	I	12/19/2013
6 F	I	12/19/2013
16 H	II	9/23/2015
12 H	I	4/28/2016

5.2 <u>Idaho National Laboratory (INL)</u>

In 1953, the Idaho Chemical Processing Plant, now the Idaho Nuclear Technology and Engineering Center (INTEC), was chartered to recover fissile uranium by reprocessing spent nuclear fuel (SNF)[58]. In 1992, the DOE officially discontinued reprocessing SNF at INTEC. The Tank Farm Facility (TFF), located within the northern portion of INTEC, comprises eleven 1,135.6-kL (300,000-gal) below grade stainless steel tanks in unlined concrete vaults of various construction, four inactive 113.5-kL (30,000-gal) stainless steel tanks, interconnecting waste transfer piping, and ancillary equipment. The TFF tanks had historically been used to store a variety of radioactive liquid waste, including wastes associated with past spent nuclear fuel reprocessing.

The four 113.5-kL (30,000-gal) (tanks WM-103, -104, -105, and -106) and seven 1,135.6-kL (300,000-gal) (tanks WM-180, -181, -182, -183, -184, -185, and -186) TFF tanks were emptied of waste, cleaned, and grouted in place in 2006 and 2007[58]. Ancillary piping and valve boxes associated with these tanks were grouted in 2008. Over 24,000 yd^3 of grout were placed to fill the tanks and vaults followed by the grouting of over 7 miles of underground piping process and cooling coil piping. The TFF remains operational to provide interim storage of radioactive liquid waste awaiting final treatment, and closure of the remaining four large tanks has yet to be accomplished.

The ingredients and proportions for the grout fill formulations at the INTEC TFF are shown in Table 14.[59] One grout was for filling pipes (Pipe Grout), and the other was for filling the bulk of the tanks and vaults (Tank Grout).

Table 14. Grout Compositions for Closing Tanks at the INTEC TFF

Ingredient	Pipe Grout	Tank Grout
Portland Cement, Type I/II (lb/yd^3)	680	320
Fly Ash, Class F (lb/yd^3)	1,600	640
Quartz Sand (lb/yd^3)	---	2,200
Water (gal/yd^3) *(lb/yd^3)*	96 max. *(800 max.)*	52 max. *(433 max.)*

5.3 <u>Hanford Grout Mix for Tank Closures</u>

It is assumed Hanford's closure configuration will be similar with the successful demonstrations being conducted at SRS and INL.[26,60,61] The overall approach for dispositioning the tank wastes at Hanford, Savannah River, and Idaho has been to remove the waste to the maximum extent practical, and separate the waste into high and low activity fractions.

In 2002, it was determined that the first set of tanks identified for closure included: C-106, C-201, C-202, C-203, C-204, S-102 and S-112.[62,63] This includes waste retrieval, tank cleaning, and filling the empty tanks with portland cement-based materials. Three grouts were designated for the tank fill:

- Stabilizing Grout (Phase 1 Grout) to eliminate residual liquid in the tanks and stabilize contaminants (Tc-99) in the residual tank heels,
- Structural Grout (Phase 2 Grout) to provide structural support for the landfill (filling the tank void space), and
- Capping Grout (Phase 3 Grout) to provide an intruder barrier at the top of the tanks.

To date, a conclusive grout formulation for Hanford tank closure has yet to be finalized and no tanks have been closed from a regulatory standpoint (the list tanks designated for closure may have evolved as well).

6.0 Other Waste Tank Closures

6.1 Savannah River Site

6.1.1 Closure of the Consolidated Incineration Facility

Operation of the CIF at SRS ended in November 2000 when it was deemed not economical for PUREX treatment.[37] Four 114 m^3 (30,000) gallon underground solvent storage tanks, Tanks 33-36, were part of the CIF.[64] Those tanks were filled with a self-leveling, zero bleed grout between May 29 and June 27, 2018. A total of 135 to 140 cubic yards of grout were placed in each tank (two lifts, 7 days apart) (see Figure 13 and Figure 14).

Figure 13. CIF Solvent Tank Grouting

Figure 14. Tank #34, Grout Nearing the Top

6.2 Oak Ridge

6.2.1 Closure of the Gunite and Associated Tanks

Several underground storage tanks were constructed in the Gunite and Associated Tanks (GAAT) Operable Unit (OU) between 1943 and 1951, designed to store liquid radioactive chemical wastes generated by ORNL operations.[65] A total of twelve gunite tanks (Note: Gunite is a mixture of portland cement, sand, and water, which was sprayed over a wire mesh and steel reinforcing rod frames) and four stainless-steel tanks were constructed, primarily in the North and South Tank Farms (see Table 15).

Table 15. Tanks located in the GAAT OU[65]

Tank number(s)	Construction material	Date stabilization with grout completed
W-11	Gunite	2000
TH-4	Gunite	April 2001
North Tank Farm Tanks		
W-1 and W-2	Gunite	2000
W-13, W-14, and W-15	Stainless-steel	FY 1998
W3 and W4	Gunite	September 2001
W-1A[b]	Stainless-steel	N/A
South Tank Farm Tanks		
W-5, W-6, W-7, W-8, W-9, and W-10	Gunite	September 2001

N/A = not applicable

[b] Tank W-1A was not stabilized/grouted in place as the other GAAT OU tanks. Due to leaks in the tank's waste transfer lines, Tank W-1A and surrounding contaminated soil(s) was excavated and removed (shipped off site for disposal) in January 2012.

The GAATs were stabilized in place – filled with a low-strength grout (basic formulation shown in Table 16).[65]

Table 16. Grout formulation used for filling the GAATs

Ingredient	Amount (lb)	% of total (wt%)
Portland cement	1.4	2.2
Sand	48.8	76.5
Water	13.6	21.3
Total:	63.8	

6.2.2 Closure of the Old Hydrofracture Facility Tanks

Five underground, carbon-steel tanks were constructed at the Old Hydrofracture Facility (OHF) and were in service from 1963 through 1980 (Tanks T-1, T-2, T-3, T-4, and T-9).[66] A small residual waste volume remained in each tank after the wastes (sludge and supernatant) were retrieved. A two-stage grouting process was used to stabilize these tanks – the initial stage targeted blending the residual waste with grout; the second bulk-fill stage filled the remaining tank structure.[67] The bulk-fill grout formulation is shown in Table 17. This flowable grout had the following purposes: Provided structural stability to the tanks, prevented subsidence and further additions to the tanks, and added waste-retention properties for the RCRA and radioactive constituents present in the tank heel.

Table 17. OHF Tank Grout Formulation[66,67]

Ingredient	Amount
Portland cement, Type II (lb/yd^3)	50
Fly Ash, Class F (lb/yd^3)	600
Concrete Sand (lb/yd^3)	2,400
Water (gal/yd^3) *(lb/yd^3)*	50 *417*

7.0 Facility Decommissioning

The International Atomic Energy Agency (IAEA) has defined the following three options for decommissioning (internationally accepted definitions)[68,69]:

- Immediate Dismantling or DECON (Early Site Release in the U.S.),
- Deferred Dismantling or SAFSTOR (also called safe storage, safe store or safe enclosure), and
- Entombment or ENTOMB.

In practice, the final approach lies somewhere between these categories (e.g. partial dismantling followed by a period of safe enclosure for the remaining parts). Many factors including available waste disposal options, security, and cost may influence the approach adopted.

The U.S. Nuclear Regulatory Commission (NRC) regulates decommissioning activities in the United States and follows the IAEA approach. The U.S. DOE follows the same nuclear facility decommissioning strategy as described above. However, slightly different terminology has been recently used to emphasize features of selected decommissioning actions. For example, Interim Safe Storage (ISS) or “cocooning” is used to describe the status of eight DOE isotope production reactors/reactor buildings at the Hanford Reservation. This status is equivalent to the SAFSTOR strategy but emphasizes the interim nature of action and acknowledges prioritization of more pressing site cleanup actions. The U.S. DOE uses the term In-situ Decommissioning (ISD) to represent a strategy that is consistent with the ENTOMB option but can include elements of the DECON and SAFSTOR. ISD emphasizes the U.S. DOE commitment to retain the site in perpetuity and to provide long-term maintenance and monitoring, hence the strategy is referred to as ISD-Land Use Control (LUC)-Monitored Natural Attenuation (MNA).

Entombment (ENTOMB) is the strategy that entails placing the facility in a condition that allows the radioactive material to remain on site without ever totally removing it. In this option, radioactive material is encased in a structurally long-lived material until radioactivity decays to a level that is no longer of concern, thereby permitting unrestricted release of the facility. The following sections are a summary of cement/grout materials and activities relating to ISD and ENTOMB strategies.

7.1 In-situ Decommissioning (ISD)

7.1.1 SRS Isotope Production Reactors

ISD - LUC - MNA was the selected decommissioning alternative for the P and R isotope production reactor facilities and for the C-Reactor Disassembly Basin at SRS. At the 105-C Disassembly Basin, water in the basin was evaporated. Rod hangers were disposed of in the basin, which was filled with grout. The above-grade structure remains in place. At the 105-P and 105-R Reactor facilities, construction debris, heat exchangers, and some equipment were disposed of as LLW in the SRS Solid Waste Disposal Facility (SWDF). The below-grade portion of each facility was physically stabilized with flowable grout/concrete. Reactor vessels were located below grade, but above the water table, so they were also filled with concrete or grout and capped. The above grade structures were left in place. All openings above- and below-grade of 105-P and 105-R were sealed with reinforced concrete, and new roofs were installed. The below-grade portions of the structures were filled with cement grout/concrete. The below-grade reinforced concrete structure performed the function of entombment at each reactor building (C, P, and R).

The SRS 105-P and 105-R reactor facilities were very similar[70]. The 105-R Disassembly Basin was the first SRS reactor facility to undergo the ISD process, but all pertinent data and information related to grout formulations and concrete mix designs, placement strategy, and concepts were also applicable to the 105-P Reactor Disassembly Basin and the below-grade portions of the 105-P and 105-R Main Reactor Buildings. The ISD process for the entire 105-P and 105-R reactor facilities required approximately 250,000 cubic yards of grout and 2,400 cubic yards of structural cement. Schematic cross sections of the ISD concept for both 105-P and 105-R are illustrated in Figure 15 and Figure 16.

Three grout mixes were developed for filling the massive below-grade voids / rooms. These grouts utilize zero bleed, flowable structural fill technology developed at the Savannah River National Laboratory (SRNL). These grouts are based on a portland cement – Class F fly ash binder and were specified for the following applications:

- Below-grade massive voids / rooms:
    - Bulk filling
    - Restricted placement and
    - Underwater placement.

A cellular (light weight) grout was also specified for filling a portion of the P-Reactor Disassembly Basin. The loading limit for the basin floor was the driver for specifying a cellular grout.

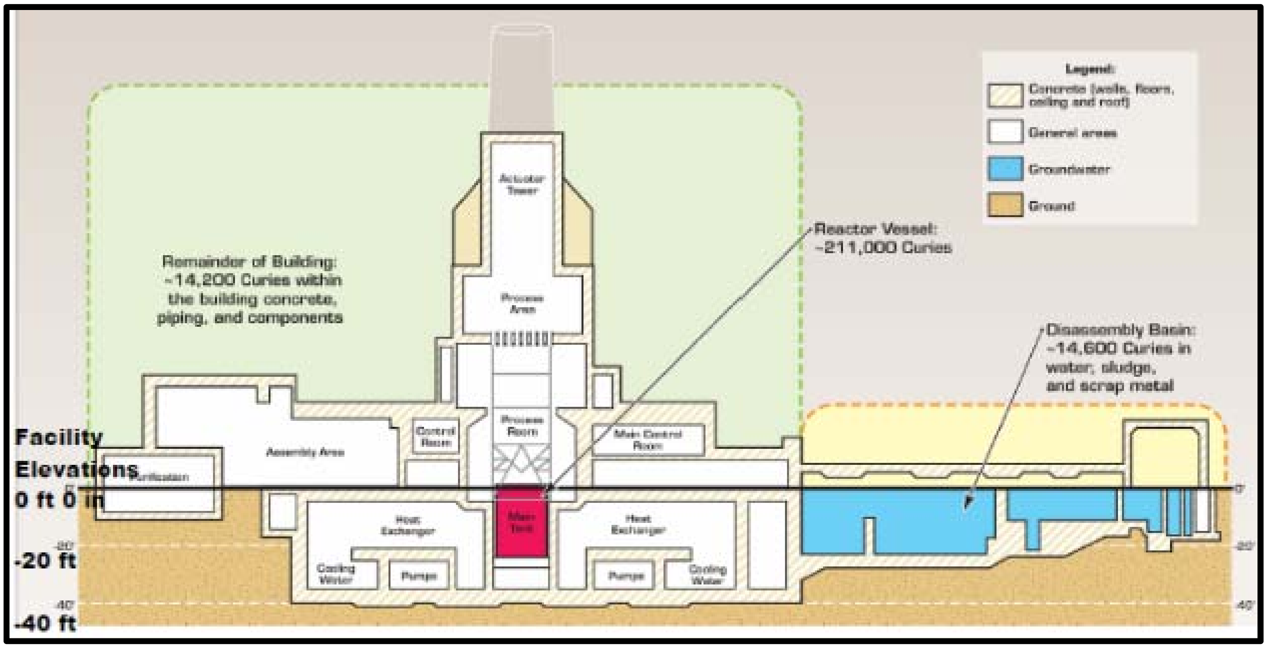

Figure 15. Schematic cross-section view through 105-P (105-R) reactor building *before* ISD grout placement[70]

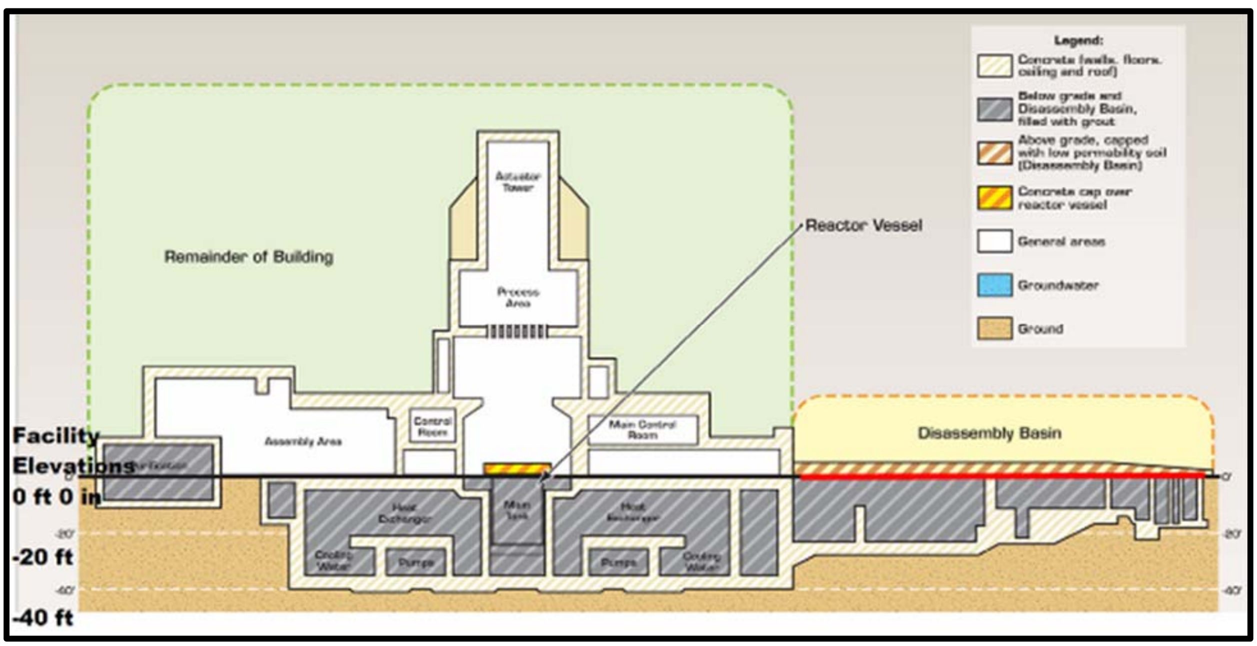

Figure 16. Schematic cross-section view through 105-P (105-R) reactor building *after* ISD grout placement[70]

Bulk Fill Grouts: Ingredients in these flowable structural fills are presented in Table 18. (These mixes were adjusted slightly by the subcontractors who supplied the cementitious materials to account for properties of their raw materials.) Selected properties of these grouts are presented in Table 19.

Table 18. SRS Reactor Facility ISD Structural Fill Grout Mix Designs.

Material (kg/m³) *(lb/yd³)*	Congested Dry Area Placements	Uncongested Dry Area Placements		Underwater Placements
	PR-ZB-FF	**PR-ZB-FF-8**	**PR-ZB-FF-8-D**	**PR-UZB-FF-8**
Portland Cement, Type I/II	89 *(150)*	89 *(150)*	89 *(150)*	89 *(150)*
Fly Ash, Class F (ASTM C-618)	297 *(500)*	297 *(500)*	297 *(500)*	297 *(500)*
Sand (quartz) (ASTM C-33)	1375 *(2318)*	1097 *(1850)*	1097 *(1850)*	1097 *(1850)*
Gravel (granite) No. 8	0	475 *(800)*	475 *(800)*	475 *(800)*
Water (kg/m³) *(lb/yd³)* *(gal/yd³)*	**311** (525) *(63)*	**262** *(441)* *(53)*	**247** *(416)* *(50)*	**205** *(346)* *(41.5)*
Polycarboxylate polymer HRWR max. (L/m³) *(fl. oz/yd³)*	0.46* *(120)**	0.30* *(79)**	0.30* *(79)**	0.26** *(68)***
VMA (g/m³) *(g/yd³)*	360W *(275)*W	360W *(275)*W	262D *(200)*D	0

* SIKA Inc. Viscocrete 2100 and 6100 and W. R. Grace Inc. Advacast 575 were tested and found to be compatible with the gum VMA. Compatibility was defined as being capable of forming a fluid slurry when premixed with the gum VMAs.
** W.R. Grace Adva 405 was tested.
W = Welan Gum
D = Diutan Gum
A calcium nitrite-based set accelerator can be added if necessary. However, set acceleration was not necessary.

Table 19. SRS Reactor Facility ISD Structural Fill Grout Properties.

Properties	Congested Dry Area Placements	Uncongested Dry Area Placements (Bulk Fill)		Underwater Placements
	PR-ZB-FF	**PR-ZB-FF-8**	**PR-ZB-FF-8-D**	**PR-UZB-FF-8**
Flow (cm) *(inches)* ASTM D-6103	29 *(11.5)*	29 *(11.5)*	33 *(13)*	24 *(9.5)*
Flow (cm) *(inches)* ASTM C-1611	Not measured	63 *(25)*	66 *(26)*	48 *(19)*
Set Time* (hr) modified ASTM C-403 and SRNL UPV method (ultrasonic pulse velocity)	< 18	< 16	< 16	< 10
Bleed Water (mL after 24 hr) modified ASTM C-232	0	0	0	0
Unit Weight (g/cc) *(lb/ft³)* ASTM C-138	2.04 *(127.5)*	2.15 *(134.5)*	2.20 *(137.5)*	2.18 *(135.8)*
Compressive Strength (avg. of 2) ASTM C-39, D-4832 for field sampling				
7 days (MPa) *(psi)*	1.1 *(160)*	1.4 *(200)*	Not measured	2.6 *(380 @ 14d)*
28 days (MPa) *(psi)*	2.7 *(390)*	3.7 *(540)*	5.4 *(780)*	5.7 *(820)*
90 days (MPa) *(psi)*	8.9 *(1300)*	7.2 *(1050)*	11.3 *(1640)*	18.8 *(2725)*
180 days (MPa) *(psi)*	TBD	TBD	TBD	TBD
Permeability (cm/s) ASTM D-5084	1E-07	Not measured	1.3E-08	1.3E-08
Temperature Rise (calculated semi-adiabatic)	< 25°C	< 25°C	< 25°C	< 25°C

* Values without set accelerator.

Two concrete ready-mix plants were set up in P-Area to support P-and R-Reactor Facilities ISD grout filling operation (see Figure 17). Additional fill material was supplied by LaFarge Ready Mix, Jackson, SC and Webb Concrete, Barnwell, SC. Portable concrete pumps and pump trucks were used to convey the grout into the P- and R- Reactor Disassembly Basins and the below-grade portions of the 105-Buildings (see Figure 18).

Figure 17. On-site Concrete Batch Plants Located in P-Area – Producing ISD fill

Figure 18. Delivery and Pumping of ISD Grout in the R-Reactor Disassembly Basin

Cellular Grout for P-Reactor Disassembly Basin: A cellular grout was specified for a portion of the P-Reactor Disassembly Basin[71]. This grout was produced in the following way: 1.40 cubic meters (1.83 cubic yards) of cement paste with a water to cement ratio of 0.50 was delivered to the job site from an off-site ready-mix plant.[c] This material was transferred from the delivery truck to a colloidal mixer where it was mechanically sheared and then transferred to another mixing truck. Approximately 351 kgs (774 pounds) of pre-formed foam were added per 1.40 cubic meters of paste and mixed into the paste. The foam was generated by mixing Varimax HS:320 Liquid Foam Concentrate (Vermillion and Associates, Chattanooga, TN) with water and air. The target density of the cellular grout was 416.5 kg/m^3 (26 lb/ft^3). The production rate for the cellular grout ranged from 12.2 to 33.16 cubic meters (16 to 44 cubic yards) per hour. Approximately, 2158 cubic meters (2824 cubic yards) of cellular grout were pumped into the P-Reactor Disassembly Basin over a 12-day period. The average compressive strength at 28 days ranged from 0.69 to 1.38 MPa (100 to 200 psi) which was above the 50-psi design requirement. The saturated hydraulic conductivity of this material was 5E-05 cm/s

Reactor Vessel ISD: Savannah River Nuclear Solutions (SRNS) committed to DOE and the stakeholders that it would fill the reactor vessels in 105-P and 105-R buildings with grout to the extent practicable as part of the SRS Reactor Facilities ISD Projects[71]. The main tank (referred to as the reactor vessel) in each reactor was constructed of 304 stainless steel and is 4.9 m (16 ft) in diameter and 4.9 m (16 ft.) high. The bottom and top of each tank are capped with Tube Sheets approximately 1.2 m (4 ft) and 1 m (3.5 ft) in height, respectively. The top tube sheet is covered with a plenum which is approximately 0.6 m (2 ft) high. A steel shell around each reactor vessel forms a Thermal Shield around each tank with a Cooling Annulus of about 0.5 m (21 in.) wide. The steel shell is surrounded by a five-foot-thick Biological Shield consisting of reinforced concrete.

General requirements for the reactor vessel grout were the same as for the 105-R and 105-P Buildings except that the flow paths in the 105-P reactor vessel are especially constricted due to numerous internal

[c] The theoretical slurry/paste unit weight was 114.8 lb/ft^3; the material measured on the job site was 117 lb/ft^3.

components (see Table 20). In addition, the need for material compatibility between the grout and reactor materials imposed additional requirements. Both the P-and R-Reactor Vessels contain aluminum components which were left in place as part of the ISD closure. After estimating the amount of aluminum metal abandoned in each reactor, calculations were performed to estimate the potential for exceeding 60 % of the Lower Flammability Limit (LFL) as the result of hydrogen generation from corrosion of the aluminum in a caustic media.[d] Results indicated that the limited amount of aluminum metal in the R-Reactor did not pose an LFL issue if portland cement-based grout was used to fill the vessel[71-73]. However, the safety factor calculated for the portland cement fill for the P-reactor vessel, which contained significantly more aluminum metal, was such that the decision was made to investigate alternative low pH grout systems. The corrosion calculations indicated that a higher safety factor could be achieved for grouts with pHs ≤ 10.5[71,73].

Table 20. SRS ISD Reactor Vessel Grout Fill Requirements.

Property	Requirement	Comments
Slurry Properties (Fresh Properties)		
pH of grout for the P-Reactor Vessel (fresh and cured grout)	≤ 10.5	Aluminum corrosion rate[72,73]
pH of grout for the R-Reactor Vessel (fresh and cured grout)	≤ 13.4	Aluminum corrosion rate[72,73]
Flow Cone (ASTM C-939)	< 50 s	Flowable, self-leveling, P-Reactor grout
Flow/Slump (ASTM C-1611)	> 24 in.	Flowable, self-leveling, R-Reactor grout
Static Working Time (SRNL test)	> 30 min.	Grout needs to remain fluid as the velocity decreases (to zero) as a function of distance from the discharge point in the reactor vessel
Dynamic Working Time (SRNL test)	> 60 min.	Longer is better in case of upset conditions
Set Time (SRNL Ultrasonic Pulse Velocity test)	2 to 24 hr	Long enough to enable placement but short enough to mitigate settling / segregation.
Density (wet unit weight) ASTM C-138	1282 to 2243 kg/m^3 80 to 140 lbs/ft^3	Conventional materials denser than water and no need for shielding properties
Air Content (ASTM C-231)	< 8 vol.%	No air entrainment required, no frothing
Bleed water (modified ASTM C-232)	None	Physically stable slurry is required
Segregation (visual exam)	None	Physically stable slurry is required
Maximum particle size	3 mm maximum	< 0.5 mm may be necessary pending further understanding of reactor vessel construction
Cured Properties		
Compressive Strength ASTM C-39		50 psi required in regulatory documentation
3 days	> 0.34 MPa (50 psi)	50 psi required in regulatory documentation
28 days	> 1.38 MPa (200 psi)	
Adiabatic temperature rise (SRNL method)	< 60°C	As low as possible and still achieve compressive strength.
Maximum placement temperature	35°C	Suitable for mass pours

R-Reactor Vessel ISD Grout: A portland cement-based grout, MIX PR-ZB-FF-8-D, which was used for filling the majority of the void space in the P- and R-Reactor Facility, was selected as the ISD grout for the R-Reactor Vessel. Ingredients and properties of this mix are listed in Table 18 and Table 19, respectively.

[d] Portland cement-based slurries are alkaline and typically have a pH between 12.4 and 13.2. The pore solution in cured portland cement-based grouts is also alkaline and has a pH similar to the wet slurry.

P-Reactor Vessel ISD Grout: Based on estimates of the amount and rate of H_2 generated as the result of corrosion of the aluminum components abandoned in place in the P-Reactor Vessel and the desire to maintain a high safety factor with respect to not exceeding 60% of the LFL, a program was initiated to develop a low pH flowable grout for P-Reactor Vessel ISD. Two alternative cement systems were investigated as potential low-pH binders for formulating a non-portland cement-based grout:

1) Magnesium potassium phosphate cement based on Ceramicrete™ technology.[74] Ceramicrete™ is a hydrated magnesium phosphate waste form patented by Argonne National Laboratory.[75]

$$\mathbf{MgO + KH_2PO_4 + 5\ H_2O \rightarrow Struvite\ MgKPO_4{\cdot}6H_2O}$$

2) Calcium sulfo-aluminate cement.

$$\mathbf{CaAl_2O_6 + 3\ CaSO_4 + H_2O \rightarrow Ettringite\ (CaO){\cdot}3(Al_2O_3){\cdot}3(CaSO_4)\cdot 32\ H_2O + Al(OH)_3}$$

Two calcium sulfo-aluminate cement formulations were developed (see Table 21), and the mix with a water to binder ratio of 1.41 was selected for scale-up testing and full-scale production.

Table 21. Calcium Sulfo-aluminate Grout Mixes Developed for the P-Reactor Vessel ISD.

Ingredient	Water to binder weight 1.41		Water to binder weight 1.24	
	(lb/yd^3)	(kg/yd^3)	(lb/yd^3)	(kg/yd^3)
Ciment Fondu® (Kerneos Aluminate Technologies)	304.3	180.5	304.3	180.5
Plaster of Paris (US Gypsum Company)	152.2	90.3	152.2	90.3
Class F Fly Ash SEMT C-616 (SEFA, Inc.)	514.8	305.4	514.8	305.4
ASTM C-404 Masonry sand or ASTM C-637 Sand for grout for pre-placed aggregate	1732.0	1027.6	1937	1149
Water	644.3	382.2	566.9	366.4
KIM 301® (Integral Water Proofing Admixture) (Kryton, International Inc.)	4.5	2.7	4.5	2.7
SIKA Visco Crete 2100 (W.R. Grace, Inc.)	3.1	1.8	3.4	2.0
Diutan Gum (CP Kelco, Inc.)	0.5	0.3	0.17	0.1
Boric Acid (if needed) (Alfa Aesar)	3.4	2.0	3.4	2.0
Total	3359	1993	3487	2069

Figure 19 and Figure 20 provide photos of the R-Reactor building complex before and after ISD, respectively.

Figure 19. R-Reactor building complex (105-R) *before* decommissioning

Figure 20. R-Reactor building complex (105-R) *after* decommissioning

7.1.2 SRS Heavy Water Component Test Reactor (HWCTR)

The Heavy Water Components Test Reactor (HWCTR) at SRS was also decommissioned using ISD technology[69]. The reactor Containment Building (70-ft diameter, 65-ft above ground with lowest floor level 52-ft below) housed the reactor and coolant systems, the refueling machine, the spent fuel basin, numerous auxiliary systems, and the reactor instrumentation. Figure 21 and Figure 22 contain photos of the HWCTR Containment Building.

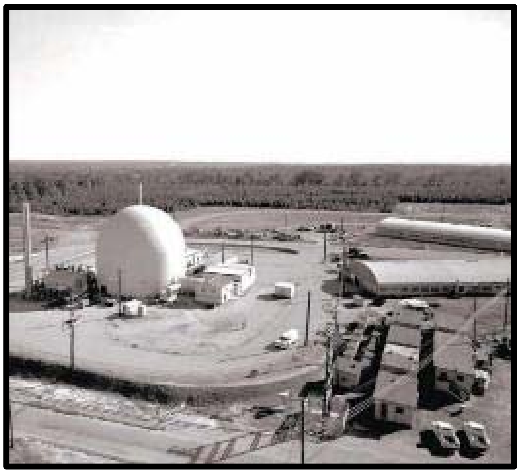

Figure 21. HWCTR during operation

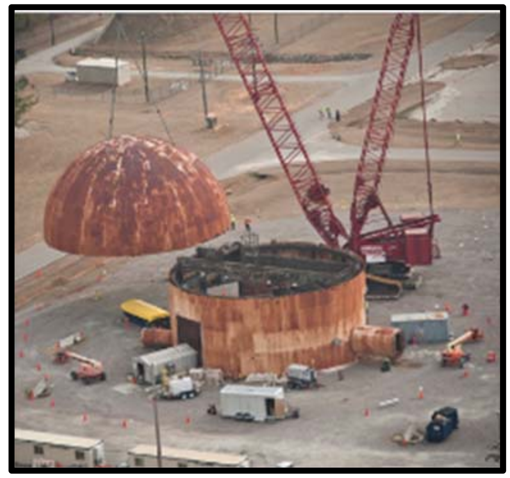

Figure 22. HWCTR during decommissioning

HWCTR was operated from March 1962 to December 1964. It was initially placed in a standby condition, and in 1965, all fuel assemblies and neutron sources were removed from the facility and all systems that contained heavy water were drained, vacuum dried and placed under a nitrogen blanket to minimize corrosion. Further, all fluid piping systems and basins were drained, de-energized, and disconnected from plant services. Demolition and ISD activities of the Containment Building, all auxiliary buildings, and outside equipment was finally completed in June 2011. The removal of the HWCTR reactor vessel from the Containment Building is shown in Figure 23; disposal of the reactor vessel in a slit trench in the SRS SWDF is shown in Figure 24 (vessel encased in grout). Figure 25 shows grouting of the below grade space and Figure 26 shows the end state of the HWCTR site with concrete cap.

Figure 23. HWCTR reactor vessel removal

Figure 24. Reactor vessel disposal

Figure 25. Grouting of below-grade space

Figure 26. HWCTR end state

7.2 Entombment or ENTOMB

The ENTOMB technology of nuclear decommissioning involves encasing portions of a structure/facility, possibly along with some facility components and/or equipment, with a long-lived structural fill (e.g., concrete or grout) at the site itself. The following (Table 22) is a list of smaller, former reactor sites throughout the United States that have been closed via entombment.

Table 22. Facilities Decommissioned by ENTOMB Technology

Reactor Description	Decommissioning
Super Kukla-Ramjet Propulsion Experimental Reactor NNSS – Nevada "Prompt Burst" neutron reactor Operation: 1964-1979 Decommissioned: 2006-2007	• The reactor core and components were disassembled and removed, and the reactor fuel was sent to the Y-12 Plant in Oak Ridge, Tennessee for storage. • Radiologically impacted equipment (primarily activated metals) from the other three buildings were placed into Building 5400 (Reactor Building) for entombment. • Grouting activities at Building 5400 took place March 5-21, 2007 using a flowable grout.[76,77]
Experimental Breeder Reactor II (EBR-II) INEL – Idaho (Operated by Argonne National Laboratory (ANL)) Sodium cooled breeder reactor Operation: 1961-1994 Decommissioned: 2013-2014	• Reactor vessel was not removed and was filled with grout. • More than 3400 cubic yards of concrete grout were pumped into the basement of the EBR-II building to fill in any remaining void spaces and effectively entomb the reactor.[78,79]
Hallam Reactor Hallam, Nebraska Sodium cooled graphite moderated power reactor Operation: 1962-1964 Decommissioned: 1967-1969	• Below grade areas of the reactor building are steel lined and surrounded by several feet of concrete and other structural materials, which provided shielding when the facility was operating (the above-grade portion of the facility was demolished) • Access points to the below-grade portion of the facility and the Intermediate Heat Exchanger Building were sealed off using welded steel closures and reinforced expanding concrete.[80,81]
Piqua Reactor Piqua, Ohio Organically cooled and moderated (terphenyl), thermal reactor built by the U.S. Atomic Energy Commission* (AEC)[69,82]. Operation: 1963-1966 Decommissioned: 1967-1969	Decommissioning activities at the Piqua Reactor facility consisted of accrediting the concrete biological shield surrounding the reactor vessel as the primary entombment structure and capping the reactor vessel and biological shield with a water proof barrier and a concrete slab (void space below concrete slab was left unfilled).[82]
Continued on following page	

Boiling Nuclear Superheater (BONUS) Reactor Punta Higuera, Puerto Rico Boiling water reactor Operation: 1965-1968[69,83] Decommissioned: 1970	• All special nuclear materials (fuel) and certain highly activated components (e.g., control rods and shims) were removed to the U.S. mainland for disposal. • All piping systems were flushed. • The reactor vessel and associated internal components within the biological shield were entombed/encased in concrete and grout, along with many contaminated and activated materials that had been placed in the main circulation pump room beneath the pressure vessel.[83]
SM-1A Reactor Fort Greely, Alaska ("SM" – stationary medium-power plant; "1A" – first field plant of its type) was built by the U.S. Army under the Army Nuclear Power Program[69]. Pressurized water reactor Operation: 1962-1972 Decommissioned: 1972	• Decommissioning consisted of removing all fuel and filling the reactor vessel (below-grade) and reactor room with grout and concrete. • A radioactive waste storage facility was left in place, and concrete was poured over the floor of the building to cover remaining contamination.

* The AEC was a predecessor agency of DOE

7.3 <u>Hanford</u>

The following facilities at Hanford have been grouted (completed 2012): U-Canyon (221-U) Facility, railcars, the Plutonium Finishing (234-5) Facility, the KE Fuel Storage Basin, the Uranium Trioxide Plant, and the Cold Vacuum Drying Facility / KW Reactor Fuel Load-Out[84].

7.3.1 U-Canyon

The U-Canyon (221-U) Facility was constructed with the intent to use it as one of three chemical separation plants for recovery of plutonium from spent nuclear fuel[85], and was subsequently used for uranium recovery operations, and later used for materials and process equipment decontamination and storage[84]. The structure is nominally 250 meters long, 20 meters wide and 23 meters high with approximately 40 percent of the structure below ground. The design approach was to fill all isolated areas below ground up to the "canyon deck" (main floor) with grout – filling of ancillary equipment within the canyon, manholes, vaults, blower pits, process sewer, electrical gallery, ventilation tunnel, etc[85]. The completion of the canyon void space grouting (below ground) prepared the 221-U Facility for the canyon demolition (above ground) phase (see Figure 27).

Figure 27. U-Canyon (221-U) Facility Grouting

7.3.2 Railcars

Railcars, acquired in the 1940-60s and generally supported Hanford Site missions by transporting fuel rods between facilities, were grouted to meet waste acceptance criteria for burial[84]. The string of railcars included: 11 cask cars (once used to transport spent nuclear fuel), 2 tanker cars (once used to transport radiologically contaminated liquid wastes), 2 diesel locomotives, and 1 flatcar (once used to transport miscellaneous equipment). These railcars were staged at the Hanford North Area rail spurs in preparation for grout stabilization and isolation as a precursor to transport for final disposition. Access to casks was through mechanical doors located on the top of each open top tank. Access to tank car internals was through piping in tank cupolas (see Figure 28).

Figure 28. Railcar Grout Placement

7.3.3 Plutonium Finishing Facility

Located in the Hanford West Area, the Plutonium Finishing (234-5) Facility was used for preparation of plutonium metal for use in DOE weapons programs[84]. The main facility contains numerous pipe trenches directly below the main floor level. The under-floor slab tunnel roof was on the order of 0.09 meters thick and was assessed as not capable of supporting equipment to be moved over the tunnel. Hence, tunnel grouting was required to provide loading capacity. Grout was injected through floor slabs via drilled core holes directly into the tunnels. Each tunnel to be grouted was isolated from other subgrade tunnels and passageways, etc., with lateral bulkheads.

7.3.4 KE Fuel Storage Basin

The KE Fuel Storage Basin located directly adjacent to the Hanford KE weapons materials production reactor consisted of three main below grade reinforced concrete pools and ancillary fuels examination and fuel handling structures (i.e., elevator, view and weasel pits, and load-out pits)[84]. Filling these with grout provided a stable platform for demolition of the overhead fuel basin structure, containment of residual contamination within the subgrade basin structure, and significant reduction of dose rates. Prior to grouting, the fuel basin and ancillary structures, were dewatered. The volume of flowable fill grout placed was approximately 6,300 cubic meters (see Figure 29).

Figure 29. KE Fuel Storage Basin Grouting

7.3.5 Uranium Trioxide Plant

The original design of the uranium trioxide plant was plutonium concentration and was later used for calcining of uranium nitrite hexahydrate for gaseous diffusion plant feed[84]. The plant was physically connected to U-Plant via subgrade piping through a lateral tunnel. A portion of the tunnel and corresponding access pit was required to be backfilled with grout as a part of plant decommissioning. The tunnel and access structure were isolated from the adjoining U-Plant by a bulkhead. The tunnel structure volume was approximately 87 cubic meters. The tunnel and associated structure also contained significant free-standing contaminated water. Dry bulk powder grout was placed first to absorb the contaminated water and cure into a structural monolith. Flowable grout was then placed into the access pit and tunnel to completely fill all accessible voids and provide a structural monolith.

7.3.6 Cold Vacuum Drying Facility / KW Reactor Fuel Load-Out

A general area was established for injection of grout into drums and waste disposal containers proximal to the Hanford Cold Vacuum Drying Facility and near the 100 KW Reactor Fuel Basin[84]. Drums and containers were injected with slurry grout on an asphalt pad and within the fuel basin rail load-out area. Drums were fitted with high efficiency particulate air filtration located at an elevation of approximately 4.9 meters above the base of each drum, for displaced air. Disposal containers were fitted with high efficiency particulate filters affixed to the top of each container such that container tops could be removed after injection to inspect void fill completeness.

8.0 Borehole Construction and Sealing

8.1 Hanford PUREX Tunnel Stabilization

Two waste storage tunnels were constructed adjacent to Hanford's Plutonium Uranium Extraction (PUREX) Facility. Tunnel 1 construction was completed in 1956 as part of the PUREX Plant construction project[86,87]. The tunnel was filled to capacity in 1965 with eight railcars (each of 40 to 42 feet in length) containing radioactive process equipment. In the anticipation of Tunnel 1 being filled, Tunnel 2 was added (construction complete in 1964)[88] (see Figure 30). Tunnel 2 also holds railcars (28 total) containing radioactive process equipment.

Figure 30. Hanford PUREX Tunnels 1 and 2

The roof of Tunnel 1 was constructed with wood timbers, a portion of which collapsed into the tunnel in May 2017[86]. Uncompacted soil fill was placed through the roof opening to stabilize the tunnel support walls and prevent further atmospheric exposure to the tunnel interior. CH2M HILL Plateau Remediation Company (CH2M) filled the remainder of the tunnel with an engineered grout (grouting occurred Oct. 3 to Nov. 11, 2017) (Tunnel 1 formulation listed in
Table 23). Approximately 4,430 cubic yards of grout were placed in the tunnel, with approximately one foot of space left between the topmost layer and the ceiling of the tunnel.

Table 23. Hanford PUREX Tunnel 1 Stabilization Grout Formulation[67]

Ingredient	Amount
Portland Cement, Type III (lb/yd^3)	376
Fly Ash, Class F (lb/yd^3)	799
Quartz Sand (lb/yd^3)	2109
Water (lb/yd^3) (*gal/yd^3*)	470 *56.4*
MasterGlenium 3030 (fl oz/yd^3)	23.00
MasterMatrix VMA 358 (fl oz/yd^3)	60.00
MasterSet Delvo (fl oz/yd^3)	60.00
MasterSure Z60 (fl oz/yd^3)	23.00
Air	1.5%

The grout formulation for the stabilization of Tunnel 2 was slightly different from that of Tunnel 1. Type II portland cement was used in Tunnel 2 versus Type III used in Tunnel 1 (Type III is more finely ground than Type II), and the Tunnel 2 formulation did not require the use of MasterMatrix VMA 358 or MasterSure Z60 (Tunnel 2 formulation listed in Table 24). The stabilization/grouting of PUREX Tunnel 2 began in October 2018 with completion forecasted for March 2019. An estimated 39,800 cubic yards of grout were to be placed in Tunnel 2.

Table 24. Hanford PUREX Tunnel 2 Stabilization Grout Formulation

Ingredient	Amount
Portland Cement, Type II (lb/yd^3)	300
Fly Ash, Class F (lb/yd^3)	500
Quartz Sand (lb/yd^3)	2685
Water (lb/yd^3) (*gal/yd^3*)	433 *52.0*
MasterGlenium 3030 (fl oz/yd^3)	40.00
MasterSet Delvo (fl oz/yd^3)	32.00
Air	2.0%

8.2 NNSS Borehole, Shaft, and Tunnel Sealing

Borehole disposal of nuclear waste is designed for waste with the following characteristics: 1) contains radionuclides too long-lived for decay storage (e.g., half-life greater than a few years), 2) radionuclides are too long-lived and/or too radioactive to be placed in a simple near-surface facility, and 3) small volume waste for which no other disposal facility is available.[89] Optimum design for borehole disposal is still being explored (facility consisting of a single borehole (deep, larger diameter shaft) or a series of boreholes (smaller, less volume)). It has been suggested that grout could be used in the waste encapsulation matrix and/or the borehole backfill material (sealing boreholes).

Sealing (grouting) of boreholes could be considered for boreholes at NNSS. A performance assessment was completed on classified TRU material stored in Greater Confinement Disposal boreholes in the Area 5 Radioactive Waste Management Site on the NNSS.[90] The materials are stored at 21 to 37 m depth (70 to 120 ft) in large diameter boreholes, and the radiological releases from the intermediate depth disposal configuration were assessed.

8.3 Waste Isolation Pilot Plant

The WIPP, located near Carlsbad, New Mexico, is a deep, geologic repository designed for the management, storage, and disposal of TRU mixed waste.[91] An assessment of the potential impacts of continuing the phased development of the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico as a geologic repository for the safe disposal of TRU waste was performed. Treatment by a shred and grout process was an Action Alternative examined. In a shred and grout treatment process, TRU waste would be shredded to achieve a relatively uniform size and then mixed with grout. An optimum shred and grout process for TRU waste treatment has yet to be selected by DOE (other treatment alternatives are still being evaluated as well).

A shaft seal system[e] is also currently being designed for WIPP and grout has been proposed as a material for the sealing process.[92] Four vertical shafts (the Waste Shaft, the Salt Handling Shaft, the Exhaust Shaft, and the Air Intake Shaft) connect the surface facility to the underground portion of WIPP. The WIPP underground structures are located in a mined salt bed 2,150 feet below the surface. An ultrafine, cementitious grout with 90% of the particles smaller than 5 microns and an average particle size of 2 microns was developed for the shaft seal design (see Table 25).[92,93] The extremely small particle size would enable the grout to penetrate fractures present in the shaft(s) with apertures as small as 6 microns.

Table 25. Ultrafine Grout Mix for the Shaft Seal System at WIPP

Ingredient	Amount (wt%)
Portland Cement, Type V	45
Pumice	55
Superplasticizer	1.5
Grout ingredients to water ratio of 0.6:1	

This developed grout has the characteristics of 1) no water separation upon hydration, 2) low permeability paste, 3) fine particle size, 4) low hydrational heat, 5) no measurable agglomeration subsequent to mixing, 6) two hours of injectability subsequent to mixing, 7) short set time, 8) high compressive strength, and 9) competitive cost.

8.4 Other

The Fernald site located near Cincinnati, Ohio, is a former DOE uranium processing facility. Silos 1 and 2 at the site stored residues generated from the processing of high assay uranium ores. In 2005, approximately 4,300 pounds of residues inside Silos 1 and 2 were blended with grout (see Table 26) to create a 15,000-pound batch that was gravity-fed into 7,000 carbon-steel canisters beneath the mixers.[94] Once filled, the containers were shipped two at a time to a storage facility in Texas. The waste removal process left a hard, residual heel containing significant amounts of lead and radium as well as depleted uranium. The heel material was mixed in-place with grout, hardened, and removed/disposed along with the contaminated concrete of the silos.

Table 26. Grout Formulation for Fernald Silos 1 & 2

Ingredient	Amount (weight parts)
Portland Cement, Type I	100
Fly Ash, Class F	150
Spersene CF	0.8
Pre-hydrated bentonite slurry	74
Water	120

[e] The WIPP Permit Renewal Application stated, “the shaft seal system will not be constructed for decades.”

9.0 Environmental Remediation

9.1 Oak Ridge Reservation (ORR)

9.1.1 Silo and Trench Grouting

At ORNL on the Oak Ridge Reservation (ORR), some solid low-level radioactive waste had been disposed of in below-grade cylindrical concrete silos[95]. Sixty-six silos were constructed (~8 feet in diameter and 20 feet deep) at Solid Waste Storage Area (SWSA) 6, but only 57 silos were made available for grouting. In the end, grout was pumped into 54 silos (grout formulation shown in Table 27).

Table 27. Grout Formulation for SWSA 6 Silos at ORNL

Ingredient	Amount
Portland Cement, Type I (lb/yd^3)	400
Fly Ash, Class F (lb/yd^3)	200
Silica Fume (lb/yd^3)	50
Sand (lb/yd^3)	2493
Water (lb/yd^3)	420

In the northeastern corner of SWSA 6, two trenches were selected for in-situ grouting with a particulate grout (Nos. 151 and 170, located in the Test Area for Remedial Actions (TARA) site)[96]. Each of the interconnected trenches are approximately 15 feet deep – trench 151 measures 42'×14' (~583 ft^2) and trench 170 measures 44'×14' (612 ft^2). In 1990, a total of 79 yd^3 of grout were injected into the two trenches (48 and 31 yd^3 in trenches 151 and 170, respectively) (see Table 28)[f]. The following summer (1991), the same two trenches (151 and 170) previously grouted with the portland Type I cement-based grout, were grouted again with another particulate-based grout made from a microfine cement and Wyoming bentonite to fill the unfilled void spaces and reduce hydraulic conductivity within these trenches[g].

Table 28. Grout Formulation for Trenches 151 and 170 at the TARA site of SWSA 6

Ingredient	Amount (wt%)
Portland Cement, Type I	39
Fly Ash, Class F	55.5
Bentonite	5.5
Water – dry ingredients mixed at 12.5 lb/gal of water	

In 1996, grouting activities occurred at Waste Area Grouping (WAG) 4 within SWSA 4 at ORNL to reduce ^{90}Sr off-site transport[97]. The sections of the waste disposal trenches targeted for grouting were 100'-175' long, 6'-12' wide, and 12'-20' deep. From July-October 1996, approximately 137,600 gallons of grout were injected in the WAG 4 trenches (multiple formulae of regular portland cement-based grouts, ultrafine cement-based grouts, and acrylamide solution grouts).

9.1.2 Melton Valley

Remedial actions at Melton Valley of the ORR were completed in September 2006[98]. Some of those remediation activities included the plugging (with grout) and abandonment of 112 wells associated with the hydrofracture process of deep waste injection at ORNL, and the grouting of the High Flux Isotope Reactor (HFIR) Tank and Tanks T-1 and T-2 at the HFIR reactor complex. Seepage Trenches 5 and 7 (300 and 200 feet long, respectively) were grouted in place with a portland cement-based grout injected under low

[f] It was found that 40 yd^3 were injected into Trench 150 (measures 56'×9.2'×11.8') in 1987 with a grout of the same formulation.
[g] This same clay-microfine-cement grout was also injected into trench 148.

pressure. Finally, more than 27,000 linear feet of pipeline and about 5,000 ft^2 of void space associated with valve boxes, pump pits, manholes, and vaults were also grouted.

9.1.3 K-25 Plant Pond Sludge

The site of the K-25 Plant (otherwise known as the Oak Ridge Gaseous Diffusion Plant) contained two ponds known as the K-1407-B and K-1407-C Ponds which were used as settling basins for precipitates from waste water treatment from plant operations (e.g., electroplating, metals cleaning, and decontamination)[99]. RCRA stipulations ordered such surface impoundments to be in compliance or closed by November 8, 1988. Removal of Pond C sludges was complete 10/31/88 and all Pond B sludges were removed by 8/3/89.

Treatment of the removed sludge(s) entailed fixing the sludges in a grout matrix – the grout mix recipe consisted of 50% waste (nominal ratio of 1:3, solids to liquid), 25% cement, and 25% fly ash, with an air-entrainment (MB-AE-100) added[99]. To meet pond closure plan deadlines though, raw sludges from both ponds were removed and drummed without treatment at times during removal, with the intent of solidifying all unprocessed drummed sludges at a later date. All drums (46,000 solidified sludge drums and 32,000 unprocessed sludge drums) were placed in the K-1417 Drum Storage Yard – 89-gallon and 96-gallon drums were primarily used, but approximately 3,000 55-gallon drums were also used).

Drums containing both solidified and unprocessed sludges began to exhibit internal corrosion (~6% of the drums leaked). Drum failure was attributed to the following main contributors: 1) Mix design development focused on the 50 psi RCRA compressive strength requirement and did not adequately address phase separation or the formation of free liquids, 2) limitations of process equipment rendered it unable to effectively solidify low-solids content sludge, 3) there was inadequate final product inspection and no waste acceptance criteria, 4) possible degrading effects of chemicals in the sludge on the cement were apparently not addressed, and 5) incompatibility of the mild steel drums with the waste form was not considered.

9.2 Rocky Flats

9.2.1 Underground Piping

The Rocky Flats Plant (Colorado) operated from 1951 to 1992 under the control of the U.S. Atomic Energy Commission, later the U.S. DOE[100]. During decommissioning, more than 800 structures were demolished, and debris removed. Site remediation efforts included filling/grouting most of the underground process waste lines (all below 6 feet and left in-place) and plugging some corrugated metal pipe openings with grout[101]. Note: Grout formulations used at Rocky Flats or amounts were not found for this report. Jurisdiction and control of a majority of the lands once occupied by the Rocky Flats nuclear weapons production facility and complex was transferred to the U.S. Department of Interior, U.S. Fish & Wildlife Service in 2007 – the land is now known as the Rocky Flats National Wildlife Refuge[100,101].

9.2.2 Solar Evaporation Pond Sludge

Five solar evaporation ponds were constructed at Rocky Flats to store and treat (by evaporation) low-level radioactive process wastes from industrial operations at the plant[102]. The ponds were designated 207A, 207B (which was actually three ponds, designated North (N), South (S), and Center (C)), and 207C, and were utilized from the mid-1950's until the 1980's. Clean out of the ponds' sludge began in the 207A pond by mixing sludge with portland I cement to form "pondcrete" (basic formula – 20 wt% solids mixed at a water/cement ratio of 1.5) and packaged in boxes (cardboard "Triwall" boxes). The boxes were cured and were labeled and transported to two outdoor asphalt pads for storage until shipment to NTS for disposal – more than 16,000 boxes of pondcrete were produced from 1986 until May 1988 and subsequently stored outside on the two storage pads. In May 1988, operations personnel noticed deformation of the pondcrete boxes – the pondcrete had deteriorated, crumbled, cracked, and at least one box had spilled open.

Degradation was due to a combination of issues – improper curing, excess water, and/or unsuitable storage conditions. The boxes were sorted and ultimately all but 8,800 boxes of pondcrete were approved for shipment to NTS in late 1989. The rejected pondcrete Triwall boxes were reprocessed or repackaged.

Approximately 750,000 gallons of sludge was removed from five solar evaporation ponds around the Rocky Flats complex during the site remediation[103]. 9,225 cubic meters of pondcrete was shipped to Envirocare in Utah for treatment and disposal in 1999. "Saltcrete" was also removed from Rocky Flats and sent to Utah. Saltcrete was formed from the mixing of concrete with the brine or salt left over from the evaporation processes during Rocky Flats operations.[103]

9.3 Fernald

A jet grouting technique was utilized at the Fernald site for environmental remediation efforts.[104] Horizontal barriers were constructed via jet grouting underneath contaminated soil to prevent/stop the vertical migration of contaminants through the soil. When the jet grouting drill pipe having orifices (jets) was thrust into the soil and beneath a waste pit/trench, a cement slurry was pumped through. The slurry exited the jets with high kinetic energy, shattered the soil and mixed it with grout. Then, moving over and replicating the process would build "blocks" that joined and served as a cut-off wall or slurry barrier.

10.0 DOE-EM Gaps and Opportunities

The use of cementitious materials for civil engineering is not directly applicable to waste treatment and conditioning. Therefore, a program focused to DOE-EM needs and issues is crucial. The DOE-EM Concrete, Binders, and Grout (CBG) Program was initiated to address this need and is a follow-on to the CBP Project. Whereas the CBP focused on prediction of long-term performance of cementitious materials in response to time and changing conditions for Performance Assessment modeling (durability), the proposed CBG scope addresses DOE Complex technology gaps. A list of areas which can benefit from technology development and technical understanding are provided below:

10.1 Aging Concrete Infrastructure – Engineering Properties to Support Condition Assessment and Improvements

DOE is operating many aging facilities constructed of concrete. These facilities are in many cases over 50 years old and are beyond their planned service life. Portions of some have experienced limited degradation. Condition assessment of these facilities includes concrete characterization, i.e., degradation processes and rates, both of which are needed to assess operational risks and develop mitigation strategies and engineering solutions. Examples of specific DOE facility needs for structural concrete include:

- **Savannah River Site (SRS) H-Canyon Exhaust Tunnel**: It is recommended that the effects of progressive alteration (changes in matrix mineralogy) on compressive strength be measured of concrete cylinders to support data needs and provide parameters for structural models to support fragility analysis. SRNL can prepare and conduct tests on concrete cylinders that have been altered as a function of depth from the surface exposed by concurrent exposure to both NOx vapor and CO_2. SRNL can develop protocols to provide compressive strength data for concrete in which the matrix has been progressively altered as a function of distance from the exposed surface.

- **SRS L-Basin:** Continued long-term storage of fuel in the SRS L-Basin is expected. The basin is not lined. A monitoring program and possibly a core sampling program are needed to monitor this structure.

- **Hanford Waste Encapsulation and Storage Facility (WESF):** Forensic characterization of concrete core sections from the WESF facility should be examined for gamma radiation damage and evidence of other degradation/alteration effects as the result of exposure to doses of high gamma radiation doses. Gamma effects on concrete are the result of either gamma exposure and other conditions, such as leaching, that degrade the concrete or both gamma and neutron exposure. This data would help reduce conservativism in safety basis calculations for both structural concrete (for DOE and the nuclear sector) and cementitious waste forms.

- **DOE Complex Condition Assessment Database for Concrete and Cementitious Materials Structures and Used Fuel Dry Storage Casks:** A DOE Complex-wide database should be assembled for structural concrete properties and past, current, and upcoming condition assessments. This database will include a compilation of mix designs, concrete properties, and approaches to parameterizing condition assessments and fragility analyses for concrete structures in the DOE Complex. The data base can provide a tracking tool to document changes in conditions as a function of time, use, and conditions and proposed repair or rehabilitation.

- **Effects of High Doses of Gamma and Alpha Radiation on Hydrated Waste Forms and Cementitious Materials in Corrosive Environments:** Several DOE waste streams include: (1) Cs and Sr capsules currently stored at the Hanford WESF, (2) waste PuO_2-containing salts and other impurities, (3) sealed sources, (4) used reactor fuel dry storage containers, and (5) other storage containers for alpha and gamma contaminated materials. Better fundamental understanding of radiolytic gas generation in cementitious materials (containing chemically bound, sorbed, and free water) and H_2 scavenging by nitrates and other chemicals is needed to evaluate conditioning, storage, transportation, and disposal options which have the potential to reduce cost and schedule for disposal.

10.2 Liquid Waste Solidification/Stabilization (S/S) and Debris Encapsulation

Currently the SRS Saltstone facility and Hanford Supplemental Law Cast Stone and Waste Treatment Plant Secondary Cast Stone are the operating and planned large cement waste form projects, respectively. These are large, long-term projects which will span decades into the future.

10.2.1 Technical Partnership

- **Technical Expertise:** National Laboratory expertise is needed to support the DOE Complex EM legacy waste cleanup and arising technical issues in operating and planned waste treatment processes. More specifically, maintaining and developing expertise in cementitious materials is needed to support alternatives analyses and the successful outcome of “cradle to grave” waste processing flowsheets. SRNL currently has the most relevant set of competencies in this area, but continued funding is necessary to maintain this proficiency.

  Both cost and schedule are expected to be reduced by maintaining and expanding expertise that can: (1) build on successful applied nuclear industry processing and material technology and lessons learned, (2) provide innovation based on fundamental science and engineering, and (3) minimize duplication of efforts and funding.

- **International Collaboration:** Maintenance and growth of this expert community within this DOE National Laboratory community is needed for successful interaction and leveraging with the international nuclear waste form community for developing and implementing waste form designs, processing equipment, and long-term interactions and material durability evaluations. Technical exchanges through workshops or other focused interactions are expected to result in meaningful input based on nuclear industry experience with respect to waste form designs and processing equipment and operation scenarios.

- **Testing Facilities:** A base level of expertise to evaluate the condition of existing structures and to assess service life extension of aging nuclear structures is needed to support current and future missions. Capabilities for sampling, analyzing, and testing concrete cores is needed and is a pre-requisite for characterization and measurement of parameters needed for structural analyses. Engineers involved in evaluating whether concrete structures meet nuclear structure codes and standards are available in the DOE Complex and private sector. However, the ability to sample, characterize, and communicate the first-hand observations concerning the condition of radioactively contaminated concrete and structures is a National Laboratory and DOE engineering function. To this end, an investment in contaminated concrete characterization methods is needed to assure capabilities are maintained and improved and that experience and knowledge are transferred. Laboratory facilities and methods for characterizing radioactive cementitious materials with respect to mechanical properties (structural assessments and modeling) and hydraulic properties (contaminant fate and transport modeling) need to be upgraded. An archive facility is also recommended for selected materials. These needs are not currently addressed at any site. Expertise and experience with the latest non-destructive testing equipment are also needed to improve and clarify specific needs to vendors and universities and thereby achieve successful outcomes.

- **Test Beds for Processing/mixing High-volume Containerized Waste Forms:** A test bed program project for 2,000 gallons of Hanford tank waste cementation is currently on-going. National Laboratory oversight of this task is essential for maximizing the information generated and for data collection and documentation in support of a successful outcome.

10.2.2 Process/Formulation Changes

The long-term availability of cementitious reagents is becoming of concern, specifically for SRS and Hanford LAW waste form viability. The risk associated with lack of Class F fly ash and blast furnace slag is a risk that has been identified at both SRS and Hanford. Examples of needs include:

- **Alternate Raw Materials:** Identify supplies of suitable raw materials in an ever-changing global market place where the need for fly ash and slag and even portland cement alternatives are expected to arise. This is a global issue and is currently impacting the British nuclear waste treatment procurement for portland cement. Raw material options from the construction industry or commercial ceramics industries need to be identified and possibly modified to meet and enhance performance of cementitious waste forms. Examples of alternatives for blast furnace slag include: (1) Reagents to chemically reduce redox sensitive contaminants such as Tc(VII), Cr(VI), and Hg(II) and organic mercury, (2) manufactured hydraulic glass with chemical reduction capacity, and (3) functionalized additives that chemically reduce redox sensitive contaminants, other chemically reducing byproduct or supplementary cementitious materials. Substitutions for fly ash which warrant evaluation include: Inert and functional fillers (including reclaimed fly ash from settling ponds), meta kaolin, plant ash, other industrial ashes.

- **Qualification Methods for Cementitious Reagents:** Essential attributes of cementitious reagents are needed to reliably qualify cementitious materials as ingredients in waste forms, grouts, and concretes used to stabilize or contain radionuclides and hazardous chemicals. Specifications and test methods for typical cementitious materials have been developed for the construction industry.

In many cases, these specifications are appropriate for radioactive applications. However, additional specifications for use in radioactive waste and D&D and closure grouts relating to chemical stabilization or rheology may be needed on a case by case basis. Rapid test methods for qualifying cementitious reagents are needed especially for radionuclide and chemical stabilization and capacity because these attributes are not covered in current construction specifications. Rapid, automated, in-line chemical characterization methods for cementitious materials will support operating facility material receipt and blending operations and provide assurance of chemical properties not covered in the current ASTM specifications.

- **Viscosity Modifying Admixtures and High Range Water Reducers for Highly Caustic and/or High Salt Waste Forms:** The current suite of concrete admixtures designed for construction applications is not effective in salt waste forms. New admixtures for eliminating bleed water and increasing flowability of saltstone are needed to reduce processing complexity and cost. Development of new viscosity modifying admixtures and high range water reducers that are effective in waste forms made with high sodium, high dissolved solids, and high pH salt solutions will enable more liquid waste to be disposed in the same volume of final waste form. Even a 5% increase in liquid/water loading of a zero-bleed waste form is expected to simplify operations and reduce overall cost.

- **Processing:** A review of current options for both continuous and batch waste form mixers that can meet the production needs (moderate to large volumes) will support processing options and identify engineering and technology gaps for producing large volume containerized radioactive waste forms. Currently several domestic and international options for mixing are commercially available. However, they need to be evaluated by a consistent set of criteria via a test bed process to determine whether any are suitable (e.g., Hanford LSW and/or SSW).

- **Evaporation or Pre-Processing:** Producing a salt waste form from concentrated/evaporated LAW solution and mixing it before it cools with cementitious reagents also has the potential to provide significant cost and schedule savings to certain options for the Hanford low activity waste project.

Design and Testing Non-Portland Cement Matrices for Special Applications: Alternative cementitious binders are documented, and some are commercially available. Matching alternative binders to special waste types and needs has the potential to reduce cost and schedule by providing a DOE experience coupled with international experience for technology screening and application. Alternative matrices include: geopolymers, low pH cements that are compatible with acid waste streams, reactive metals, and geologic/environmental media, and phosphate matrices which have excellent bonding to metal and stabilization of amphoteric metals. Experimental studies are needed to refine fresh properties and cured properties so selected alternative matrices can be extended to flowable grouts and concretes for tank and facility closures.

Additive Manufacturing Evaluation – Cement Waste Form Processing: New grout waste forms are being considered for SLAW and Secondary Low Activity Waste at Hanford. In the past, SRS has considered mixing saltstone at the disposal unit rather than in a central facility and pumping slurry to disposal units.

Evaluating the feasibility and opportunities for applying additive manufacturing concepts and processes including new batch mixing equipment and continuous mixing using 3-D printing to waste form processing has the potential to provide new options for SRS saltstone, Hanford Cast Stone, and cementation processes at other sites. Given the recent advancements in 3-D printing of cementitious materials, investigating this technology for manufacturing small (200 L) and large (structures) concrete waste disposal containers and containment structures offers potential with respect to reliability, safety, operational efficiency, and cost.

11.0 Summary

This report has been prepared to document the use of cementitious materials for liquid and solid waste, processing waste conditioning, debris microencapsulation, environmental restoration, and nuclear facility closures. This information and lessons learned will provide a basis for future projects in these areas. In addition, experience with cementitious materials has been extended to condition assessments of DOE-processing structures. The examples documented here are not intended to be an all-inclusive list but demonstrate the broad range of applications in the DOE Complex. The information is expected to be used in decision making for new cementitious processes to support the DOE closure mission by DOE and contractor engineers and project managers to design of new materials and processing facilities.

This literature review covers work performed in the DOE Complex up to and including work performed under the CBP multi-disciplinary, multi-institutional, 8-year project funded by DOE-EM. The focus of this project was to provide fundamental understanding and prediction capabilities for chemical degradation of portland cement-based concrete, grout, and waste forms. This extensive body of work of research and software development is documented in an annotated bibliography in Attachment A. Characterization, methodology, and algorithms generated by this project have been used to support long-term durability predictions in recent SRS Performance Assessments.

Cementitious materials have worldwide acceptance for waste conditioning and containment, environmental restoration, and construction of nuclear facilities. DOE-EM funded research and development is aligned with and complimentary to international programs. Continued support and collaboration in this area is expected to reduce cost and schedule of DOE-EM projects and contribute to and take advantage of international technology developments.

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Appendix A. Annotated Summary of Documents Regarding the Cementitious Barriers Partnership (2008-2016)

Doc. #: **CBP-QAP-2008-001**
Title: ***Quality Assurance Program: Cementitious Barriers Partnership***
Authors: **J.P. Vaughan and Christine Langton – SRNL**

The goals of the Cementitious Barrier Partnership (CBP) Project Quality Assurance Program (QAP) are to ensure that all work performed under the CBP Cooperative Research and Development Agreement (CRADA) 1) will achieve the intended R&D objectives and 2) can be understood, and, if necessary, reproduced successfully by others. Application of this document should be focused on these goals. This CBP QAP represents an integration of common elements of partners' existing quality assurance plans as well as agreed-upon elements new to this purpose. This document is a general statement of good R&D practices that will be used on all CBP tasks. SRNS endorses the content and intent of this document as a means of ensuring a base level of quality for the work performed under CBP. The designated Principal Investigator (PI) has first-line responsibility. The PI is responsible to ensure that this document is applied and followed during the performance of each applicable task. Additional requirements may be identified and implemented. Any conflicts between the basic quality requirements in this document and specific QA requirements imposed on the various implementing tasks should be identified by the PI and referred to SRNS for resolution. Although the PI has primary responsibility, it is the responsibility of all persons, technical and non-technical, associated with the task to ensure the quality of the work they perform for the task. The PI shall ensure that all personnel actively supporting the conduct of a CBP task should have an understanding of the requirements that are stated in this document and how the quality of their work affects the products developed under each task. This document will help to ensure that appropriate steps have been taken to protect the accuracy and reproducibility of technical results.

Doc. #: **CBP-RP-2010-012**
Title: ***Cementitious Barriers Partnership Experimental and Characterization Plan***
Author: **Christine Langton – SRNL**

The CBP Experimental and Characterization Plan will focus on the following specific needs:
1. **Enhance Partner Models so they can better support PAs -** Provide data to reduce uncertainty and improve conceptual models, including improved representation of phenomena (e.g., sulfate attack, oxidation, carbonation and cracking) and boundary conditions for surface and near surface environments.
2. **Characterize CBP Reference Materials -** Develop a CBP database that supports the partner models for representative materials using existing and emerging characterization methodologies. This will provide the data necessary to demonstrate improved models and reduced uncertainty on relevant cases.
3. **Characterize Cementitious Barrier Materials and Facilities -** Extend the CBP database to include materials from existing facilities. This will facilitate use of CBP developed models to evaluate performance of cementitious materials in existing and proposed facilities.
4. **Provide Data to Develop More Robust (Inclusive) Reactive Transport Codes -** Work jointly with code developers to include additional phenomena and improve coupling amongst phenomena (e.g., fractured porous media, two-phase flow, and geochemistry). This data is needed to verify interactions amongst individual phenomena in contexts analogous to anticipated field conditions.
5. **Test Beds -** Large-scale laboratory and/or field experiments to better understand and more accurately represent complex, larger-scale effects, such as, cracks on transport of water, gas, and contaminants.

Doc. #: **CBP-RP-2012-002, R0**
Title: ***Cementitious Barriers Partnership 2012 Mid-Year Status Report***
Authors: **Flach, Langton, and Burns – SRNL; Garboczi – NIST; Samson – SIMCO; Meeussen and van der Sloot – Netherlands; Kosson and Brown – Vanderbilt University/CRESP**

In FY2012 the Cementitious Barriers Partnership (CBP) completed development of sulfate ingress and attack models and developed an initial carbonation model for assessing chemical and physical damage to cementitious materials. A beta-version of the combined software bundle, referred to as the CBP Software Toolbox, was achieved in March 2012. Software demonstrations and PA end-user workshops were held April 9-10 in Gaithersburg MD for NIST, NRC, and DOE-EM, and April 18-19 at Savannah River for SRNL, SRR, DOE-SR, and DOE-EM/ASCEM. A third workshop is anticipated for Hanford in May 2012. On the experimental front, through mid-FY2012 the CBP has characterized the physical and chemical properties of several cementitious (concrete and grout) materials used as barriers and for waste stabilization in the DOE-EM complex. This information is organized in a materials database in LeachXS™ format and used to define the modeling scenarios implemented in the CBP Software Toolbox. In early FY2012, the CBP started several longer-term exposure experiments intended for model validation. Specific tests include sulfate attack on hardened cement paste samples, longer-term saltstone-concrete interfacial contact, and embedded steel (rebar) corrosion tests in a CO2 (carbonation) environment.
Through the remainder of FY2012 the CBP plans to a) refine the CBP Software Toolbox based on beta-user feedback and release version 1.0 to the DOE-EM Performance Assessment community, b) continue development of carbonation and other models, and c) continue material characterization and model validation experiments. A lack of funding for NIST and SIMCO for the remainder of FY2012 will preclude THAMES model development, and delay or disrupt model validation experiments at SIMCO.

Doc. #: **CBP-TR-2009-001**
Title: ***Overview of the U.S. Department of Energy and Nuclear Regulatory Commission Performance Assessment Approaches: Cementitious Barriers Partnership***
Authors: **Langton, Seitz, and Marra – SRNL; Suttora – U.S. DOE (EM-41)**

Engineered barriers including cementitious barriers are used at sites disposing or contaminated with low-level radioactive waste to enhance performance of the natural environment with respect to controlling the potential spread of contaminants. Drivers for using cementitious barriers include: high radionuclide inventory, radionuclide characteristics (e.g., long half-live, high mobility due to chemical form / speciation, waste matrix properties, shallow water table, and humid climate that provides water for leaching the waste). This document comprises the first in a series of reports being prepared for the Cementitious Barriers Partnership. The document is divided into two parts which provide a summary of: 1) existing experience in the assessment of performance of cementitious materials used for radioactive waste management and disposal and 2) sensitivity and uncertainty analysis approaches that have been applied for assessments. Each chapter is organized into five parts: Introduction, Regulatory Considerations, Specific Examples, Summary of Modeling Approaches, and Conclusions and Needs. The objective of the report is to provide perspective on the state of the practice for conducting assessments for facilities involving cementitious barriers and to identify opportunities for improvements to the existing approaches. Examples are provided in two contexts: (1) performance assessments conducted for waste disposal facilities and (2) performance assessment-like analyses (e.g., risk assessments) conducted under other regulatory regimes.

Doc. #: **CBP-TR-2009-002**
Title: ***Review of Mechanistic Understanding and Modeling and Uncertainty Analysis Methods for Predicting Cementitious Barrier Performance***
Authors: **Christine Langton – SRNL; D.S. Kosson -Vanderbilt University/CRESP**

Cementitious barriers for nuclear applications are one of the primary controls for preventing or limiting radionuclide release into the environment. At the present time, performance and risk assessments do not fully incorporate the effectiveness of engineered barriers because the processes that influence performance are coupled and complicated. Better understanding the behavior of cementitious barriers is necessary to evaluate and improve the design of materials and structures used for radioactive waste containment, life extension of current nuclear facilities, and design of future nuclear facilities, including those needed for nuclear fuel storage and processing, nuclear power production and waste management. The focus of the Cementitious Barriers Partnership (CBP) literature review is to document the current level of knowledge with respect to 1) mechanisms and processes that directly influence the performance of cementitious materials 2) methodologies for modeling the performance of these mechanisms and processes and 3) approaches to addressing and quantifying uncertainties associated with performance predictions. This will serve as an important reference document for the professional community responsible for the design and performance assessment of cementitious materials in nuclear applications. This review also provides a multi-disciplinary foundation for identification, research, development and demonstration of improvements in conceptual understanding, measurements and performance modeling that would be lead to significant reductions in the uncertainties and improved confidence in the estimating the long-term performance of cementitious materials in nuclear applications. This report identifies; 1) technology gaps that may be filled by the CBP project and also 2) information and computational methods that are in currently being applied in related fields but have not yet been incorporated into performance assessments of cementitious barriers.

Doc. #: **CBP-TR-2009-002-C2**
Title: ***Mineralogical and Microstructural Evolution in Hydrating Cementitious Systems***
Author: **Kenneth Snyder – NIST**

The mineralogical and microstructural changes that occur in cementitious systems during hydration are summarized. These changes depend, in large part, on the proportions of the cementitious binders (e.g., portland cement, fly ash, silica fume, and slag). Moreover, these changes are discussed in the context of hydration under sealed (no chemical exchange with the environment) and isothermal conditions. Under these conditions, the hydration reactions, and commensurate mineralogical and microstructural changes, continue over the time scale of months or years. The few very slow reactions are discussed in the context of thermodynamic modeling.

The mineralogical and microstructural stability at very long timescales (e.g., centuries, millennia) is relevant to performance assessment for nuclear applications. The very long-term stability of the hydrated phases is discussed in the context of natural and ancient analogs.

Microstructural changes due to degradation are discussed in the general context of physico-chemical service life computer modeling; the mineralogical changes due to degradation are discussed in the chapter on chemical degradation. Because there are no analytical expressions for the microstructural changes that occur during degradation (besides changes in the porosity), computer models must be used that are applied to all chemical degradation mechanisms simultaneously. As a result, the microstructural changes are discussed in the broad context of modeling, without reference to specific degradation mechanisms.

For relevance to nuclear applications, various cementitious systems are considered. These include systems having a broad range of proportions of cement, fly ash, slag, and silica fume. Moreover, the possible effects of waste stabilization, through incorporation into the mix water, are discussed.

Doc. #: **CBP-TR-2009-002-C3**
Title: ***Early-Age Cracking Review: Mechanisms, Material Properties, and Mitigation Strategies***
Author: **D.P. Bentz – NIST**

The goal of long-lasting concrete for critical infrastructure applications can only be achieved when early-age cracking is avoided. This includes nuclear facilities, including waste processing, containment and storage facilities and power plant facilities. Consequently, this topic is crucial to the mission of the Cementitious Barriers Partnership (CBP). Since most concrete is cast in place, field conditions, including environmental and workmanship parameters, can significantly influence early-age cracking tendencies. Beyond this, two inherent contributions to early-age cracking are thermal and autogenous deformations. In this chapter, these latter two contributions are reviewed from the three perspectives of basic mechanisms, relevant material properties, and successful mitigation strategies for portland cement-based concrete. Cementitious waste forms have unique chemistry and will need to be considered on a case by case basis.
For thermal deformations, key considerations are hydration rates and the thermophysical properties of the cement paste or concrete. The heat of hydration of the binder sets the limit on the ultimate possible temperature rise of the concrete. Equally important to this ultimate heat of hydration is the hydration rate that governs when and how fast this heat is produced within a cement paste or concrete element. Thermophysical properties of relevance include heat capacity, thermal conductivity, and coefficient of thermal expansion.
Methods for measuring these properties are discussed and representative data presented. Autogenous deformations are driven by the volumetric chemical shrinkage that accompanies the reactions of cementitious binders. Under non-saturated conditions, this chemical shrinkage leads to self-desiccation and the creation of internal stresses and strains. Autogenous shrinkage is generally increased in lower water-to-cementitious materials ratio *(w/cm)* systems and in systems that contain fi ne supplementary cementitious materials such as silica fume and slag. Measurement of internal relative humidity provides a convenient method for onsite monitoring of the self-desiccation process.
A wide variety of mitigation strategies have been successfully employed to mitigate thermal and autogenous contributions to early-age cracking. Modifications to the mixture proportions such as an increase in *w/cm* ratio, the utilization of a coarser cement, or a partial replacement of cement with a coarse limestone powder can effectively reduce both the maximum temperature rise and the autogenous shrinkage experienced by a concrete mixture. Two other well-developed mitigation strategies, specifically for reducing autogenous shrinkage, are the utilization of shrinkage-reducing admixtures and the application of internal curing, using pre-wetted lightweight aggregates for example. Both of these have progressed from laboratory evaluation to field applications in recent years and their ability to reduce plastic shrinkage cracking (as well as early-age cracking after set) has been recently documented.

Doc. #: **CBP-TR-2009-002-C4**
Title: ***Chemical Degradation Review***
Authors: **Samson, Henocq, and Marchand – SIMCO**

This report reviews the most common mechanisms associated with the chemical degradation of cementitious materials. The review focuses on cases where the chemical degradation of the materials is triggered by the exchange of ionic species at the material/environment interface. In some cases, ionic species are leached out of the material while in other cases, external contaminants enter the material and affect the microstructure. Many situations involve simultaneous species ingress and leaching.
Since the transport of species is prominently involved in the chemical degradation of cementitious materials, the various mechanisms affecting the movement of ions in the pore solution of cementitious materials was first reviewed. Part of the review is dedicated to moisture transport. A more detailed report on this topic can be found in Chapter 2d.

Following this, common chemical degradation mechanisms were reviewed, namely chloride ingress and corrosion, carbonation, decalcification due to the leaching of hydroxide and calcium and external sulfate attack.
As mentioned earlier, only cases involving the exchange of ions at the material/environment interface were considered. "Internal" degradation mechanisms such as delayed ettringite formation (DEF) and alkali-silica reaction (ASR) were left aside. Although they are commonly observed on many existing structures, they can be avoided with proper material selection and concrete practice.
Various types of cementitious materials were described in the paper reviewed. The papers dealing with chloride ingress featured mostly mortar and concrete mixtures, while the carbonation studies were primarily made on hydrated cement pastes and mortars. In the case of external sulfate attack and decalcification, the papers reviewed in this chapter were mostly based on hydrated cement pastes, which make characterization easier due to the absence of aggregates. No studies dedicated specifically to waste forms were reviewed.

Doc. #: **CBP-TR-2009-002-C5**
Title: ***Mechanical Damage Review***
Authors: **Eric Samson – SIMCO; Sarkar and Kosson – Vanderbilt University**

This report summarizes modeling approaches used to predict the formation of cracks in cementitious materials. General considerations related to cracks such as the origin, detection, and prevention are first outlined. Following this, a section is dedicated to the general description of approaches to model the formation of cracks in materials. The first method reviewed is called damage mechanics. It is based on a damage parameter that indicates the level of damage in a continuous material. The second method is called the fracture mechanics. In this approach, the geometry and localization of cracks is predicted instead of relying on a smeared damage parameter. The other sections are dedicated to the description of models developed for specific damage phenomena. Early age cracking caused by the heat generated during the hydration process and the drying shrinkage is first discussed. This is followed by reviews on damage models dealing with sulfate ingress in concrete, rebar corrosion, alkali-silica reaction and freezing/thawing cycles.

Doc. #: **CBP-TR-2009-002-C6**
Title: ***Moisture Transport Review***
Authors: **Arnold and Garrabrants – Vanderbilt University; Samson – SIMCO; Flach and Langton – SRNL**

Moisture transport plays a key role in determining how cementitious materials respond to exposure conditions and release contaminants to the external environment. Moisture presence and movement, whether in the form of liquid water and/or water vapor, affect the concentration and transport rates of dissolved and vapor constituents. The fundamentals of moisture transport in cementitious materials are discussed. Various moisture transport formulations and associated properties are summarized with particular emphasis on moisture transport in fractured or otherwise damaged cementitious materials.

Doc. #: **CBP-TR-2009-002-C7**
Title: ***Review of the Physical and Chemical Aspects of Leaching Assessment***
Authors: **van der Sloot and Meeussen – Energy Research Centre of the Netherlands; Garrabrants and Kosson – Vanderbilt University; Fuhrmann – NRC**

The objective of this chapter is to provide a summary of the latest developments in leaching from cementitious barrier materials consisting of different concrete formulations and cement stabilized waste forms. The chemical retention of substances in the matrix, which is controlled physically by material hydraulic and diffusion properties and chemically by precipitation/dissolution processes, sorption processes onto iron oxides and organic matter, incorporation in solid solutions and interactions with clay, is addressed. The influence of external factors such as oxidation and carbonation on constituent release can be very important because large pH and redox gradients may exist initially, but the chemistry within and surrounding the matrix will change with time and consequently different release behaviors may occur at over different time intervals. In addition, physical stresses may occur that change the physical and hydraulic properties of the material (this aspect is addressed in other report chapters). From a leaching perspective, the release controlling phases are not necessarily the primary matrix minerals, but also may be phases only present in very minor quantities. An integrated set of tools for testing and evaluation of release is presented, which lend themselves for chemical speciation modeling and subsequent chemical reaction transport modeling. The important role of field verification in lysimeters and testbed studies is stressed and experiences in nuclear waste management are identified.

Doc. #: **CBP-TR-2009-002-C8**
Title: ***Review of Thermodynamic and Adsorption Databases***
Authors: **Meussen, van der Sloot, and Dijkstra – Energy Research Centre of the Netherlands; Kosson – Vanderbilt University**

The objective of this chapter provide a summary of thermodynamic databases that have been used and are available to predict 1) equilibrium phase assemblages in cementitious materials and 2) the impact of sorption processes on the concentrations of ionic species in an aqueous phase in contact with cementitious materials and soils. In addition, a brief summary of approaches to thermodynamic modeling is provided.

Doc. #: **CBP-TR-2009-002-C9**
Title: ***Review of Approaches to Coupling Physical, Structural and Chemical Mechanisms***
Authors: **Samson – SIMCO; Meussen and van der Sloot – Energy Research Centre of the Netherlands; Garrabrants – Vanderbilt University**

This chapter reviews approaches used to model coupling between different degradation mechanisms affecting concrete structures. Two main categories of models were identified: reactive transport modeling and thermo-hydro-mechanical models.

Reactive transport models are concerned with the transport of chemical species in porous materials and the multiple interactions they can have with the solid matrix. These models couple transport equations with complex chemical models. They ignore the mechanical aspects of deleterious chemical reactions such as crack formation upon sulfate attack.

On the other hand, there are models that couple fluid transport with thermal and mechanical equations, called thermo-hydro-mechanical (THM) models. These models can be used to simulate crack formation caused by drying shrinkage or heat release during the hydration of cement. However, classic THM models

do not incorporate the transport of species in the fluid phases and the chemical exchange with the solid minerals.
Reactive transport models incorporating mechanical considerations, or THM models dealing with detailed transport and chemistry relationships, are nearly non-existent. Given the mechanisms and time scales involved in nuclear waste storage problems, models incorporating detailed reactive transport with a THM framework could be used to provide a global durability assessment for those structures.

Doc#: **CBP-TR-2009-002-C10**
Title: ***Review of Integrating Programs and Code Structure Used for DOE Environmental Assessments***
Authors: **Brown – Vanderbilt University/CRESP; Flach – SRNL**

A fundamental understanding of the behavior of cementitious barriers will be needed to reduce uncertainty in performance evaluations and to improve designs. These barriers are often one of the primary control mechanisms to prevent or limit radionuclide releases from nuclear facilities. Improved tools are needed to allow performance assessments to fully incorporate and consider the effectiveness of cementitious barriers, which in part limits the types and quantities of contaminants that may be disposed of in shallow land disposal. A set of simulation tools are needed to predict 1) the hydraulic properties, 2) the stability of the relevant cement matrix phases and 3) the release fluxes of contaminants in response to variable boundary conditions and system stresses over relevant time periods. The developed tools should include explicit evaluation of uncertainty in the resulting performance estimates. In this chapter, examples of relevant integration frameworks and couplings are described in the context of the CBP modeling needs. Each of the frameworks described has strengths and weaknesses based on the models that will be selected and the extent and nature of the interactions among the models.

Doc#: **CBP-TR-2009-002-C11**
Title: ***Uncertainty Analysis Methods***
Authors: **Mahadevan and Sarkar – Vanderbilt University/CRESP**

This report surveys available analysis techniques to quantify the uncertainty in performance assessment (PA) arising from various sources. Three sources of uncertainty – physical variability, data uncertainty, and model error – are considered. The uncertainty quantification methods are described in the context of four types of analyses needed, namely, (1) quantification of uncertainty in the inputs to the PA models, (2) propagation of input uncertainty through the PA models, (3) model error quantified through verification and validation activities, and (4) probabilistic PA. Random variable and random process descriptions of physical variability are outlined. Methods for handling data uncertainty through flexible families of probability distributions, confidence bounds, interval analysis and Bayesian analysis are described. Useful surrogate modeling and sensitivity analysis techniques for efficient uncertainty propagation analysis are discussed, as well as methods to quantify the various sources of model error. Statistical hypothesis testing techniques (both classical and Bayesian) are discussed for the validation of PA models, and a Bayesian approach to quantify the confidence in model prediction with respect to field conditions is developed. First-order approximations as well as efficient Monte Carlo sampling techniques for probabilistic PA are described.

Doc. #: **CBP-TR-2009-003**
Title: ***Description of the Software and Integrating Platform***
Author: **Greg Flach – SRNL**

Doc#: **CBP-TR-2009-003C1**
Title: ***CBP Software Summaries for LeachXS™/ORCHESTRA, STADIUM®, Thames, and GoldSim***
Authors: **Brown – Vanderbilt University; Flach – SRNL**

The goal of the Cementitious Barriers Partnership (CBP) is to develop a reasonable and credible set of tools to predict the structural, hydraulic and chemical performance of cement barriers used in nuclear applications over extended time frames (e.g., >100 years for operating facilities and >1000 years for waste management). The simulation tools and data produced will be used to evaluate and predict the behavior of cementitious barriers used in near surface engineered waste disposal systems including waste forms, containment structures, entombments and environmental remediation. The tools will also support analysis of structural concrete components of nuclear facilities (i.e., spent fuel pools, dry spent fuel storage units, and recycling facilities).
Model parameters will be obtained from literature sources and experimentally measured under this project, when needed, to demonstrate application of the simulation tools to three prototype applications (i.e., waste form in concrete vault, high level waste tank grouting, and spent fuel pool).
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 critical aging and degradation phenomena. STADIUM® has been used to predict the behavior of concrete structures exposed to chemically aggressive environments including chloride and sulfate. LeachXS™ is a database and expert decision tool that can seamlessly call the ORCHESTRA geochemical code to model chemical attack as well as carbonation, oxidation, and leaching of cementitious materials. THAMES is being developed to describe cementitious binder microstructures and calculate important engineering properties during hydration and degradation. Through the CBP, conceptual models and computational tools will be developed or modified to improve the assessment of long-term structural, hydraulic, and chemical performance of cementitious materials.
Characterizing properties and understanding the mechanistic behavior of cementitious barriers is necessary to evaluate and improve system designs. Uncertainty reductions require coupling multi-scale and multi-physics processes, including physical-chemical evolution and transport phenomena applied to heterogeneous materials with changing boundary conditions. The selected codes will be coupled using a GoldSim probabilistic simulation framework. Uncertainty evaluation will be included with simulations at both the phenomenological and integrated system level.

Doc. #: **CBP-TR-2010-006**
Title: ***Reference Cases for Use in the Cementitious Partnership Project***
Authors: **Christine Langton – SRNL; Kosson and Garrabrants – Vanderbilt University**

The Cementitious Barriers Partnership Project (CBP) is a multi-disciplinary, multi-institution cross-cutting collaborative effort supported by the US Department of Energy (DOE) to develop a reasonable and credible set of tools to improve understanding and prediction of the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. The period of performance is >100 years for operating facilities and > 1000 years for waste management. The CBP has defined a set of reference cases to provide the following functions: (i) a common set of system configurations to illustrate the methods and tools developed by the CBP, (ii) a common basis for evaluating methodology for uncertainty characterization, (iii) a common set of cases to develop a complete set of parameter and changes in parameters as a function of time and changing conditions, (iv) a basis for experiments and model validation, and (v) a basis for improving conceptual models and reducing model uncertainties. These reference cases include the following two reference disposal units and a reference storage unit: (i) a cementitious low activity waste form in a reinforced concrete disposal vault, (ii) a concrete vault containing a steel high-level waste tank filled with grout (closed high-level waste tank), and (iii) a spent nuclear fuel basin during operation. Each case provides a different set of desired performance characteristics and interfaces between materials and with the environment. Examples of concretes, grout fills and a cementitious waste form are identified for the relevantreference case configurations.

Doc. #: **CBP-TR-2010-006, R1**
Title: ***Reference Cases for Use in the Cementitious Partnership Project***
Authors: **Christine Langton – SRNL; Kosson and Garrabrants – Vanderbilt University**

The Cementitious Barriers Partnership Project (CBP) is a multi-disciplinary, multi-institution cross-cutting collaborative effort supported by the US Department of Energy (DOE) to develop a reasonable and credible set of tools to improve understanding and prediction of the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. The period of performance is >100 years for operating facilities and > 1000 years for waste management. The CBP has defined a set of reference cases to provide the following functions: (i) a common set of system configurations to illustrate the methods and tools developed by the CBP, (ii) a common basis for evaluating methodology for uncertainty characterization, (iii) a common set of cases to develop a complete set of parameter and changes in parameters as a function of time and changing conditions, (iv) a basis for experiments and model validation, and (v) a basis for improving conceptual models and reducing model uncertainties. These reference cases include the following two reference disposal units and a reference storage unit: (i) a cementitious low activity waste form in a reinforced concrete disposal vault, (ii) a concrete vault containing a steel high-level waste tank filled with grout (closed high-level waste tank), and (iii) a spent nuclear fuel basin during operation. Each case provides a different set of desired performance characteristics and interfaces between materials and with the environment. Examples of concretes, grout fills and a cementitious waste form are identified for the relevant reference case configurations.

Doc. #: **CBP-TR-2010-007-C1**
Title: ***Demonstration of LeachXS Orchestra Capabilities by Simulating Constituent Release from a Cementitious Waste Form in a Reinforced Concrete Vault***
Authors: **Meeussen and van der Sloot – Energy Research Centre of the Netherlands; Kosson and Sarkar – Vanderbilt University**

This report provides an overview of the current capabilities of the LeachXS™/ORCHESTRA database reactive transport model combination and how these relate to the objectives and development efforts of the Cementitious Barriers Partnership (CBP). LeachXS includes a database with an extended set of experimental data on different waste and building materials, including cementitious materials. Within LeachXS, ORCHESTRA is used as the geochemical speciation and reactive transport code for simulating experimental results and the chemical behavior of materials in specific application scenarios. ORCHESTRA can calculate chemical speciation in thermodynamic equilibrium systems in a similar way as other geochemical speciation programs (e.g., PHREEQC or MINTEQ) by using the same thermodynamic database format. ORCHESTRA contains state-of-the-art adsorption models for oxide and organic surfaces as well as solid solutions. The ORCHESTRA chemical speciation module can be used in combination with previously established transport algorithms (modules) that calculate single or multi-phase diffusion or convection in single or multi-regime porous media models. Within the CBP context, LeachXS™/ORCHESTRA will be used to calculate transport rates of reactive substances through reactive porous media, including release of material constituents and ingress of external reacting substances (e.g., sulfate, oxygen, or carbon dioxide).

This report illustrates the use of LeachXS™/ORCHESTRA for the following applications:

1. Comparing model and experimental results for leaching tests for a range of cementitious materials including cement mortars, grout, stabilized waste, and concrete. The leaching test data includes liquid-solid partitioning as a function of pH and release rates based on laboratory column, monolith, and field testing.
2. Modeling chemical speciation of constituents in cementitious materials, including liquid-solid partitioning and release rates.
3. Evaluating uncertainty in model predictions based on uncertainty in underlying composition, thermodynamic, and transport characteristics.
4. Generating predominance diagrams to evaluate predicted chemical changes as a result of material aging using the example of exposure to atmospheric conditions.
5. Modeling coupled geochemical speciation and diffusion in a three-layer system consisting of a layer of Saltstone, a concrete barrier, and a layer of soil in contact with air. The simulations show developing concentration fronts over a time period of 1000 years.
6. Modeling sulfate attack and cracking due to ettringite formation. An example case is provided in a separate article by the authors. Finally, based on the computed results, the sensitive input parameters for this type of modeling are identified and discussed.

Doc. #: **CBP-TR-2010-007-C2**
Title: ***Task 7 Demonstration of Thames for Microstructure and Transport Properties***
Authors: **Bullard, Stutzman, Snyder, and Garboczi – NIST**

The goal of the Cementitious Barriers Partnership (CBP) is to develop a reasonable and credible set of tools to reduce the uncertainty in predicting the structural, hydraulic and chemical performance of cement barriers used in nuclear applications that are exposed to dynamic environmental conditions over extended time frames.

One of these tools, the responsibility of NIST, is THAMES (Thermodynamic Hydration And Microstructure Evolution Simulator), which is being developed to describe cementitious binder microstructures and calculate important engineering properties during hydration and degradation.

THAMES is designed to be a "micro-probe", used to evaluate changes in microstructure and properties occurring over time because of hydration or degradation reactions in a volume of about 0.001 mm^3. It will be used to map out microstructural and property changes across reaction fronts, for example, with spatial resolution adequate to be input into other models (e.g., STADIUM®, LeachXS™) in the integrated CBP package.

THAMES leverages thermodynamic predictions of equilibrium phase assemblages in aqueous geochemical systems to estimate 3-D virtual microstructures of a cementitious binder at different times during the hydration process or potentially during degradation phenomena. These virtual microstructures can then be used to calculate important engineering properties of a concrete made from that binder at prescribed times. In this way, the THAMES model provides a way to calculate the time evolution of important material properties such as elastic stiffness, compressive strength, diffusivity, and permeability. Without this model, there would be no way to update microstructure and properties for the barrier materials considered as they are exposed to the environment, thus greatly increasing the uncertainty of long-term transport predictions.

This Task 7 report demonstrates the current capabilities of THAMES. At the start of the CBP project, THAMES did not exist, so that it is in the early stages of development. However, extensive experience with 3-D microstructure models at NIST is making possible a timely development process.

Doc. #: **CBP-TR-2010-007-C3**
Title: ***Task 7 Demonstration of Stadium ® for the Performance Assessment of Concrete Low Activity Waste Storage Structures***
Author: **Samson – SIMCO**

This report summarizes the simulation results obtained with the model STADIUM® for typical Cementitious Barrier Partnership (CBP) problems. The model was used to simulate the transport of ions from the pore solution of a salt waste form surrogate material through a concrete barrier in order to estimate the long-term durability of low activity waste storage structures. The simulations were performed before improvements to STADIUM® planned in the CBP research program were completed. Accordingly, the version of the model used in Task 7 could not predict the formation of cracks due to the presence of expansive sulfate-bearing minerals in the hydrated cement paste.
Simulations were performed to estimate the long-term impact of several factors: thickness of the waste form material, flow field around the concrete barrier, finite element mesh density, concrete transport properties and initial mineral assemblage in the waste form material. The simulations were performed with transport properties estimated from laboratory tests performed on concretes corresponding to the Vault 1/4 and Vault 2 mixtures. The properties of the waste form were also obtained from laboratory experiments. The calculations made in this report showed the capacity of STADIUM® in handling complex multilayer cases to predict the durability of concrete barriers in contact with sulfate bearing Saltstone-type material. The results highlighted important factors

to consider in long-term analyses. For instance, the thickness of the Saltstone layer considered in the simulation has a significant impact on the model prediction. The results obtained in this report indicate that at least 3 m of salt waste material should be used to simulate the long-term durability of the barrier.
At the soil/concrete barrier interface, the simulations indicated that the thickness of the soil layer considered has very little impact on the kinetics of the ettringite front penetration that starts at the Saltstone/concrete boundary. The soil layer does have an influence on the rate of decalcification of C-S-H at the soil/concrete barrier interface. However, the most important result concerns the influence of different mineral assemblages in the Saltstone mixture. One set of minerals used for the simulations did not initiate the penetration of an ettringite front in the concrete barrier despite the high sulfate concentration in the pore solution. The absence of ettringite means that the concrete is not subject to sulfate attack and could prove highly durable for an extensive period of time. This surprising result emphasizes the need for experimental research work in order to have a better understanding of the complex interaction between the salt waste material and the concrete barrier.

Doc. #: **CBP-TR-2010-009-1**
Title: ***Conceptual Design for Phase I of CBP Software Integration***
Authors: **Flach and Smith – SRNL; Brown – Vanderbilt University**

The Cementitious Barriers Partnership (CBP) is a collaborative program sponsored by the US DOE Office of Waste Processing. An objective of the CBP is to develop a set of computational tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers and waste forms used in nuclear applications. Selected components of the computational toolset include LeachXS™/ORCHESTRA developed by the Energy Research Centre of the Netherlands (ECN 2007, Meeussen 2003), STADIUM® developed by SIMCO Technologies, Inc. (SIMCO 2008), and THAMES under development by the US National Institute of Standards and Technology (NIST). GoldSim (GTG 2009a, b) developed by the GoldSim Technology Group has been selected as the code integration and probabilistic simulation platform for the CBP computational toolbox (Brown and Flach 2009a, b).
Currently these software tools exist in isolation to each other. Goals of the CBP code integration project are to 1) couple LeachXS™/ORCHESTRA, STADIUM® and THAMES in a synergistic manner, 2) enable convenient access to their combined capability through a more unified user interface using GoldSim and custom integration software, and 3) provide a probabilistic uncertainty/sensitivity analysis wrapper for the CBP partner codes, whether used alone or in combination. A phased software integration strategy has been adopted. Phase I will involve integration of current CBP partner code versions in their "as-is" state using GoldSim as the primary integration platform and a Graphical User Interface (GUI). The GoldSim Player, a free version of GoldSim that allows the user to read and run but not edit GoldSim applications, will be used to distribute the integration software without requiring purchase of a GoldSim license. Phase I development will provide an early tangible product and serve as a prototyping step toward development of the Phase II integration framework. In Phase II, plans call for modification of the improved CBP partner codes to facilitate active coupling and information exchange within a GoldSim-driven overall transient simulation. Preliminary successful interfacing of ORCHESTRA and STADIUM to GoldSim using links to Visual Basic for Application (VBA) code embedded in Excel spreadsheets has been demonstrated.

Doc. #: **CBP-TR-2010-009-2**
Title: ***CBP Code Integration GoldSim DLL Interface***
Authors: **Flach and Smith – SRNL; Brown – Vanderbilt University**

A general dynamic-link library (DLL) interface has been developed to link GoldSim with external codes. The overall concept behind this development is to use GoldSim as top-level modeling software with interfaces to external codes for specific calculations. The DLL that performs the linking function is designed to take a list of code inputs from GoldSim, create an input file for the external application, run the external code, and return a list of outputs, read from files created by the external application, back to GoldSim. Instructions for creating the input file, running the external code, and reading the output are contained in an instructions file (`DLL.dat`) that is read and interpreted by the DLL. As an example, a prototype model linking GoldSim with the STADIUM® code used to predict concrete service life has been developed and successfully run. While the example is for an interface between GoldSim and STADIUM® (Brown & Flach 2009), the DLL is designed to be general and should be readily adaptable to interfacing other codes to GoldSim.

Doc. #: **CBP-TR-2011-009-1**
Title: ***CBP Phase I Code Integration***
Authors: **Flach and Smith – SRNL; Brown and Sarkar – Vanderbilt University**

The goal of the Cementitious Barriers Partnership (CBP) is to develop a reasonable and credible set of software tools to predict the structural, hydraulic, and chemical performance of cement barriers used in nuclear applications over extended time frames (greater than 100 years for operating facilities and greater than 1000 years for waste management). The simulation tools will be used to evaluate and predict the behavior of cementitious barriers used in near surface engineered waste disposal systems including waste forms, 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) (ECN 2007, Meeussen 2003) and
- STADIUM® developed by SIMCO Technologies, Inc. (SIMCO 2008).

These partner codes were selected based on their maturity and ability to address the problems outlined above. The GoldSim Monte Carlo simulation program (GTG 2010a, GTG 2010b) was chosen as the code integration platform (Brown & Flach 2009b). GoldSim (current Version 10.5) is a Windows based graphical object-oriented computer program that provides a flexible environment for model development (Brown & Flach 2009b). The linking of GoldSim to external codes has previously been successfully demonstrated

(Eary 2007, Mattie et al. 2007). 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 (Smith III et al. 2010). 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.

Doc. #: **CBP-TR-2012-009-1**
Title: ***CBP Software Toolbox, Version 1.0 User Guide***
Authors: **Brown – Vanderbilt University; Flach and Smith - SRNL**

The Cementitious Barriers Partnership (CBP) has developed a set of software tools, namely the **CBP Software ToolBox**, to predict the structural, hydraulic, and chemical performance of cement barriers used in nuclear applications over extended time frames. These tools can be used to evaluate the behavior of cementitious barriers used in near surface engineered waste disposal systems including waste forms, containment structures, entombments, and environmental remediation. Cementitious materials can be exposed to various dynamic environmental conditions that cause changes in material properties; the current CBP Software ToolBox models (i) sulfate attack, (ii) carbonation, (iii) oxidation and (iv) primary constituent leaching.
Two state-of-the-art software tools were selected as a starting point to capture important phenomena:

- LeachXS™/ORCHESTRA developed by the Energy Research Centre of the Netherlands (ECN) (ECN 2007, Meeussen 2003) and
- STADIUM® developed by SIMCO Technologies, Inc. (SIMCO 2008).

The GoldSim Monte Carlo simulation program (GTG 2010d, GTG 2010e) was chosen as the code integration platform to allow LeachXS™/ORCHESTRA and STADIUM® to be run probabilistically (Brown & Flach 2009b). GoldSim (current Version 10.5) is a Windows based graphical object-oriented computer program that provides a flexible environment for model development (Brown & Flach 2009b). A general Dynamic-link Library (DLL) interface was developed by the CBP that links GoldSim with the external codes (Smith III et al. 2010a). The DLL uses an instructions file, updated by GoldSim for each realization, 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. GoldSim provides: 1) a consistent user interface to the selected external applications, 2) the capability of performing probabilistic analysis with individual codes, and 3) the capability of ultimately coupling selected codes in a synergistic manner.
A GoldSim Player version is made available by the GoldSim Technology Group that allows running but not editing GoldSim models (GTG 2010c). 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.
This user guide describes use of the CBP Software ToolBox in detail and discusses the following topics:

- What is the CBP Software ToolBox?
- How does the CBP Software ToolBox work?
- What Partner codes are in the CBP Software ToolBox?
- CBP Software ToolBox File Structure

- Basic CBP Software ToolBox Concepts including model elements, navigating, and running
- Tutorials for both STADIUM® and LeachXS™/ORCHESTRA

The information provided in this user guide supersedes previous information.

Doc. #: **CBP-TR-2012-009-2**
Title: ***Cementitious Barriers Partnership, Version 1.0, Installation Guide***
Authors: **Brown – Vanderbilt University; Flach and Smith - SRNL**

The Cementitious Barriers Partnership (CBP) has developed the CBP Software ToolBox, an integrated suite of software tools, to predict the structural, hydraulic, and chemical performance of cement barriers used in nuclear applications over extended time frames. The ToolBox can be used to evaluate the behavior of cementitious barriers used in near surface engineered waste disposal systems including waste forms, containment structures, entombments, and environmental remediation. Cementitious materials can be exposed to various dynamic environmental conditions that cause changes in material properties including: (i) sulfate attack, (ii) carbonation, (iii) oxidation and (iv) primary constituent leaching.

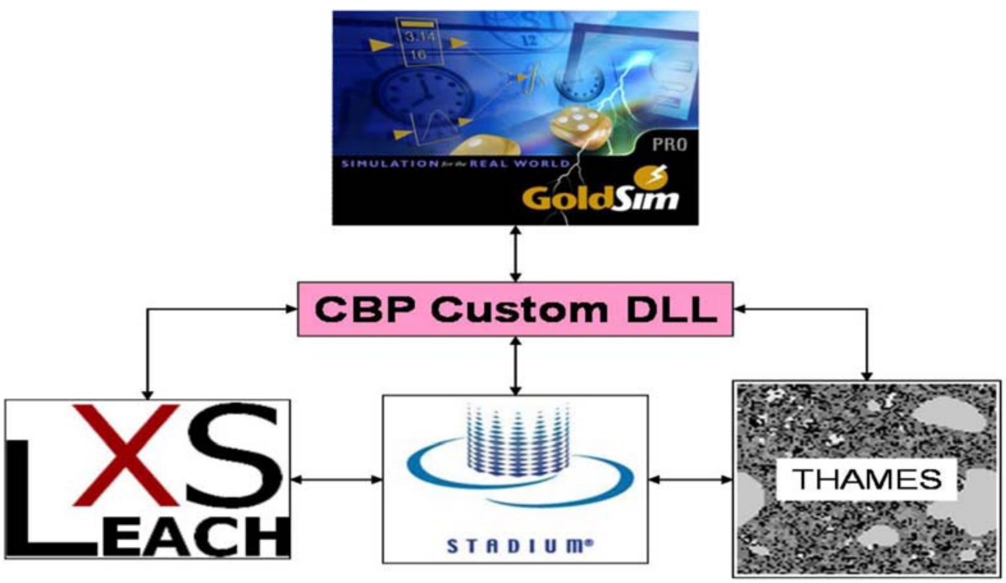
Two state-of-the-art software tools were selected as a starting point to capture the important phenomena: LeachXS™/ORCHESTRA developed by the Energy Research Centre of the Netherlands (ECN) (ECN 2007, Meeussen 2003) and STADIUM® developed by SIMCO Technologies, Inc. (SIMCO 2008). The GoldSim Monte Carlo simulation program (GTG 2010b, GTG 2010c) was chosen as the code integration platform to allow LeachXS™/ORCHESTRA and STADIUM® to be run probabilistically for a set of important, pre-defined degradation scenarios (Brown & Flach 2009). A GoldSim "Player" version allows running but not editing GoldSim models (GTG 2010a). A general Dynamic-link Library (DLL) interface was developed by the CBP that links GoldSim with the Partner codes (Smith III et al. 2010). For each realization, the DLL uses an instructions file that controls creating the appropriate 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 the GoldSim model.

This user guide describes use of the CBP Software ToolBox in detail and discusses the following topics:

- What do you need to get started?
- Installing the CBP Software ToolBox
- Setting System Options after installation
- Preparing a new simulation workspace for the Software ToolBox

Doc. #: **CBP-TR-2013-01**
Title: ***Cementitious Barriers Partnership FY13 Mid-Year Report***
Authors: **Burns, Flach, and Langton – SRNL; Kosson and Brown – Vanderbilt University; Samson – SIMCO; Meeussen and van der Sloot – Netherlands; Garboczi – NIST**

In FY2013, the Cementitious Barriers Partnership (CBP) is continuing in its effort to develop and enhance software tools demonstrating tangible progress toward fulfilling the objective of developing 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. In FY2012, the CBP released the initial inhouse "Beta-version" of the CBP Software Toolbox, a suite of software for simulating reactive transport in cementitious materials and important degradation phenomena. The current primary software components are LeachXS/ORCHESTRA, STADIUM, and a GoldSim interface for probabilistic analysis of selected degradation scenarios as shown in Figure 1. THAMES is a planned future CBP Toolbox component (FY13/14) focused on simulation of the microstructure of cementitious materials and calculation of resultant hydraulic and constituent mass transfer parameters needed in modeling. This past November, the CBP Software Toolbox Version 1.0 was released that supports analysis of external sulfate attack (including damage mechanics), carbonation, and primary constituent leaching. 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.).



The CBP issued numerous reports and other documentation that accompanied the "Version 1.0" release including a CBP Software Toolbox User Guide and Installation Guide. These documents, as well as, the presentations from the CBP Software Toolbox Demonstration and User Workshop, which are briefly described below, can be accessed from the CBP webpage at http://cementbarriers.org/. The website was recently modified to describe the CBP Software Toolbox and includes an interest form for application to use the software.
The CBP FY13 program is continuing research to improve and enhance the simulation tools as well as develop new tools that model other key degradation phenomena not addressed in Version 1.0. Also, efforts to continue to verify the various simulation tools thru laboratory experiments and analysis of field

specimens are ongoing to quantify and reduce the uncertainty associated with performance assessments are ongoing. This mid-year report also includes both a summary on the FY13 software accomplishments in addition to the release of Version 1.0 of the CBP Software Toolbox and the various experimental programs that are providing data for calibration and validation of the CBP developed software. The focus this year for experimental studies was to measure transport in cementitious material by utilization of a leaching method and reduction capacity of saltstone field samples. Results are being used to calibrate and validate the updated carbonation model.

Doc. #: **CBP-TR-2013-02**
Title: ***Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-Containing Waste Forms***
Authors: **Almond, Stefanko, and Langton – SRNL**

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 $Tc(VII)O_4^-$ 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.
In this study, small monoliths of a sodium salt waste form were spiked with sodium chromate, $Na_2Cr(VI)O_4$. The waste forms contained blast furnace slag and were formulated to be chemically reducing. After curing and exposure to air for up to 300 days, the samples were sectioned perpendicular to the exposed surface (depth-discrete samples), crushed and leached in de-aerated, deionized water for 18 ± 2 hours and also for 28 days. Leachates were analyzed for Na, NO_3^-, NO_2^-, and Cr.

Doc. #: **CBP-TR-2013-03**
Title: ***CBP Toolbox Version 2.0 Code Integration Enhancements***
Authors: **Flach and Smith – SRNL; Brown – Vanderbilt University**

This report describes enhancements made to code integration aspects of the Cementitious Barriers Project (CBP) Toolbox as a result of development work performed at the Savannah River National Laboratory (SRNL) in collaboration with Vanderbilt University (VU) in the first half of fiscal year 2013. Code integration refers to the interfacing to standalone CBP partner codes, used to analyze the performance of cementitious materials, with the CBP Software Toolbox. The most significant enhancements are:
1) Improved graphical display of model results.
2) Improved error analysis and reporting.
3) Increase in the default maximum model mesh size from 301 to 501 nodes.
4) The ability to set the LeachXS/Orchestra simulation times through the GoldSim interface.
These code interface enhancements have been included in a new release (Version 2.0) of the CBP Toolbox.

Doc. #: **CBP-TR-2014-001**
Title: ***Cementitious Barriers Partnership FY2013 End-Year Report***
Authors: **Flach, Langton, Burns, and Smith – SRNL; Kosson and Brown – Vanderbilt University; Samson – SIMCO; Meeussen and van der Sloot – Netherlands; Garboczi – NIST**

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.

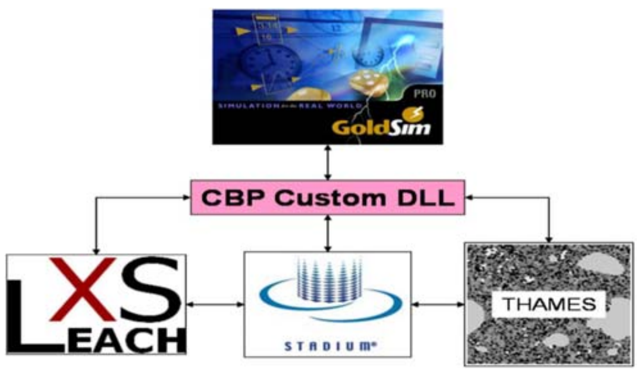


Figure 1. CBP Software Toolbox Software

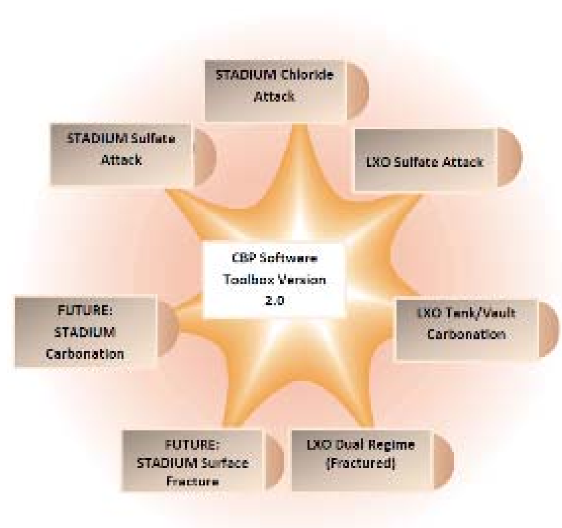


Figure 2. CBP Software Toolbox Software Modules in Version 2.0

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 (S 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.

Doc. #: **CBP-TR-2014-004**
Title: ***X-ray Diffraction of Slag-Based Sodium Salt Waste Forms***
Authors: **Langton and Missimer – SRNL**

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.

This report documents sample preparation and x-ray diffraction results for a series of mixtures of sodium salt waste and cementitious binders. The objective of this study was to provide initial phase characterization for the CBP reference case cementitious salt waste form. This information can be used to: 1) generate a base line for the evolution of the waste form as a function of time and conditions, 2) potentially to 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.

More specifically, identification of hydrated phases capable of sequestering anions in the structures and crystallinity of the calcium silicate binder phases were of particular interest. The intent was to use this characterization data as a starting point for more detailed phase characterization using neutron diffraction techniques in addition to quasi-elastic neutron scattering techniques for characterization of water at the ORNL Spallation Neutron Source, Oak Ridge, TN. The initial characterization is complete. Due to extensive substitutions of cations and anions in the layered double hydroxide phases and the very fine intermixing of poorly crystalline hydrated phases in the reference case blend (10 : 45 : 45 cement : slag : fly ash), electron diffraction and transmission electron spectroscopy are recommended as the next step for characterization.

In summary, the hydrated mixtures of Type II portland cement, Grade 100 ground granulated blast furnace slag (GGBFS) and carbon burn-out (CBO) Class F Fly ash contained hydrated phase assemblages which were typical of those reported in the literature. Based on x-ray diffraction results, 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 5 M Na salt solution resulted in the most crystalline matrix. In addition to poorly to non-crystalline 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 trace amounts in slag blends containing 30 to 45 mass percent fly ash. The calcium silicate binder in the 10:45:45 mixture of cement : slag : fly ash was primarily non crystalline to poorly crystalline 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. Sodium nitrate is distributed throughout the matrix of samples cured under non-drying conditions as very small crystals which are not obvious in SEM micrographs at magnification of a few 1000X. Drying conditions during curing, especially when coupled with elevated temperatures, result in formation of large sodium nitrate crystals which exhibit a twisted, bundle morphology. These crystals are often associated with localized cracking and a damaged microstructure not observed in samples cured under non-drying conditions.

Sodium sulfate, aluminate, and carbonate were to a large extent 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].

The mineralogy of the cured cementitious material influences the physical properties (strength, stiffness, etc.) of the cured material due to the degree of polymerization (chain length) and tetrahedron arrangement. Information about the mineralogy of hydrated cementitious materials and blends of these ingredients is needed to design waste form matrices, select ingredients and make adjustments in material proportions. Information presented in this report is an initial step in developing phases diagrams for the hydrated systems in which caustic sodium salt solutions are used as the hydration fluid for waste forms.

Doc. #: **CBP-TR-2014-005**
Title: ***Tc Oxidation in Slag-Based Sodium Salt Waste Forms Exposed to Water and Moist Hanford Soil***
Author: **Christine Langton – SRNL**

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.

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.

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 ($Tc(VII)O_4^-$) typical of near surface environments, and 2) Tc-99 is a long-lived isotope with a half-life of 2.1E+05 years which poses a great challenge to prediction performance and 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 then cutting a fresh surface 2 to 2.5 cm from the original top surface to eliminate sample inhomogeneity as the result of settling as a reason from observed results and provides 1-D soluble ion transport and gas transport information.

Based on nitrate (assumed to 100 % soluble during curing and exposure and used as a reference) 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 Hanford sediment) and Tc2-10 (DI water), respectively. 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.

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 was 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 or to block the transport or gas as efficiently as DI water.

Additional data are required to fully understand and quantify the progression of the region depleted in soluble ions and the rate of oxygen ingress and oxidation of redox sensitive contaminants such as Tc. However, these scoping studies have provided insights to the multiple mechanisms affecting the solubility and leachability of redox sensitive contaminants.

In conclusion, leaching monolithic porous cementitious waste forms in water appears to be conservative for non-redox sensitive contaminants such as nitrate and sodium. However, leaching data obtained under saturated exposure conditions do not appear to be conservative for redox sensitive contaminants such as

Tc(IV) phases which are easily and whose mobility is dependent on oxidation state. Leaching crushed samples in water still seems to be a conservative approach to estimating the concentrations of soluble contaminants in a waste form.

Doc. #: **CBP-TR-2015-001**
Title: ***Cementitious Barriers Partnership: OPC Paste Samples Exposed to Aggressive Solutions***
Authors: **Protière and Samson – SIMCO**

The study presented in this report focused on a low-activity wasteform containing a high pH pore solution with a significant level of sulfate. The purpose of the study was to improve understanding of the complex concrete/wasteform reactive transport problem, in particular the role of pH in sulfate attack.

Paste samples prepared at three different water-to-cement ratios were tested. The mixtures were prepared with ASTM Type I cement, without additional admixtures. The samples were exposed to two different sodium sulfate contact solutions. The first solution was prepared at 0.15M Na_2SO_4. The second solution also incorporated 0.5M NaOH, to mimic the high pH conditions found in Saltstone.

After three months of exposure, various techniques were used to quantify the penetration of sulfate in the paste samples and the damage sustained as a result of sulfate exposure:

• Layer-by-layer analysis of sulfate content through acid dissolution,
• Microprobe analysis,
• Mercury intrusion porosimetry,
• X-ray diffraction.

The data collected indicated that in Na_2SO_4 solution, damage occurs to the pastes. Sulfate profiles, either from layer-by-layer acid dissolution analysis or by microprobe, confirm the penetration of sulfate in the material. Limited XRD data show that in the damaged portion next to the surface, ettringite and gypsum was formed. Alterations to the microstructure were confirmed by MIP measurements. Close to the surface, where the paste is most damaged, some of the finer pores were filled, as indicated by a reduction of the pore volume in the 10nm-100nm pore range. However, for pores in the 20nm–2µm pore range, pore volume increased. This newly created volume can be associated with microcracks, likely created by the formation of ettringite and gypsum. These observations are valid for all three paste mixtures. The rate of sulfate ingress and degradation was directly related to the mix characteristics: higher water-to-cement ratio showed higher rates of degradation.

In the case of the high pH sulfate solution (Na_2SO_4 + NaOH), no signs of damage was observed on any of the paste mixtures. Contrary to the previous case, the deleterious mineral phases associated with sulfate exposure did not form in the high pH environment. A possible explanation for this is the absence of gypsum formation at high pH. Similar conclusions were drawn on the basis of numerical simulations in Task 7 of the CBP project.

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. Good quality mixtures could thus prove durable over the long term and act as an effective barrier to prevent radionuclides from reaching the environment. Additional experiments with contact solutions that mimic more closely wasteform pore solution are needed to confirm this.

Doc. #: **CBP-TR-2015-002**
Title: ***Cementitious Barriers Partnership: Transport Properties of Damaged Materials***
Authors: **Protière and Samson – SIMCO**

The objective of the Cementitious Barriers Partnership (CBP) project is to develop tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in low level waste storage applications. One key concern for the long-term durability of concrete is the degradation of the cementitious matrix, which occurs as a result of aggressive chemical species entering the material or leaching out in the environment, depending on the exposure conditions. The objective of the experimental study described in this report is 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 creates additional pore space in the microstructure but likely creates new thin pathways between existing pore space for species to travel.

These results have a significant impact on modeling efforts. Models relating porosity to tortuosity and permeability are unlikely to provide the correct basis for predicting long-term durability of concrete sustaining internal pressures and microcrack formation. Other avenues like the modeling of internal crystallization pressure need to be explored.

Doc. #: **CBP-TR-2015-007**
Title: ***Cementitious Barriers Partnership: SCM Paste Samples Exposed to Aggressive Solutions***
Authors: **Protière and Samson – SIMCO**

This report summarizes experimental work performed by SIMCO Technologies Inc. (SIMCO) as part of the Cementitious Barriers Partnership (CBP) project. The test series followed an experimental program (Protière 2014) dedicated to the study of ordinary Portland cement (OPC) hydrated cement pastes exposed to aggressive solutions. In the present study, the scope is extended to hydrated cement pastes incorporating supplementary cementitious materials (SCM) such as fly ash and ground granulated blast furnace slag (GGBFS). Also, the range of aggressive contact solutions was expanded.

The experimental program aimed at testing aggressive contact solutions that more closely mimic the chemical composition of saltstone pore solution. Five different solutions, some of which incorporated high levels of carbonate and nitrate, were placed in contact four different hydrated cement paste mixes. In all solutions, 150 mmol/L of SO_4^{2-} (14 400 ppm) were present. The solutions included different pH conditions and different sodium content.

Two paste mixes were equivalent to Vault 1/4 and Vault 2 concrete mixes uses at SRS in storage structures. Two additional paste mixes, cast at the same water-to-cement ratio and using the same cements but without SCMs, were also tested.
The damage evolution in samples was monitored using ultrasonic pulse velocity (UPV) and mass measurements. After three and twelve months of exposure conditions, samples were taken out of solution containers and analyzed to perform migration tests and porosity measurements.
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. 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 possible that the pozzolanic reaction of these SCMs could not be activated due to the low alkali content, a direct consequence of low cement content. In this scenario, the material ends up having a lot of silica available to react upon contact with sodium hydroxide, possibly forming a gel that may be similar to the gel formed in alkali-silica reactions. This scenario needs further experimental confirmation, but it may well explain the poor behavior of mix PV2 in presence of NaOH.

Doc. #: **CBP-TR-2015-008**
Title: ***Cementitious Barriers Partnership: Concrete Mixture Characterization***
Authors: **Protière and Samson – SIMCO**

This report summarizes the characterization study performed on two concrete mixtures used for radioactive waste storage. The mixtures were designed at the Savanah 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 WK37029: 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.
Chloride ponding tests were also performed on test samples. They showed limited chloride ingress, in line with measured transport properties. These test results also showed that both materials react differently with chloride, a consequence of the differences in the binder chemical compositions.

Doc. #: **CBP-TR-2015-014**
Title: ***Cementitious Barriers Partnership: FY2015 End-Year Report***
Authors: **Flach, Langton, Burns, and Smith – SRNL; Kosson and Brown – Vanderbilt University; Samson – SIMCO; Meeussen, Seignette, and van der Sloot – Netherlands**

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:

- <u>*The Cementitious Barriers Partnership Experimental Programs and Software Advancing DOE’s Waste Disposal/Tank Closure Efforts*</u> *– 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.
- <u>*Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the*</u>

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

Doc. #: **CBP-TR-2015-015, R1**
Title: ***CBP [Task 12] Experimental Study of the Concrete/Saltstone Two-Layer System***
Authors: **Protière and Samson – SIMCO**

EXECUTIVE SUMMARY

This report presents the results of a study which intended to study the behavior of concrete samples placed in contact with a wasteform mixture bearing high level of sulfate in its pore solution. A setup was prepared which consisted in a wasteform poured on top of vault concrete mixes (identified as Vault 1/4 and Vault 2 mixes) cured for approximately 6 months. The main characteristics of the mixes are:
• Vault 1/4 concrete: water-to binder ratio (w/b) of 0.38 prepared with ASTM Type I/II cement and slag;
• Vault 2 concrete with a w/b ratio of 0.38 prepared with ASTM Type V cement, slag, fly ash, and silica fume.

The concrete mixtures were characterized in a separate study, as reported in CBP Report CBP-TR-2015-003, Rev. 0. The wasteform grout was prepared in laboratory according to the proportions of the saltstone mix designed by the Savanah River National Laboratory: 10% cement, 45% flay ash, 45% slag.

The first portion of the study presented in this report focused on the characterization of transport properties of the cured saltstone mixture. Porosity and tortuosity were measured over a 2-year period, to assess the potential impact of hydration. Porosity measurements showed that the saltstone grout is very porous, with an average of 62.9%. The test results also showed that porosity did not vary with time after 28 days of curing.

Tortuosity and diffusion coefficient values were measured on the basis of the migration test procedure, where species transport is accelerated using applied electrical potential. The measurements showed a decrease in electrical current values between 28 and 91 days but was stable after that. The reduction in current values was attributed to hydration of cementitious materials. Analysis of the current curves revealed that despite its high porosity, the material exhibits very low tortuosity. The tortuosity value of the saltstone is lower than the tortuosity measured on Vault 1/4 and Vault 2 concrete mixtures. It is thus very resistant to species ingress or leaching.

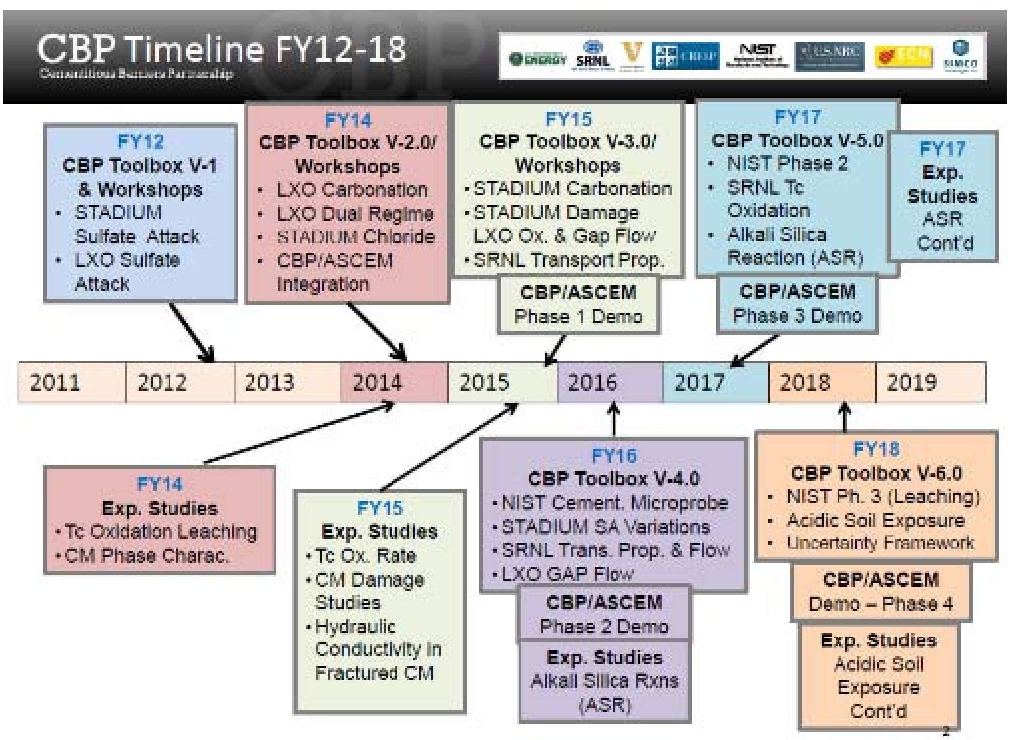
In the second portion of the experimental program, a setup was prepared which consisted of saltstone poured on top of Vault concrete mixes cured for approximately 6 months. The system was sealed to maintain saturated conditions throughout the duration of the test. After 2 years, the materials were separated. Upon separation, no signs of chemical degradation were observed. This contrasted with another study (CBP Report CBP-TR-2015-007, Rev. 1) where hydrated paste samples with the same cement, slag, fly ash and silica fume proportions as the Vault 2 mix were immersed in contact solutions with sulfate levels similar to those found in saltstone and showed alterations. One possible explanation for the absence of damage in the two-layer system is the slow exchange rate between the saltstone and concrete, owing to the low tortuosity of saltstone.

Concrete samples were analyzed to quantify the extent of species that diffused from saltstone. The concrete samples were milled over small depth increment. The collected powder samples were dissolved in acid before being analyzed to measure sodium, potassium, magnesium, calcium, nitrate/nitrite and sulfur content. Overall, only very concentrated species, such as sodium and nitrate/nitrite, showed clear signs of diffusing into concrete. Other species such as sulfate did not show significant ingress.

Limited SEM/EDS observations were also performed on the Vault 2 concrete near the saltstone interface. Although ettringite could be observed in air bubbles near the concrete/saltstone interface, the concrete paste did not show signs of damage. A silica gel was also observed in some air bubbles. It was hypothesized that a silica-rich gel was the cause of severe degradation observed in hydrated pastes from the previous study on hydrated pastes. This siliceous phase observed in the present study may fit with this assumption, but more evidence is needed before this hypothesis can be confirmed.

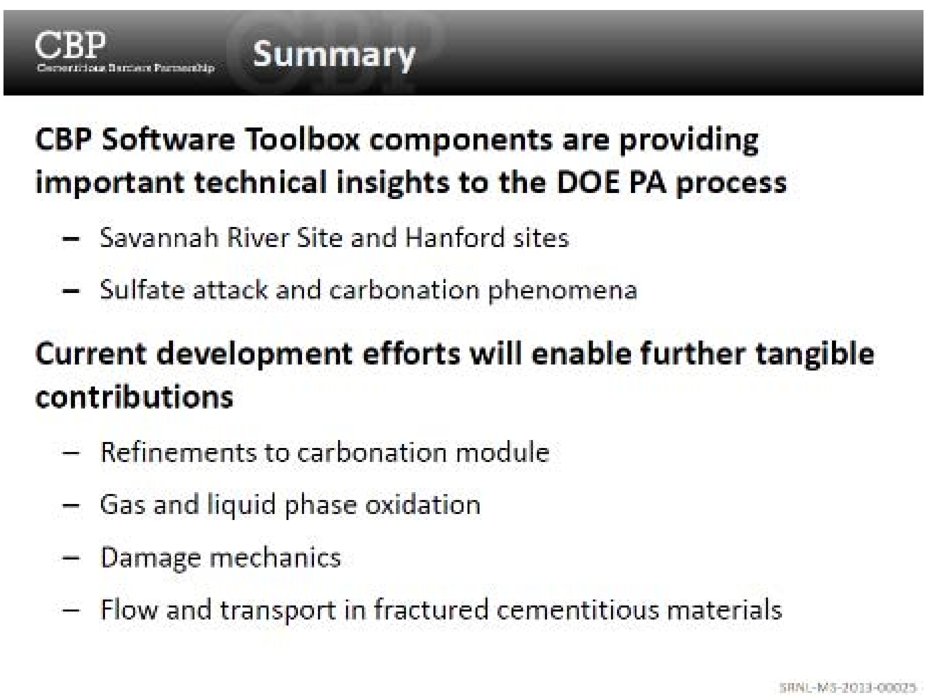
SRNL STI doc. #: **SRNL-EM-2015-00004**
Internal doc. #: **SRNL-MS-2014-00155**
Title: ***Cementitious Barriers Partnership Team Meeting May 2015***
Author: **Heather Burns – SRNL**

Presentation:



Doc. #: **SRNL-MS-2013-00025**
Title: ***CBP Software Toolbox Capabilities in Assessing the Degradation of Cementitious Barriers – 13487***
Author: **Christine Langton – SRNL**

Presentation:



Doc. #: **SRNL-MS-2014-00083**
Title: ***Cementitious Barriers Partnership, EM Office of Tank Waste Management Program Review, June 17, 2014***
Author: **Heather Burns – SRNL**

Presentation:

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Tank Waste Management Challenge

- Cementitious materials are broadly needed to accomplish the DOE-EM mission in a ***cost-effective manner*** while achieving technical performance objectives.
  - Low-Activity Waste (LAW) forms (Saltstone at SRS and potentially Cast Stone at ORP-WTP)
  - High-Level Waste (HLW) Tank Integrity and Tank Closure requirements
  - Secondary waste treatment (Cast Stone at ORP-WTP)
  - Grouting for vadose zone remediation
  - Facility Decommissioning & Decontamination (D&D) and entombment (P-Reactor at SRS)
  - Alternative waste forms for near surface disposal (i.e., grouted waste forms)
  - Nuclear power plant (NPP) structures and used nuclear fuel storage facilities
- Long-lived radionuclides require ***effective containment for thousands of years***, which is beyond our experience base
- Thus mechanistic modeling tools and supporting data are needed to ***predict long-term performance to provide greater confidence.***

3

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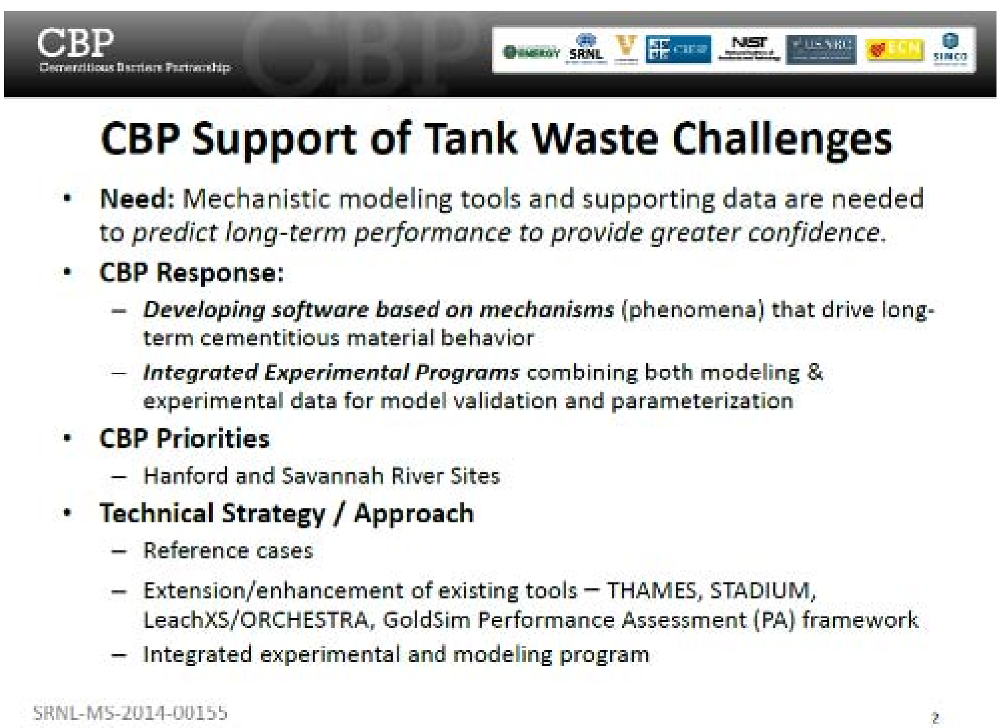
CBP Response

- ***Developing software based on mechanisms*** (phenomena) that drive long-term cementitious material behavior
  - Material degradation: sulfate attack, chloride ingress, carbonation, primary constituent leaching, cracking
  - Contaminant and radionuclide leaching: waste transport across pH/Eh spectrum coupled with the above
  - Coupled species transport, chemical reaction, damage mechanics
  - Complex cement chemistry; wide range of pH/Eh conditions
  - Unique formulations, exposure environments, requirements
- ***Integrated Experimental Programs*** combining both modeling & experimental data for model validation and parameterization
- Rigorous ***uncertainty quantification*** framework

4

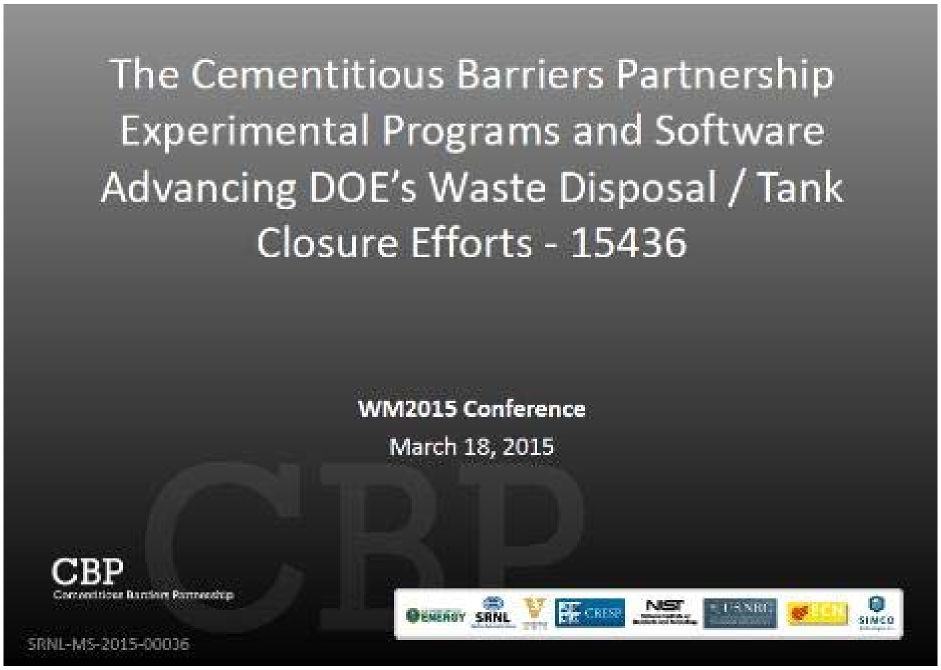
Doc. #: SRNL-MS-2014-00155
Title: *Cementitious Barriers Partnership EM-21 Office of Tank Waste Management Program Review*
Author: Greg Flach – SRNL

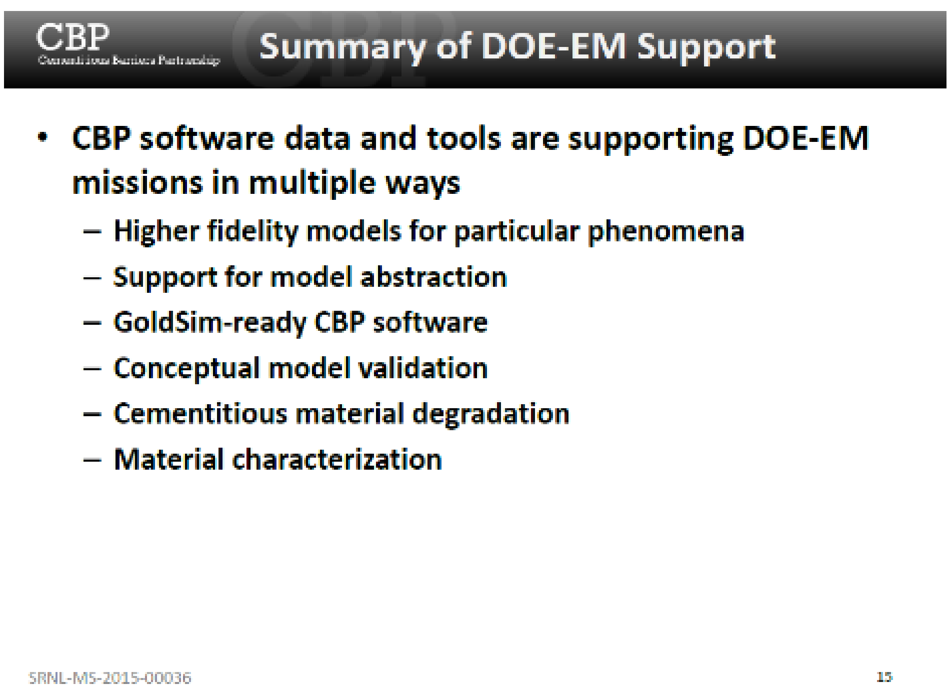
Presentation:



Doc. #: **SRNL-MS-2015-00036**
Title: ***The Cementitious Barriers Partnership Experimental Programs and Software Advancing DOE's Waste Disposal / Tank Closure Efforts – 15436***
Author: **Greg Flach – SRNL**

Presentation:

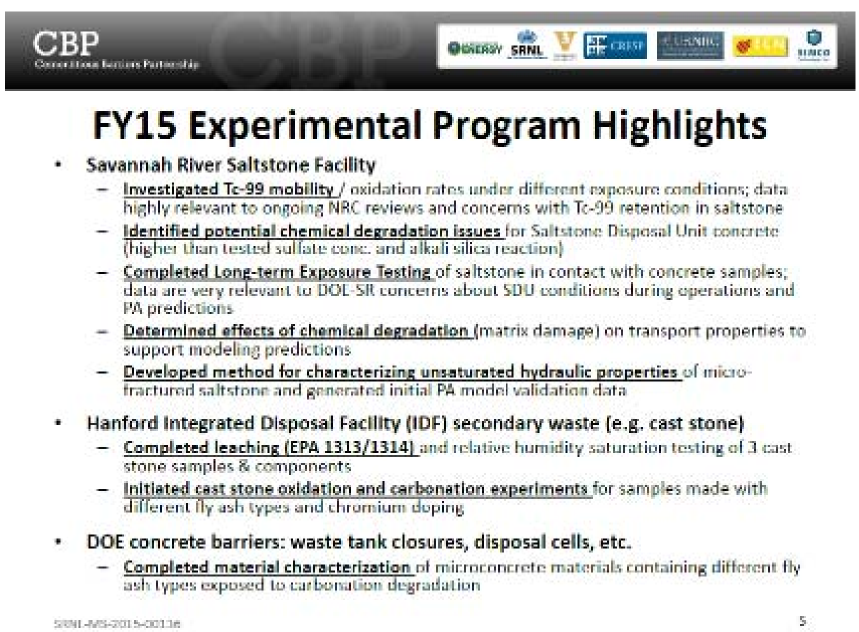




Doc. #: **SRNL-MS-2015-00136**
Title: ***Cementitious Barriers Partnership, EM-21 Office of Tank Waste Management Program Review, July 29, 2015***
Author: **Greg Flach – SRNL**

Doc. #: **SRNL-MS-2015-00136, R1**
Title: ***Cementitious Barriers Partnership, EM-21 Office of Tank Waste Management Program Review, July 29, 2015***
Author: **Greg Flach – SRNL**

Presentation:



CBP
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FY15 Software Program Highlights

- **Three user workshops** following CBP Software Toolbox 2.0 release (65 attendees)
  - **End-user training and consultation**
  - **Emerging DOE needs identified** and incorporated into CBP out-year program (e.g., ASR, dual mechanisms, acidic soil)
- **Collaboration with DOE-SR** to address Saltstone operational exposure concerns
- **Modeling support for IDF PA** under consideration by WRPS and Intera subcontractor (July 2015)
- **Fall 2015 release of CBP Software Toolbox Version 3.0** with NQA-1 graded QA pedigree, and new and enhanced modules:

  <u>New Modules</u>
  - Carbonation (STADIUM)
  - Damage Model for Sulfate Attack (STADIUM)
  - Coupled Oxidation, Carbonation and Leaching (LXO)
  - Hydraulic Property/Flow Database (SRNL)

  Enhanced Modules
  - Sulfate Attack with New Surface Fracture Damage Model (STADIUM)
  - Enhanced Carbonation coupled with Leaching (LXO)
  - Enhanced Sulfate Attack (LXO)

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FY15 SIMCO Experimental & Model Development

- **Key findings and contributions**
  - SDU Paste Exposure:
    - Phase 1 – No damage under high pH conditions in the presence of sulfate
    - Phase 2 – Damage to paste with silica-fume exposed to sulfate, nitrate, and hydroxides (approx. 8 months)
      - Characterized paste damage through acoustic methods
      - Measured effect of paste damage on transport properties needed for PA modeling and prediction
  - SDU Concrete exposure to Saltstone:
    - No apparent damage after two-years
  - New prediction capabilities added to CBP Software Toolbox Version 3.0
  - Software QA documentation for STADIUM

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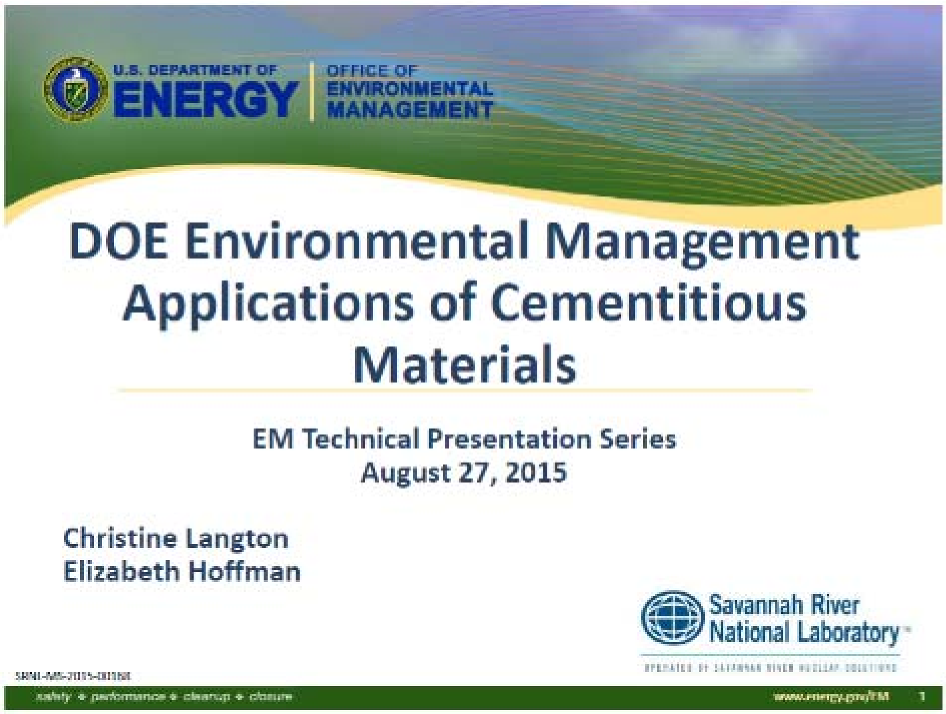
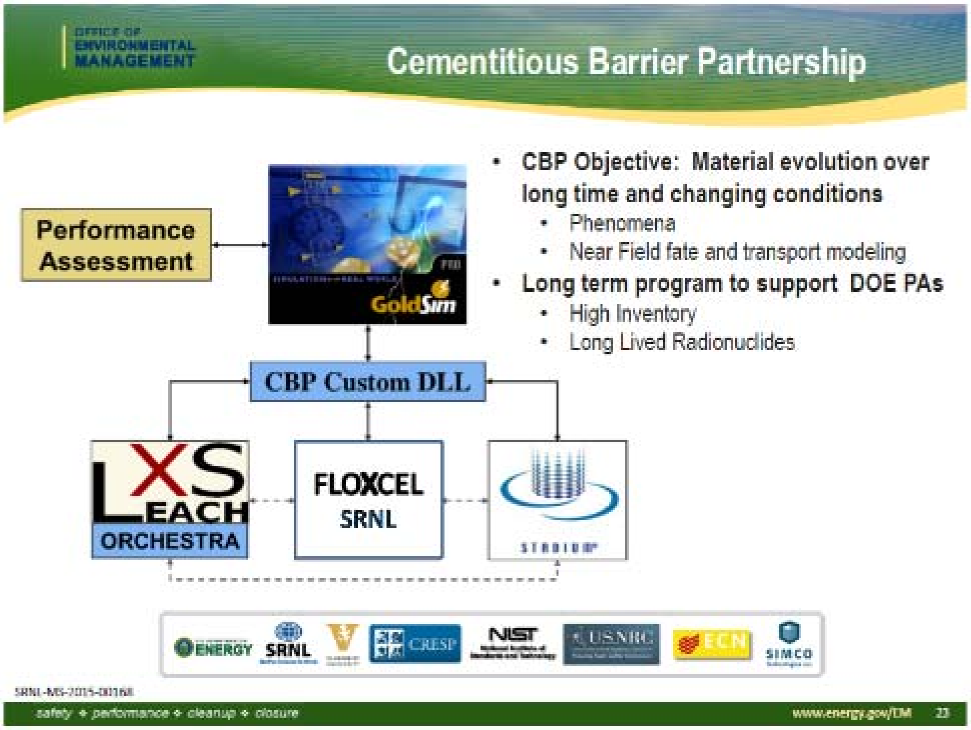
Doc #: **SRNL-MS-2015-00168**
Title: ***DOE Environmental Management Applications of Cementitious Materials***
Authors: **Langton and Hoffman – SRNL**

Presentation:

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Cementitious Barrier Partnership
Performance Assessment
GoldSim
CBP Custom DLL
LXS LEACH
ORCHESTRA
FLOXCEL
SRNL
STADIUM
• CBP Objective: Material evolution over long time and changing conditions
• Phenomena
• Near Field fate and transport modeling
• Long term program to support DOE PAs
• High Inventory
• Long Lived Radionuclides
ENERGY
SRNL
CRESP
NIST
U.S.NRC
ECN
SIMCO
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Summary
• DOE is a leader in innovative cementitious materials and technologies for radioactive/nuclear applications
• Cementitious materials are used in a wide variety of DOE applications, commercial nuclear industry and international nuclear community
– Waste forms
– Containers / Containment structures / Engineered Barriers
– HLW Tank Closure
– In-Situ Decommissioning
– Environmental Restoration
• Materials are tailored to provide performance (both fresh and cured properties) including long term durability
• Emerging needs and unique applications result in new developments and improved understanding
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safety ♦ performance ♦ cleanup ♦ closure
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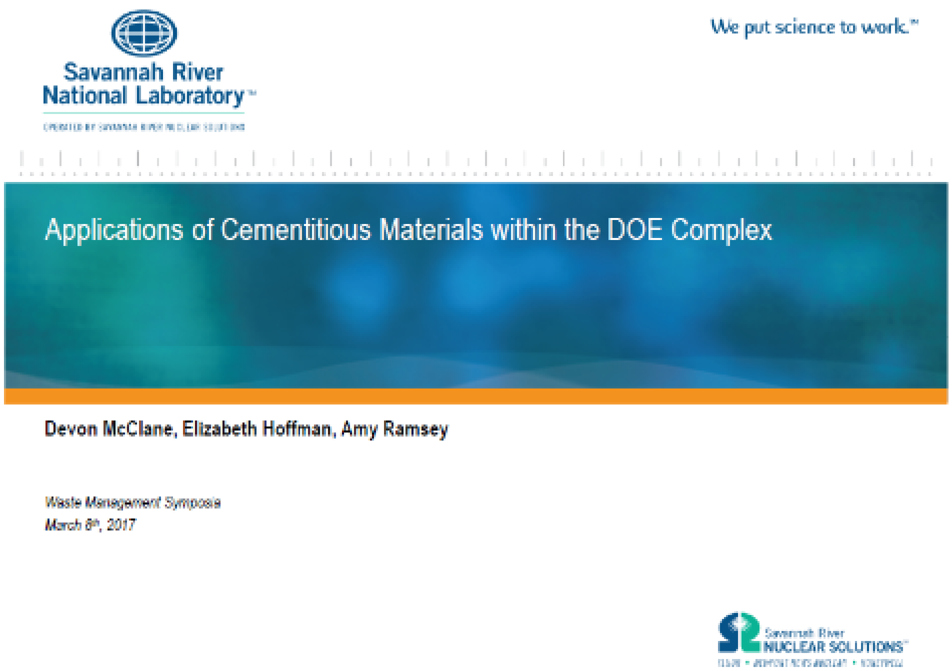
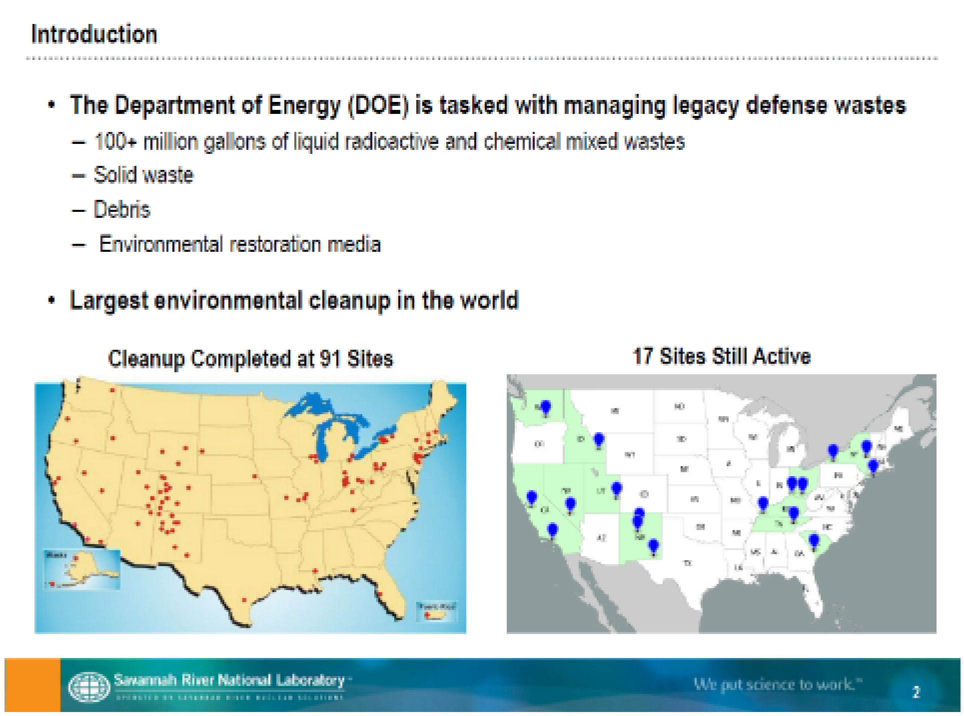
Doc #: **SRNL-MS-2017-00014**
Title: ***Applications of Cementitious Materials Within the DOE Complex***
Authors: **McClane, Hoffman, and Ramsey – SRNL**

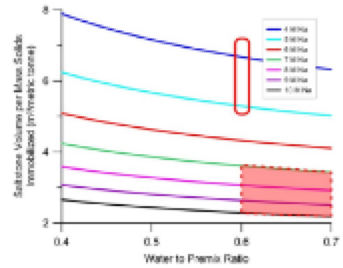
Presentation:

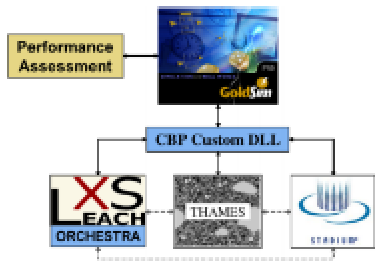




Waste Treatment

- **Focus of the majority of experimental work**
  - Increasing/maximizing waste loading
  - Improving contaminant retention
    - *Tc, I, Hg*
  - Elucidating structural changes
    - *Aging under various environmental conditions*
      - Supports long-term performance modelling efforts
        - *Cementitious Barriers Partnership (CBP)*





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Conclusions

- **To date cementitious materials have been used in a variety of ways for the containment, treatment and disposal of large quantities of waste within the DOE complex.**
  - Applications range from:
    - *Treating waste*
    - *Containing/isolating waste materials*
    - *Closing tanks*
    - *Decommissioning facilities*
    - *Environmental restoration*
  - Significant work has been done to identify the processing/performance parameters required for specific applications
  - Research/modeling efforts have been focused on methods to increase waste loading and predicting and improving long term material performance

- **Cementitious materials have numerous beneficial uses**

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Doc. #: **SRNL-RP-2009-01152**
Title: ***The Cementitious Barriers Partnership (CBP) Project: Task Technical & QA Plan***
Author: **Tim Jones – SRNL**

The Cementitious Barriers Partnership (CBP) Project is a multidisciplinary effort supported by the US DOE to develop a set of tools to improve prediction of the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications over extended time frames (e.g.,>100 years for operating facilities and > 1000 years for waste management) [1]. The CBP partners in addition to the US DOE, are the U.S. Nuclear regulatory Agency (NRC), the National Institute of Standards and Technology (NIST), 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 project is focused on reducing uncertainties associated with current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will support long-term performance predictions and performance-based decision making and are applicable to several of the strategic initiatives in the U. S. Department of Energy (DOE) Environmental Management Engineering & Technology Roadmap [2].

Doc #: **SRNL-RP-2009-01152, R1**
Title: ***Task Technical and Quality Assurance Plan for Cementitious Barriers Partnership - Task 6b. Description of Prototype Reference Cases (U)***
Author: **Tim Jones – SRNL**

The objective of this task is to:
1. Establish an inventory of materials for preparing reference case specimens for testing by the CBP partners and
2. Prepare reference case cementitious materials at the request of the CBP partners.

The reference case scenarios include: a cementitious waste form, vault/basin containment concrete, and tank fill grout. The reference scenarios were developed to provide benchmark data to validate the computational methods and the individual physical models in the contributing modules. Reference materials will be fabricated for property measurements that will be used in the physical modules and physical property test methods will be reviewed and selected for making the property measurements.

Doc. #: **SRNL-RP-2010-00850**
Title: ***Task Technical and Quality Assurance Plan for Development of Leach Methods, Sample Tracking and Archive Storage for Samples Associated with the Cementitious Barriers Program (CBP) (U)***
Author: **Charles Crawford – SRNL**

Draft Environmental Protection Agency (EPA) leach methods for a wide range of solid materials have been made available. SRNL was contacted in January 2010 by EPA personnel in regards to participating in an inter-laboratory study to evaluate the draft leach methods on a standard fly ash solid granular sample. (1) The purpose of such an inter-laboratory project is to establish a data set that can become part of a package submitted to the EPA for a draft test method to be approved. (See http://www.epa.gov/osw/hazard/testmethods/methdev.htm). The EPA requested SRNL to test two of the four draft methods in an initial phase of testing and possibly perform the remaining final two draft EPA methods at a later time. The two draft EPA methods for initial testing, Draft Methods 1313 and 1316 (2,3) covered by this Task Plan, are similar to the EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP). (4) The other two EPA draft Methods involve a flowing leachant method with particulate solids Draft Method 1314, and a monolith sample leaching Draft Method 1315. (5,6)

Savannah River National Laboratory (SRNL) is participating in a Cooperative Research and Development Agreement (CRADA) with the Cementitous Barriers Partnership (CBP). (7,8) The CBP is providing cost sharing for the leach test evaluations as part of the SRNL experimental program to support this project. The two leach tests being evaluated have been proposed by the CBP partners for evaluation of chemical extraction characteristics of cementitious materials.

This TT&QAP also addresses 'cradle to grave' tracking and accounting for various cementitious test samples that arise, and a program for archive sample storage. This task will support the CBP experimental program at SRNL. SRNL will develop an electronic database for managing and tracking the various CBP test samples and relevant data. The sample tracking database will be made available over the CBP FTP site. Facilities and methodologies will be developed for archiving both radioactive and non-radioactive cementitous test samples and materials for a period of up to ten years to support the CBP experimental program. Archiving capabilities will be developed and implemented for cementitious test samples including inerted storage, and storage at constant humidity and temperature (field exposed sample archiving will be addressed separately).

The purpose of this task planning document is to provide details of the activities to be undertaken at SRNL in support of the EPA request for test method evaluation and the CBP project plan tasks. (9) Task 6 of the CBP project plan pertains to 'Description of Prototype Reference Case Materials and Material Management'. Task 12 of the CBP project plan pertains to 'Experimental Program to Support Model Development'. The EPA will provide the standard fly ash samples to be tested under Draft Method 1313 and Draft Method 1316. SRNL will apply these methods under guidance and interaction with EPA personnel. SRNL will develop a cradle-to-grave system for logging, tracking and controlling various cementitious test samples.

Doc. #: **SRNL-STI-2009-00005**
Title: ***Reference Cases for Use in the Cementitious Partnership Project***
Authors: **Langton – SRNL; Kosson, Garrabrants, and Brown – Vanderbilt University**

The Cementitious Barriers Project (CBP) is a multidisciplinary cross cutting project initiated by the US Department of Energy (DOE) to develop a reasonable and credible set of tools to improve understanding and prediction of the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. The period of performance is >100 years for operating facilities and > 1000 years for waste management. The CBP has defined a set of reference cases to provide the following functions: (i) a common set of system configurations to illustrate the methods and tools developed by the CBP, (ii) a common basis for evaluating methodology for uncertainty characterization, (iii) a common set of cases to develop a complete set of parameter and changes in parameters as a function of time and changing conditions, and (iv) a basis for experiments and model validation, and (v) a basis for improving conceptual models and reducing model uncertainties. These reference cases include the following two reference disposal units and a reference storage unit: (i) a cementitious low activity waste form in a reinforced concrete disposal vault, (ii) a concrete vault containing a steel high-level waste tank filled with grout (closed high-level waste tank), and (iii) a spent nuclear fuel basin during operation. Each case provides a different set of desired performance characteristics and interfaces between materials and with the environment. Examples of concretes, grout fills and a cementitious waste form are identified for the relevant reference case configurations.

Doc #: **SRNL-STI-2009-00021**
Title: ***Cementitious Barriers Modeling for Performance Assessments of Shallow Land burial of Low Level Radioactive Waste – 9243***
Author: **Glenn Taylor – SRNL**

The Cementitious Barriers Partnership (CBP) was created to develop predictive capabilities for the aging of cementitious barriers over long timeframes. The CBP is a multi-agency, multi-national consortium working under a U.S. Department of Energy (DOE) Environmental Management (EM-21) funded Cooperative Research and Development Agreement (CRADA) with the Savannah River National Laboratory (SRNL) as the lead laboratory. Members of the CBP are SRNL, Vanderbilt University, the U.S. Nuclear Regulatory Commission (USNRC), National Institute of Standards and Technology (NIST), SIMCO Technologies, Inc. (Canada), and the Energy Research Centre of the Netherlands (ECN). A first step in developing advanced tools is to determine the current state-of-the-art. A review has been undertaken to assess the treatment of cementitious barriers in Performance Assessments (PA).
Representatives of US DOE sites which have PAs for their low-level waste disposal facilities were contacted. These sites are the Idaho National Laboratory, Oak Ridge National Laboratory, Los Alamos National Laboratory, Nevada Test Site, and Hanford. Several of the more arid sites did not employ cementitious barriers. Of those sites which do employ cementitious barriers, a wide range of treatment of the barriers in a PA was present. Some sites used conservative, simplistic models that even though conservative still showed compliance with disposal limits. Other sites used much more detailed models to demonstrate compliance. These more detailed models tend to be correlation-based rather than mechanistically-based. With the US DOE's Low-Level Waste Disposal Federal Review Group (LFRG) moving towards embracing a risk-based, best estimate with an uncertainties type of analysis, the conservative treatment of the cementitious barriers seems to be obviated. The CBP is creating a tool that adheres to the LFRG chairman's paradigm of continuous improvement.

Doc. #: **SRNL-STI-2010-00478**
Title: ***Waste Management 10 Abstract: Cementitious Barriers Partnership Accomplishments and Relevance to the DOE Complex***
Authors: **Langton, Flach, and Burns – SRNL; Kosson, Brown, and Garrabrants – Vanderbilt University; van der Sloot and Meeussen – Netherlands; Garboczi and Snyder – NIST; Samson and Marchand – SIMCO; Suttora and Mallick – U.S. DOE; Esh, Fuhrmann, and Philip – U.S. NRC**

Use and performance of cementitious barriers for waste disposal units are summarized in this paper. Recent work by the Cementitious Barriers Partnership (CBP) provides defensibility and consistency of data and assumptions used for these materials in the Department of Energy (DOE) performance assessments (PAs). The CBP is a multi-disciplinary partnership of DOE, the U.S. Nuclear Regulatory Commission, academia, private sector, and international expertise. The CBP has developed/enhanced a credible set of simulation and modeling tools that predict the structural, hydraulic, and chemical performance of cement barriers used in nuclear applications over extended time frames (e.g., up to or longer than 100 years for operating facilities and longer than 1000 years for waste management). The CBP tools have been structured to reduce the uncertainties of current methodologies for assessing cementitious barrier performance and to increase the consistency and transparency of the assessment process. The bottom line goal of the CBP is to establish a forum for technical collaboration of nationally recognized experts, DOE and NRC for increasing the defensibility and reducing the uncertainty of cementitious barrier performance predictions.
Examples of information provided by the CBP to support DOE operations and regulatory compliance and the accomplishments over the past 2 years are provided. Impacts of this work include: 1) a forum for DOE-NRC technical exchange, 2) material characterization to support PA predictions, 3) reducing uncertainty in PA predictions, 4) establishing base case performance to improve PA predictions, and 5) improving understanding and quantification of moisture and contaminant transport used in PAs. Additional CBP accomplishments include: sponsorship of a national test bed workshop to obtain collaboration in establishing the path forward in obtaining actual data to support future predictions on cementitious barrier performance evaluations, and participation in an International Atomic Energy Agency (IAEA) Cooperative Research Project on the use of cementitious barriers for low-level radioactive waste treatment and disposal.

Doc. #: **SRNL-STI-2010-00735, R2**
Title: ***Cementitious Barriers Partnership Accomplishments and Relevance to the DOE Complex***
Authors: **Langton, Flach, and Burns – SRNL; Kosson, Brown, and Garrabrants – Vanderbilt University; van der Sloot and Meeussen – Netherlands; Garboczi, Bullard, and Stutzman – NIST; Samson and Marchand – SIMCO; Suttora and Mallick – U.S. DOE; Esh, Fuhrmann, and Philip – U.S. NRC**

ABSTRACT
The Cementitious Barriers Partnership (CBP) was initiated to reduce risk and uncertainties in the performance assessments that directly impact U.S. Department of Energy (DOE) environmental cleanup and closure programs. The CBP is supported by the DOE Office of Environmental Management (DOE-EM) and has been specifically addressing the following critical EM program needs: (i) the long-term performance of cementitious barriers and materials in nuclear waste disposal facilities and (ii) increased understanding of contaminant transport behavior within cementitious barrier systems to support the development and deployment of adequate closure technologies. To accomplish this, the CBP has two initiatives: 1) an experimental initiative to increase understanding of changes in cementitious materials over long times (> 1000 years) over changing conditions and 2) a modeling initiative to enhance and integrate a

set of computational tools validated by laboratory and field experimental data to improve understanding and prediction of the long-term performance of cementitious barriers and waste forms used in nuclear applications.

In FY10, the CBP developed the initial phase of an integrated modeling tool that would serve as a screening tool which could help in making decisions concerning disposal and tank closure. The CBP experimental programs are underway to validate this tool and provide increased understanding of how CM changes over time and under changing conditions. These initial CBP products that will eventually be enhanced are anticipated to reduce the uncertainties of current methodologies for assessing cementitious barrier performance and increase the consistency and transparency of the DOE assessment process. These tools have application to low activity waste forms, high level waste tank closure, D&D and entombment of major nuclear facilities, landfill waste acceptance criteria, and in-situ grouting and immobilization of vadose zone contamination.

This paper summarizes the recent work provided by the CBP to support DOE operations and regulatory compliance and the accomplishments over the past 2 years. Impacts of this work include: 1) a forum for DOE-NRC technical exchange, 2) material characterization to support PA predictions, 3) reducing uncertainty in PA predictions, 4) establishing base case performance to improve PA predictions, and 5) improving understanding and quantification of moisture and contaminant transport used in PAs. Additional CBP accomplishments include: sponsorship of a national test bed workshop to obtain collaboration in establishing the path forward in obtaining actual data to support future predictions on cementitious barrier performance evaluations, and participation in an International Atomic Energy Agency (IAEA) Cooperative Research Project on the use of cementitious barriers for low-level radioactive waste treatment and disposal.

CONCLUSIONS

The CBP has made a significant impact in reducing risk and uncertainties in the performance assessments that directly impact U.S. Department of Energy (DOE) environmental cleanup and closure programs. The CBP has developed the initial phase of an integrated modeling tool that would serve as a screening tool. The initial CBP products are anticipated to reduce the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the DOE assessment process. This CBP integrated tool will predict the hydraulic properties and chemical stability of the radionuclides and cement matrix phases and release fluxes of constituents, in response to variable boundary conditions.

The CBP is reducing the uncertainty by coupling multi-scale and multi-physics processes, including physical-chemical evolution and transport phenomena applied to heterogeneous materials with changing boundary conditions. The CBP is characterizing, quantifying and effectively communicating the principal uncertainties. In addition, the CBP experimental program has been designed to provide test data to support chemical and physical degradation mechanisms for cementitious barriers. These tools have application to low activity waste forms, high level waste tank closure, D&D and entombment of major nuclear facilities, landfill waste acceptance criteria, and in-situ grouting and immobilization of vadose zone contamination.

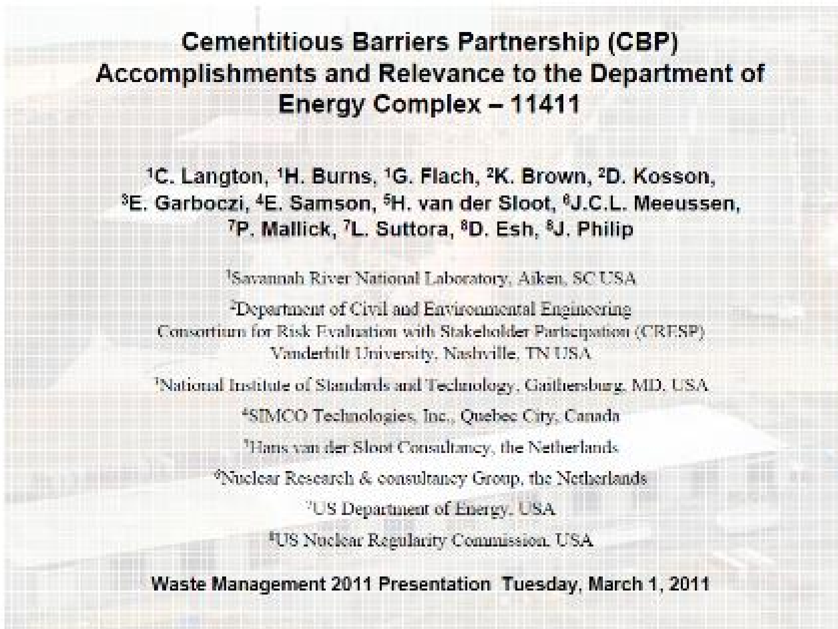
The CBP, in its 2-year existence, has already provided: 1) a forum for DOE-NRC technical exchange, 2) material characterization to support PA predictions, 3) uncertainty reduction in PA predictions, 4) base case performance to improve PA predictions, and 5) improvement in understanding and quantification of moisture and contaminant transport used in PAs. Additional CBP accomplishments include: sponsorship of a national test bed workshop to obtain collaboration in establishing the path forward in obtaining actual data to support future predictions on cementitious barrier performance evaluations, and participation in an International Atomic Energy Agency (IAEA) Cooperative Research Project on the use of cementitious barriers for low-level radioactive waste treatment and disposal.

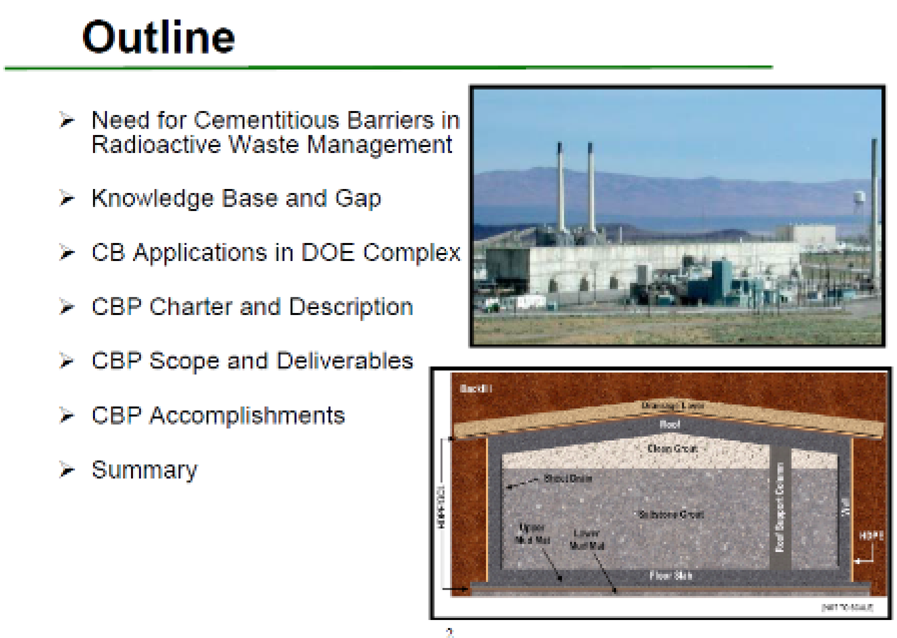
Doc. #: **SRNL-STI-2011-00122-S**

Title: ***Cementitious Barriers Partnership Accomplishments and Relevance to the Department of Energy Complex – 11411***

Authors: **Langton, Burns, and Flach – SRNL; Kosson and Brown – Vanderbilt University; van der Sloot and Meeussen – Netherlands; Garboczi, Bullard, and Stutzman – NIST; Samson – SIMCO; Suttora and Mallick – U.S. DOE; Esh and Philip – U.S. NRC**

Presentation:





Summary of Relevance

- Providing a Forum for DOE-NRC Technical Exchanges
- Providing More Defensible DOE PAs by providing Additional Modeling and Experimental Support
  - Providing Additional Material Characterization to Support PA Predictions
  - Reducing Uncertainty in PA Predictions
  - Establishing Base Case Performance to Improve PA Predictions
- Advancing Understanding of CM Degradation
  - Through Quantification of Moisture and Contaminant Transport for Engineered Barriers in PAs

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Project Mid Point Summary

- CBP is half way through a 5 year project
- Deliverables
  - New Data
  - Reports
  - Publications
  - Enhanced Partner Codes
  - Coupled Sulfate Attack-Damage-Stochastic Analysis Code
  - Integrated Codes that provide stochastic analysis
- End Users
  - DOE Site Operations (SRR, SRNS, MOX) and DOE Complex (PAs)
    - Concrete Vaults for Solid Waste and Saltstone
    - LLW and ILW Components In Grout
    - Tank Closure and Facility Closures
  - ASCEM (DOE Performance Evaluations)
  - NRC and DOE NE
    - Spent Fuel Storage Casks and Pads
    - Next Generation Nuclear Facilities

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Doc. #: **SRNL-STI-2012-00562**
Title: ***Cementitious Materials for SRS Reactor In-Situ Decommissioning***
Authors: **Langton, Stefanko, and Serrato – SRNL**

Presentation:

Cementitious Barrier Business Areas and End Users

- Environmental remediation: soil, basin sludge stabilization
- In-situ Decommissioning of nuclear facilities
- Tank Closure
  - Physical and chemical stabilization
- Liquid aqueous waste treatment / conditioning
  - Decontaminated salt solution from HLW tanks
  - Other aqueous waste streams (MOX)
- Concrete containment structures
  - E-Area solid waste disposal vaults and fills
  - Z-Area Disposal Units
- On Site
  - SRNS (EC&ACP, Solid Waste Disposal)
  - SRR (HLW Tank Closure, Saltstone)
- Off Site
  - Hanford, ORR
  - DOE-EM (Cementitious Barriers Partnership Project)
  - IAEA, TEPCO, and other International End Users
  - University outreach (FIU, USC)

P-Reactor Facility before ISD

SRNL

Feedback / Technology Exchange / Out Reach

- **ISD Sensor Network Test Bed (DOE-EM-13)**
  - **SRNL: Project coordination and technical oversight**
  - **FIU Applied Research Center: Meso-scale test bed host site**
  - **Sensor Network Array**
    - INL: Electrical Resistivity Tomography -Thermocouple and Advanced Tensiometer
    - MSU: Fiber Optic Sensor - Loop Ring-down
    - U of Houston: Fiber Optic Sensor - Bragg Grating & Piezoelectric - Smart Aggregate
    - USC: Piezoelectric - Acoustic Emission & pH

  Demonstrate the feasibility of installing and operating remote sensor networks to assess cementitious material durability and moisture-fluid flow
- **Cementitious Barrier Partnership (EM 31)**
- **SRNS, Hanford, ORR**
- **IAEA Cooperative Research Program**
- **TEPCO, ANSTO**
- **Work force development: 8 Summer Interns**
- **NSF Sustainability Research Network proposal (NWU, USC)**

SRNL

Doc. #: **SRNL-STI-2013-00015**
Title: ***The Cementitious Barriers Partnership (CBP) Software Toolbox Capabilities in Assessing the Degradation of Cementitious Barriers***
Authors: **Flach, Burns, Langton, and Smith III – SRNL; Brown, Kosson, Garrabrants, and Sarkar – Vanderbilt University; van der Sloot and Meeussen – Netherlands; Samson – SIMCO; Mallick and Suttora – U.S. DOE; Esh, Fuhrmann, and Philip – U.S. NRC**

ABSTRACT

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the U.S. Department of Energy (US DOE) Office of Tank Waste and Nuclear Materials Management. The CBP program has developed a set of integrated tools (based on state-of-the-art models and leaching test methods) that help improve understanding and predictions of the long-term structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. Tools selected for and developed under this program have been used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems for periods of performance up to 100 years and longer for operating facilities and longer than 1000 years for waste disposal. The CBP Software Toolbox has produced tangible benefits to the 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 many opportunities to bring defense in depth in prediction of the performance of cementitious barriers over time.

CONCLUSIONS

Components of the CBP Software Toolbox have been used to provide important technical insights to the DOE PA process regarding sulfate attack on the DOE Saltstone Disposal Facility. Current development efforts in the areas of carbonation, gas and liquid phase oxidation of ground blast furnace slag and Tc-99, damage mechanics, and flow and transport in fractured cementitious materials will enable further tangible contributions to DOE PAs.

Doc. #: **SRNL-STI-2013-00118, R2**
Title: ***Degradation of Cementitious Materials Associated with Saltstone Disposal Units***
Authors: **Flach and Smith – SRNL**

The Saltstone facilities at the DOE Savannah River Site (SRS) stabilize and dispose of low-level radioactive salt solution originating from liquid waste storage tanks at the site. The Saltstone Production Facility (SPF) receives treated salt solution and mixes the aqueous waste with dry cement, blast furnace slag, and fly ash to form a grout slurry which is mechanically pumped into concrete disposal cells that compose the Saltstone Disposal Facility (SDF). The solidified grout is termed "saltstone".

Cementitious materials play a prominent role in the design and long-term performance of the SDF. The saltstone grout exhibits low permeability and diffusivity, and thus represents a physical barrier to waste release. The waste form is also reducing, which creates a chemical barrier to waste release for certain key radionuclides, notably Tc-99. Similarly, the concrete shell of a saltstone disposal unit (SDU) represents an additional physical and chemical barrier to radionuclide release to the environment. Together the waste form and the SDU compose a robust containment structure at the time of facility closure. However, the physical and chemical state of cementitious materials will evolve over time through a variety of phenomena, leading to degraded barrier performance over Performance Assessment (PA) timescales of thousands to tens of thousands of years. Previous studies of cementitious material degradation in the context of low-level waste disposal have identified sulfate attack, carbonation influenced steel corrosion, and decalcification (primary constituent leaching) as the primary chemical degradation phenomena of most relevance to SRS exposure conditions.

In this study, degradation time scales for each of these three degradation phenomena are estimated for saltstone and concrete associated with each SDU type under conservative, nominal, and best estimate assumptions. The nominal value (NV) is an intermediate result that is more probable than the conservative estimate (CE) and more defensible than the best estimate (BE). The combined effects of multiple phenomena are then considered to determine the most limiting degradation time scale for each cementitious material. Degradation times are estimated using a combination of analytic solutions from literature and numerical simulation codes provided through the DOE Cementitious Barriers Partnership (CBP) Software Toolbox. Task Technical Requests HLW-SSF-2013-0001 Rev. 3, HLW-SSF-TTR-2013-0021 Rev. 2, and G-TTR-Z-00007 Rev. 0 define the scope of the analysis and certain input data.

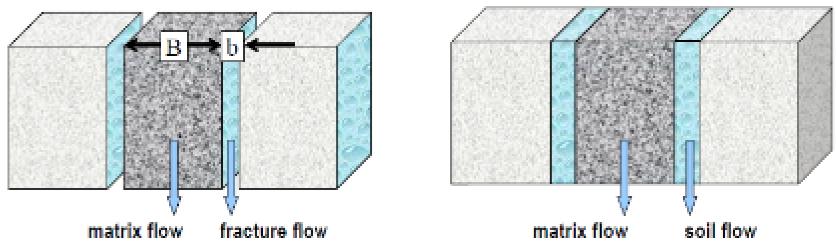
For the SDU 2 design with a clean cap fill, the roof, wall, and floor components are projected to become fully degraded under Nominal conditions at 3855, 922, and 1413 years, respectively. For SDU 4 the roof and floor are estimated to be fully degraded under Nominal conditions after 1106 and 1404 years, respectively; the wall is assumed to be fully degraded at time zero in the most recent PA simulations. Degradation of these concrete barriers generally occurs from combined sulfate attack and corrosion of embedded steel following carbonation. Saltstone is projected to degrade very slowly by decalcification, with complete degradation occurring in excess of 200,000 years for any SDU type. Complete results are provided in Table 5-1 through Table 5-3. Additional results for the SDU 2 and SDU 6 designs are provided in Table 5-5 through Table 5-7 assuming the absence of the traditional clean cap fill and column degradation by carbonation-influenced steel corrosion. For the SDU 6 design, the roof and floor components are projected to fully degrade by 1413 years while the tapered wall fully degrades at 815 years for the thinnest section and 1822 years for the thickest section. Additional degradation results are presented in Table 5-12 through Table 5-16 for SDU 2 and 6 assuming column degradation by sulfate attack.

Doc. #: **SRNL-STI-2014-00042**
Title: ***Unsaturated Hydraulic Properties of Fractured Cementitious Materials***
Author: **Greg Flach – SRNL**

Presentation:

Hydraulic Properties from Fracture – Soil Analogy

- Assume a seam of coarse-grained porous material behaves similar to a fracture



- Define soil fraction (f) by equating saturated hydraulic conductivities

$$\frac{B}{B+b} K_{matrix} + \frac{b}{B+b} K_{fracture} = K_{blend} = (1-f) \cdot K_{matrix} + f \cdot K_{soil}$$

$$f = \frac{K_{blend} - K_{matrix}}{K_{soil} - K_{matrix}}$$

Experimental Validation Based on *Multi-Step Outflow Extraction* Method for Soils

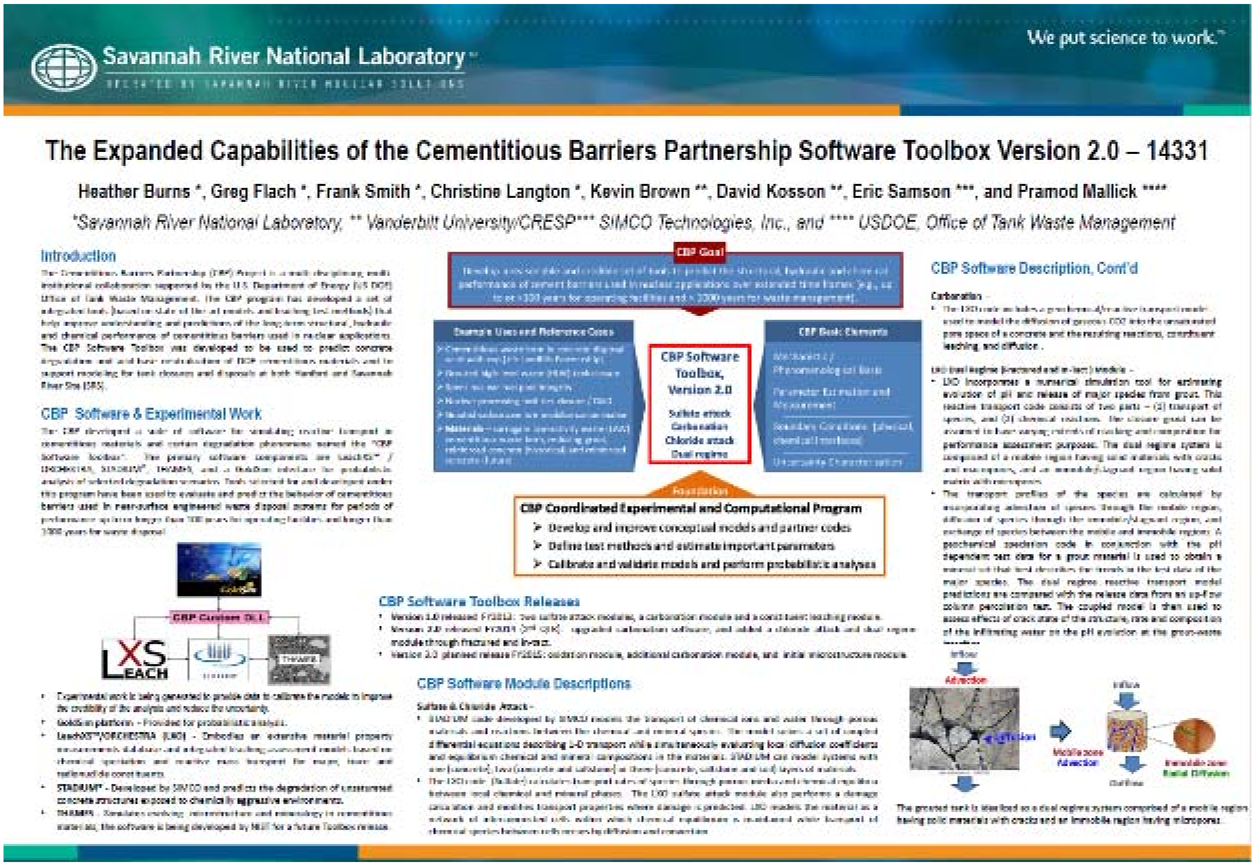
- Method development with Cementitious Barriers Partnership funding

Doc. #: **SRNL-STI-2014-00078**

Title: ***The Expanded Capabilities of the Cementitious Barriers Partnership Software Toolbox Version 2.0 Poster***

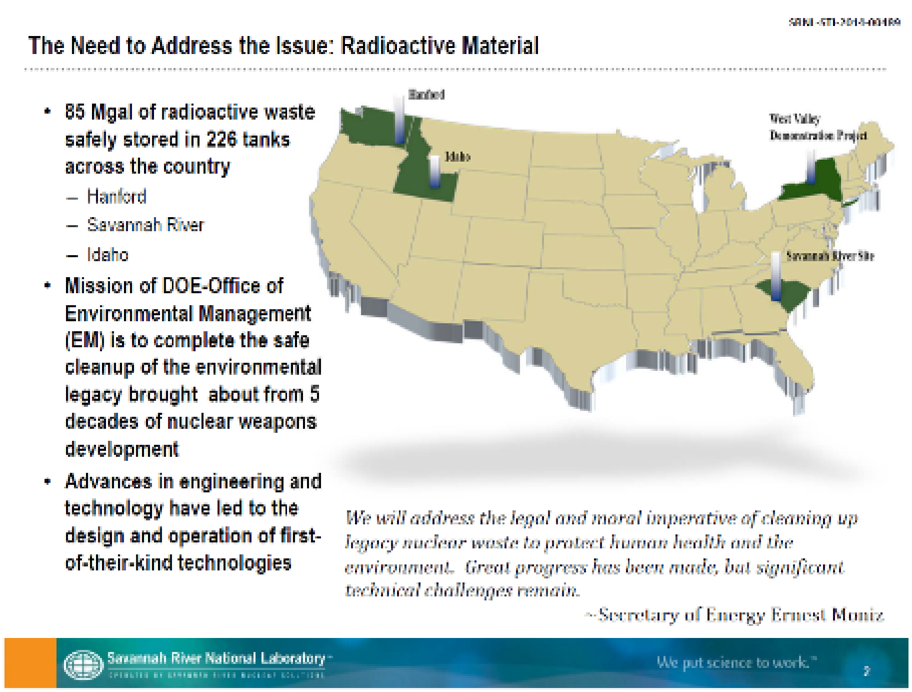
Authors: **Burns, Flach, Smith, and Langton – SRNL; Brown and Kosson – Vanderbilt University/CRESP; Samson – SIMCO; Mallick – U.S. DOE, Office of Tank Waste Management**

Poster:



Doc. #: **SRNL-STI-2014-00489**
Title: ***Cementitious Waste Forms: A Program Overview of Synthesis and Characterization for Radioactive Material Disposal***
Authors: **Hoffman, Cozzi, and Langton – SRNL**

Presentation:



Cementitious Barriers Partnership – Objective and Approach

Objective

- Mechanistic modeling tools and supporting data are needed to predict long-term performance of cementitous materials to provide greater confidence.
- Developing Software for end user support: Released CBP Software Toolbox, Version 2.0 including modules on sulfate attack, carbonation, and cracking
- Integrated experimental programs combining both modeling and experimental data and model validation
- Rigorous uncertainty qualification framework

Approach

- Reference cases – provide basis for comparison and demonstration of CBP tools
- Extension and enhancement of existing tools
- Integrated experimental and modeling program
  - Conceptual model improvements
  - Define test methods and parameter measurements
  - Model validation and experimental data

Cementitious Barriers Partnership – Members and Roles

- Department of Energy – Office of Environmental Management – Tank Waste Management
  - Primary end-user
- Nuclear Regulatory Commission
  - Primary end-user
- Savannah River National Laboratory
  - Performance Assessment Interface
  - Model Integration
  - Experimental Programs
  - Test Beds
- National Institute of Standards and Technology
  - Microstructure Evolution & Properties; Experimental Studies
- SIMCO Technologies, Inc.
  - Physical & Hydraulic Performance; Experimental Studies
- Energy Research Centre of the Netherlands (w/ Nuclear Research Group & Hans van der Sloot Consultancy)
  - Chemical Performance & Constituent Release; Experimental Studies
- Vanderbilt University
  - Chemical Performance & Constituent Release (experimental)
  - Uncertainty Analysis Framework

Doc. #: **SRNL-STI-2015-00022**
Title: ***The Cementitious Barriers Partnership Experimental Programs and Software Advancing DOE's Waste Disposal / Tank Closure Efforts – 15436***
Authors: **Burns, Flach, Smith and Langton – SRNL; Brown and Kosson – Vanderbilt University/CRESP; Samson – SIMCO; Mallick – U.S. DOE**

ABSTRACT
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 1) including:

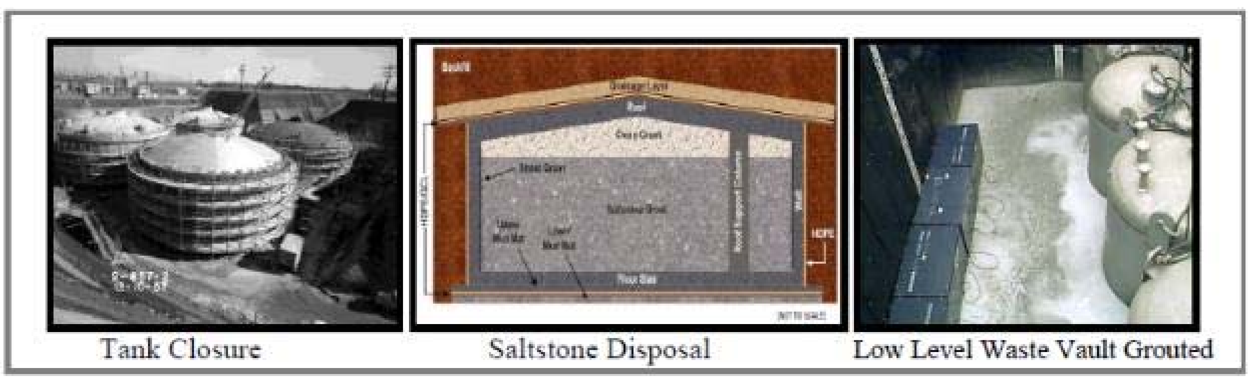


Figure 1: Various DOE Cementitious Barriers in Waste Management

Future SRS Saltstone and HLW tank performance assessments and special analyses

- Hanford site HLW tank closure projects 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.

Doc. #: **SRNL-STI-2015-00190**
Title: ***Development and Demonstration of Material Properties Database and Software for the Simulation of Flow Properties in Cementitious Materials***
Authors: **Smith and Flach – SRNL**

This report describes work performed by the Savannah River National Laboratory (SRNL) in fiscal year 2014 to develop a new Cementitious Barriers Project (CBP) software module designated as FLOExcel. FLOExcel incorporates a uniform database to capture material characterization data and a GoldSim model to define flow properties for both intact and fractured cementitious materials and estimate Darcy velocity based on specified hydraulic head gradient and matric tension. The software module includes hydraulic parameters for intact cementitious and granular materials in the database and a standalone GoldSim framework to manipulate the data. The database will be updated with new data as it comes available. The software module will later be integrated into the next release of the CBP Toolbox, Version 3.0. This report documents the development efforts for this software module.
The FY14 activities described in this report focused on the following two items that form the FLOExcel package:

1) Development of a uniform database to capture CBP data for cementitious materials. In particular, the inclusion and use of hydraulic properties of the materials are emphasized.
2) Development of algorithms and a GoldSim User Interface to calculate hydraulic flow properties of degraded and fractured cementitious materials. Hydraulic properties are required in a simulation of flow through cementitious materials such as Saltstone, waste tank fill grout, and concrete barriers. At SRNL these simulations have been performed using the PORFLOW code as part of Performance Assessments for salt waste disposal and waste tank closure.

SRNL STI doc. #: **SRNL-STI-2015-00210**
Internal doc. #: **CBP-TR-2015-009**
Title: ***Cementitious Barriers Partnership FY2014 End-Year Report***
Authors: **Flach, Langton, Burns, Smith – SRNL; Kosson and Brown – Vanderbilt University/CRESP; Samson – SIMCO; Meeussen, Seignette, and van der Sloot – Netherlands**

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

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

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

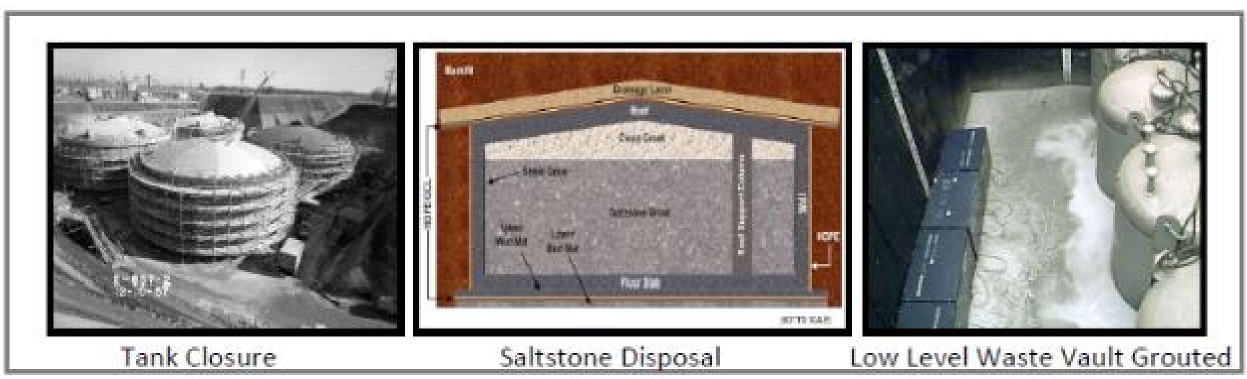


Figure 1: Various DOE Cementitious Barriers in Waste Management

- Future SRS Saltstone and HLW tank performance assessments and special analyses
- Hanford site HLW tank closure projects, secondary waste treatment, and other projects in which cementitious barriers are used
- The Advanced Simulation Capability for Environmental Management (ASCEM) project, which requires source terms from cementitious containment structures as input to their flow simulations

- Regulatory reviews of DOE performance assessments
- Nuclear Regulatory Commission reviews of commercial nuclear power plant (NPP) structures which are part of the overall US Energy Security program to extend the service life of NPPs.

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

- SRNL experimental studies related to Tc mobility indicate that conventional leaching protocols may not be conservative for direct disposal of Tc-containing waste forms in vadose zone environments. These results have the potential to influence the current Hanford supplemental waste treatment flow sheet and disposal conceptual design.
- SRNL mineralogy characterization discussed in this paper illustrates that sodium salt waste form matrices are somewhat similar to but not the same as those found in blended cement matrices which to date have been used in long-term thermodynamic modeling and contaminant sequestration as a first approximation. Utilizing the CBP generated data in long-term performance predictions provides for a more defensible technical basis in performance evaluations.
- In 2014, SIMCO Technologies, Inc. (SIMCO) completed a two phase study with surprising results in the second phase study. The SIMCO experimental work was aimed at supporting the assessment of long-term durability of concrete barriers containing sulfate-bearing salt wasteform, present at both SRS and Hanford. In the Phase 1 experimental study, ordinary Portland cement hydrated cement pastes were exposed to aggressive solutions. In the 2014 Phase II study, the scope was extended to include hydrated cement blend pastes representative of DOE cementitious barrier materials that included slag and flyash. Also, the range of aggressive contact solutions was expanded. The experimental program was aimed at testing aggressive contact solutions that more closely mimic the chemical composition of saltstone pore solution. Phase I experimental results showed that damage does not occur in high pH solutions in the presence of sulfate. However, Phase II results showed that this was not the case (i.e., damage was observed) for concrete barriers that contained additional silica fume.
- Vanderbilt University experimental studies characterized changes in the microstructure and chemical speciation from carbonation in cementitious materials (a primary waste tank degradation mechanism) as a function of material alkalinity and exposure conditions to evaluate the carbonation front, transport of gases, and reaction chemistry. The improved LeachXS/ORCHESTRA carbonation model was then used to assess impact of carbonation on contaminant migration for a representative tank closure scenario.

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

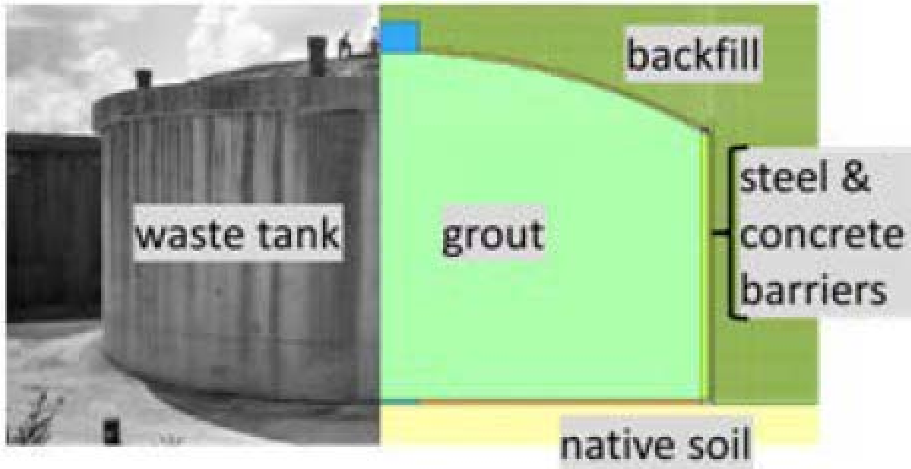


Figure 2: Cementitious Barriers – Tank Integrity and Closure Model Constructs

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

SRNL STI doc. #:	**SRNL-STI-2015-00237**
Internal doc. #:	**CBP-TR-2015-010**
Title:	***Cementitious Barriers Partnership FY2014 End-Year Report***
Authors:	**Flach, Langton, Burns, Smith – SRNL; Kosson and Brown – Vanderbilt University/CRESP; Samson – SIMCO; Meeussen, Seignette, and van der Sloot – Netherlands**

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.

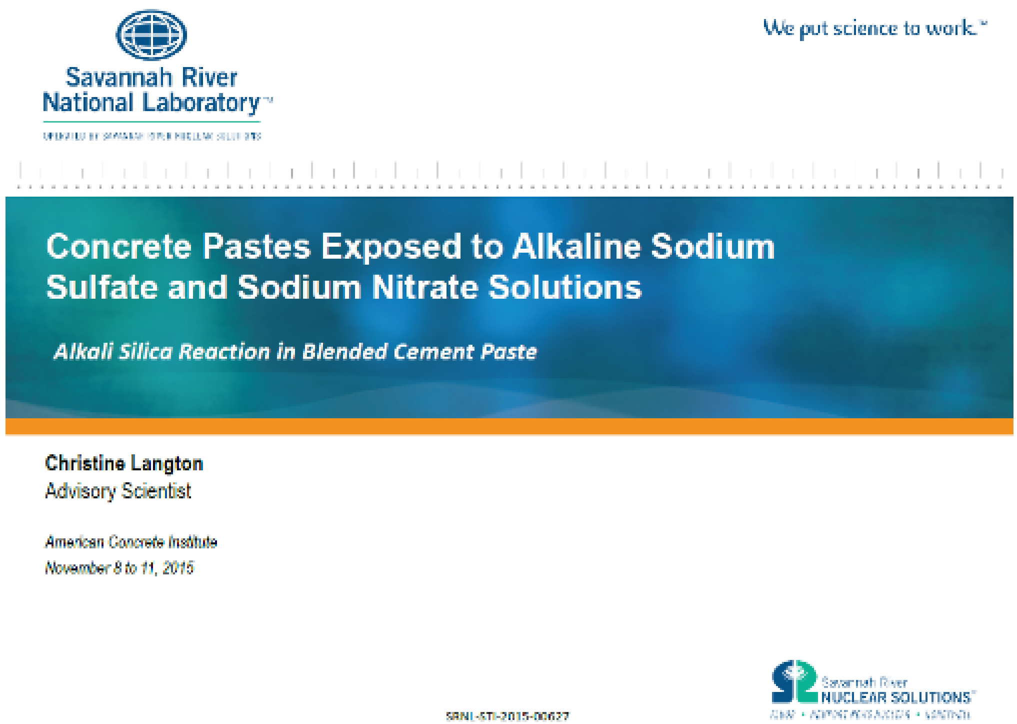
In 2015, the CBP plans to release its newest version, the CBP Software Toolbox – "Version 3.0", which will include new STADIUM carbonation and damage models, a new SRNL module for transport properties and flow in fractured and in-tact cementitious materials, and a new LeachXS/ORCHESTRA (LXO) oxidation module. In addition, improved STADIUM sulfate attack and chloride models will be included.

This is in addition to the LXO modules for sulfate attack, carbonation, constituent leaching, and percolation with radial diffusion (for leaching and transport in cracked cementitious materials), of which will also be improved for Version 3.0. These STADIUM and LXO 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.
In 2015, the Cementitious Barriers Partnership is providing 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 and are currently drafting many reports including six papers that were presented at WM2015:

- **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.

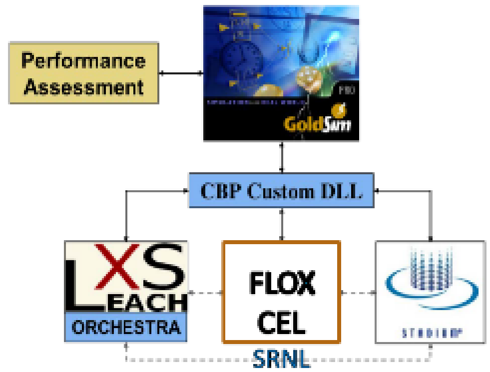
Doc. #: **SRNL-STI-2015-00627**
Title: ***Concrete Pastes Exposed to Alkaline Sodium Sulfate and Sodium Nitrate Solutions - Alkali Silica Reaction Blended Cement Paste***
Author: **Christine Langton – SRNL**

Presentation:



Cementitious Barrier Partnership

- **Material evolution over long time (1000 yr.) and changing conditions**
  - Phenomena
  - Near field fate and transport modeling
- **Support DOE Performance Assessments**
  - High Inventory
  - Long Lived Radionuclides



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Summary

- **Conditions encountered in radioactive waste disposal scenarios can be significantly different than conditions on which engineering codes and standards are based**
- **Durability of concrete and other cementitious materials used for radioactive waste containment must be evaluated for chemical environments expected in the disposal setting.**
- **Concrete paste bulk oxide composition is an important parameter in understanding chemical degradation and durability**
  - The effect of pozzolans and supplemental cementitious materials on bulk oxide composition should be evaluated for unusual exposure environments
  - Higher $(CaO + MgO) / (SiO_2 + Al_2O_3)$ result in better chemical durability in highly alkaline environments typical of legacy salt waste solutions and cement waste forms
  - Alkali silica reaction of the binder was observed in binders with low a (0.8) $(CaO + MgO) / (SiO_2 + Al_2O_3)$ after 3 and 8 months immersion in (a) NaOH, Na_2SO_4 and (b) NaOH + Na_2SO_4 + $NaNO_3$ solutions
  - $NaNO_3$ in the immersion solution accelerated deterioration

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Doc. #: **SRNL-STI-2016-00638**
Title: ***CRADA Final Report for CRADA No. CR-08-001 Cementitious Barriers Partnerships***
Authors: **Burns, Langton, and Flach – SRNL**

The Cementitious Barriers Partnership (CBP), led by the Savannah River National Laboratory, has achieved its ultimate purpose to support progress in final treatment and disposal of legacy waste and closure of High-Level Waste (HLW) tanks in the DOE complex. The CBP achieved its goal by developing experimental programs with results that supported the development of a reasonable and credible set of software tools to improve understanding and prediction of the structural, hydraulic and chemical performance of cementitious barriers and waste forms used in nuclear applications. These experimental data and software tools are and will continue to reduce the uncertainties in the current methodologies for assessing cementitious barrier performance and increase the consistency and transparency of the assessment process. The CBP has made a significant impact in reducing risk and uncertainties in the performance assessments that directly impact U.S. Department of Energy (DOE) environmental cleanup and closure programs. The CBP has developed an experimentally-based, integrated modeling tool that serves as a screening tool known as the CBP Software Toolbox, Version 3.0. The CBP products reduce the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the DOE assessment process. This CBP Software Toolbox predicts the hydraulic properties and chemical stability of cement matrix phases and release fluxes of constituents, in response to variable boundary conditions. Therefore, the CBP tools are reducing the uncertainty by coupling multi-scale and multi-physics processes, including physical-chemical evolution and transport phenomena applied to heterogeneous materials with changing boundary conditions. In addition, the CBP Experimental and Characterization Program has provided test data to support chemical and physical degradation mechanisms for cementitious barriers. These tools have application to low activity waste forms, high level waste tank closure, D&D and entombment of major nuclear facilities, landfill waste acceptance criteria, and in-situ grouting and immobilization of vadose zone contamination.
The CBP also provided: 1) a forum for DOE-NRC technical exchange, 2) material characterization to support performance assessment (PA) predictions, 3) uncertainty reduction in PA predictions, 4) base case performance to improve PA predictions, and 5) improvement in understanding and quantification of moisture and contaminant transport used in PAs. Additional CBP accomplishments include: sponsorship of a national test bed workshop to obtain collaboration in establishing the path forward to obtain actual data supporting future predictions of cementitious barrier performance, and participation in an International Atomic Energy Agency (IAEA) Cooperative Research Project on the use of cementitious barriers for low-level radioactive waste treatment and disposal.

Doc. #: **SRNL-STI-2016-00689, R1**
Title: ***Applications of Cementious Materials Within the DOE Complex***
Authors: **McClane, Langton, and Hoffman – SRNL**

ABSTRACT
Cementitious materials are used in a variety of ways for the disposal of waste. This document explores some of these applications and acts as a review on how cementitious materials have been used in the nuclear waste industry, across several Department of Energy (DOE) complexes. Specifically, this document highlights formulations, installations, experimental work, and modeling efforts supported by a variety of DOE programs and focuses on how/where cementitious materials are: used in deactivation and decommissioning (D&D) of reactors, used in the closure of tanks, used to produce containment structures, and how they are used to treat waste streams. In addition to these topics, the material requirements and expected future research needs are discussed.

Degradation
Since it is necessary to ensure waste is properly contained for up to thousands of years, it has been deemed critical to understand how/why the cementitious waste forms and structural barriers degrade. Because of this importance, there have been numerous studies on a wide variety of exposure conditions that have investigated the chemistry of the materials [49-53] as well as the influence of radiation [54, 55].
Much of the work on degradation in support of long term modeling has been conducted under the cementitious barriers partnership (CBP). For example Langton et al. investigated the phases that formed within the cementitious waste form to provide a basis for the starting compositions utilized within software models [49], and Kubilius et al. investigated gas transport through a cementitious material [53].
The most common forms for degradation within a cementitious material include: cracking (chemical and thermal), alkali-silica reactions, sulfate attack, and carbonation [4, 56-58]. In an attempt to further understanding on long-term performance, several organizations (including SIMCO and CRESP) have developed various models for predicting this performance for a given cementitious material [56, 57, 59-61].

Doc. #:	**SRNS-STI-2008-00097**
Title:	***Development of Reference Cases for Use in the Cementitious Barriers Partnership Long Term Performance Evaluation***
Authors:	**Langton – SRNL; Kosson and Garrabrants – Vanderbilt University**

The U.S. DOE has initiated a multidisciplinary cross cutting project, Cementitious Barriers Partnership Project, to develop a reasonable and credible set of tools to predict the structural, hydraulic and chemical performance of cement barriers used in nuclear applications over extended time frames (e.g., >100 years for operating facilities and > 1000 years for waste management). The results of this project will enable improved risk informed, performance-based decision making, and supports several of the strategic initiatives in the U. S. Department of Energy's (DOE's) Environmental Management Engineering & Technology Roadmap.

A set of reference cases are being defined for the CBP project to serve the following functions: (i) provide a common set of examples to illustrate use of methods and tools developed, (ii) provide a basis of comparison to evaluate reductions in uncertainty achieved through use of improved methods and tools by comparison evaluations of the same cases using current approaches, (iii) provide a common set of cases to develop a complete parameter set, and (iv) to provide a basis for improving conceptual models by comparison with laboratory and field data.
The three reference cases being defined are (i) a cementitious low activity waste form in a reinforced concrete disposal vault, (ii) grouting of a high-level waste tank for closure, (iii) a spent nuclear fuel pool. Each case provides a different set of desired performance characteristics and interfaces between materials and with the environment. The primary materials being used as reference materials are (i) a simulated waste form, (ii) reinforced concrete designs typical of historic and future construction, and (iii) a reducing grout. Various levels of system abstraction are required to achieve desired evaluations. The rationale for selection of each reference case, reference case specifications, and approaches to model abstraction will be discussed in this paper.

Doc. #: **SRNS-STI-2014-00019**
Title: ***The Expanded Capabilities of the Cementitious Barriers Partnership Software Toolbox Version 2.0 – 14331***
Authors: **Burns, Flach, Smith, and Langton – SRNL; Brown and Kosson – Vanderbilt University/CRESP; Samson – SIMCO; Mallick – U.S. DOE**

ABSTRACT
The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the U.S. Department of Energy (US DOE) Office of Tank Waste Management. The CBP program has developed a set of integrated tools (based on state-of-the-art models and leaching test methods) that help improve understanding and predictions of the long-term structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. The CBP Software Toolbox – "Version 1.0" was released early in FY2013 and was used to support DOE-EM performance assessments in evaluating various degradation mechanisms that included sulfate attack, carbonation and constituent leaching. The sulfate attack analysis predicted the extent and damage that sulfate ingress will have on concrete vaults over extended time (i.e., > 1000 years) and the carbonation analysis provided concrete degradation predictions from rebar corrosion. The new release "Version 2.0" includes upgraded carbonation software and a new software module to evaluate degradation due to chloride attack. Also included in the newer version are a dual regime module allowing evaluation of contaminant release in two regimes – both fractured and un-fractured. The integrated software package has also been upgraded with new plotting capabilities and many other features that increase the "user-friendliness" of the package. Experimental work has been generated to provide data to calibrate the models to improve the credibility of the analysis and reduce the uncertainty. Tools selected for and developed under this program have been used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems for periods of performance up to or longer than 100 years for operating facilities and longer than 1000 years for waste disposal. The CBP Software Toolbox is and will continue to produce tangible benefits to the working DOE Performance Assessment (PA) community.

CONCLUSIONS
The CBP Software Toolbox has been used to provide important technical insights to the DOE PA process regarding sulfate attack on the DOE Saltstone Disposal Facility and carbonation on a typical high-level waste tank. Current development efforts in the areas of carbonation, transport in fractured and intact media, and chloride attack have resulted in the second release of the Toolbox. Future development efforts on gas and liquid phase oxidation of ground blast furnace slag and Tc-99 mobility, damage mechanics, and flow and transport in fractured cementitious materials will enable further tangible contributions to DOE PAs and future upgrades of the CBP Toolbox.
Since the 2009 CBP review of DOE PAs, the influence of carbonation on the corrosion rate of steel embedded within cementitious materials has been identified by the CBP as another critical need for improved predictive capabilities. Embedded steel occurs in the common form of reinforcing bar (rebar) material, and as the primary tank liner in the context of DOE liquid radioactive waste tank closures. Damage to cementitious barriers and waste forms is considered a primary degradation phenomenon in many DOE applications. In response, development efforts to add carbonation modules to the CBP Software Toolbox began in 2012 and the initial Toolbox release includes one based on LeachXS™/ORCHESTRA. Refinement of that module was realized in the Version 2.0 release and addition of a STADIUM®-based module is anticipated in FY2014.
Recognizing that physical damage to cementitious materials typically occurs in the form of cracking, ongoing CBP development efforts are also focused on predicting damage through fracture mechanics considerations, determining the hydraulic and transport properties of fractured materials, and implementing corresponding Toolbox simulation capabilities. Version 2.0 includes software that differentiates transport through a dual regime of fractured and intact cementitious material. Future versions of the Toolbox

anticipated in FY2014 will include software that calculates the unsaturated hydraulic properties of fractured and intact media.

Doc. #: **WSRC-STI-2008-00055**
Title: ***Partnership for the Development of Next Generation Simulation Tools to Evaluate Cementitious Barriers and Materials Used in Nuclear Application – 8388***
Authors: **Langton and Dimenna – SRNL; Suttora and Chee – U.S. DOE (EM-20); Esh, Fuhrmann, and Philip – U.S. NRC; Kosson, Mahadevan, and Garrabrants – Vanderbilt University/CRESP; van der Sloot, Comans, Meeussen, and Seignette – Netherlands; Garboczi and Snyder – NIST; Samson and Marchand – SIMCO**

ABSTRACT
The US DOE has initiated a multidisciplinary cross cutting project to develop a reasonable and credible set of tools to predict the structural, hydraulic and chemical performance of cement barriers used in nuclear applications over extended time frames (e.g., >100 years for operating facilities and > 1000 years for waste management). A partnership that combines DOE, NRC, academia, private sector, and international expertise has been formed to accomplish the project objectives by integrating existing information and realizing advancements where necessary.
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., waste forms, containment structures, entombments and environmental remediation, including decontamination and decommissioning (D&D) activities. The simulation tools will also support analysis of structural concrete components of nuclear facilities (spent fuel pools, dry spent fuel storage units, and recycling facilities, e.g., 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 (waste form 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.
This is a national issue that affects all waste disposal sites that use cementitious waste forms and structures, decontamination and decommissioning activities, service life determination of existing structures, and design of future public and private nuclear facilities. The problem is difficult because it requires projecting conditions and responses over extremely long times. Current performance assessment analyses show that engineered barriers are typically the primary control to prevent the release of radionuclides from nuclear facilities into the environment. In the absence of an adequate predictive tool, assessments cannot fully incorporate the effectiveness of the concrete barriers, and the inventory of radionuclides (especially the long-lived radionuclides) that may be safely disposed of in shallow land disposal and the predicted service life of operating nuclear facilities.
This project is a 5-year effort focused on reducing uncertainties associated with 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 supports several of the strategic initiatives in the DOE-EM Engineering & Technology Roadmap.

CONCLUSIONS
In 2007 the US DOE formed the Cementitious Barriers Partnership to identify scope for a multidisciplinary cross cutting project to develop a reasonable and credible set of tools to predict the structural, hydraulic and chemical performance of cement barriers used in nuclear applications over extended time frames (e.g., >100 years for operating facilities and > 1000 years for waste management). A project plan was developed which

supports several of the strategic initiatives identified as part of the DOE-EM Engineering & Technology Roadmap. Work on the five-year project is expected to begin in the second quarter of FY08.

Doc. #: **WSRC-STI-2008-00056, R2**
Title: ***Project Plan for the Partnership for the Development of Next Generation Simulation Tools to Evaluate Cementitious Barriers and Materials Used in Nuclear Applications (Cement Barriers Partnership)***
Author: **Christine Langton – SRNL**

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Consortium for Risk Evaluation with Stakeholder Participation/ Vanderbilt University
Energy Research Centre of the Netherlands
SIMCO, Inc.
Savannah River National Laboratory

ABSTRACT
The objective of this project is to develop a reasonable and credible set of tools to predict the structural, hydraulic and chemical performance of cement barriers used in nuclear applications over extended time frames (e.g., >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., waste forms, containment structures, entombments and environmental remediation, including decontamination and decommissioning (D&D) activities. The simulation tools will also support analysis of structural concrete components of nuclear facilities (spent fuel pools, dry spent fuel storage units, and recycling facilities, e.g., 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 (waste form 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.
A multidisciplinary partnership of DOE, NRC, academia, private sector, and international expertise has been formed to accomplish the project objectives by integrating existing information and realizing advancements where necessary. This project is a 5-year effort focused on reducing uncertainties associated with 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 supports several of the strategic initiatives in the DOE-EM Engineering & Technology Roadmap.