

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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Cementitious Grout for Closing SRS High Level Waste Tanks - #12315

C. A. Langton, D. B. Stefanko, and H. H. Burns, Savannah River National Laboratory
J. Waymer and W. B. Mhyre, URS Quality and Testing
J. E. Herbert and J. C. Jolly, Jr., Savannah River Remediation,
Savannah River Site, Aiken, SC 29808

ABSTRACT

In 1997, the first two United States Department of Energy (US DOE) high level waste tanks (Tanks 17-F and 20-F: Type IV, single shell tanks) were taken out of service (permanently closed) at the Savannah River Site (SRS). In 2012, the DOE plans to remove from service two additional Savannah River Site (SRS) Type IV high-level waste tanks, Tanks 18-F and 19-F. These tanks were constructed in the late 1950's and received low-heat waste and do not contain cooling coils. Operational closure of Tanks 18-F and 19-F is intended to be consistent with the applicable requirements of the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and will be performed in accordance with South Carolina Department of Health and Environmental Control (SCDHEC).

The closure will physically stabilize two 4.92E+04 cubic meter (1.3 E+06 gallon) carbon steel tanks and isolate and stabilize any residual contaminants left in the tanks. The closure will also fill, physically stabilize and isolate ancillary equipment abandoned in the tanks. A Performance Assessment (PA) has been developed to assess the long-term fate and transport of residual contamination in the environment resulting from the operational closure of the F-Area Tank Farm (FTF) waste tanks.

Next generation flowable, zero-bleed cementitious grouts were designed, tested, and specified for closing Tanks 18-F and 19-F and for filling the abandoned equipment. Fill requirements were developed for both the tank and equipment grouts. All grout formulations were required to be alkaline with a pH of 12.4 and chemically reduction potential (Eh) of -200 to -400 to stabilize selected potential contaminants of concern. This was achieved by including Portland cement and Grade 100 slag in the mixes, respectively.

Ingredients and proportions of cementitious reagents were selected and adjusted, respectively, to support the mass placement strategy developed by closure operations. Subsequent down selection was based on compressive strength and saturated hydraulic conductivity results. Fresh slurry property results were used as the first level of screening. A high range water reducing admixture and a viscosity modifying admixture were used to adjust slurry properties to achieve flowable grouts. Adiabatic calorimeter results were used as the second level screening. The third level of screening was used to design mixes that were consistent with the fill material parameters used in the F-Tank Farm Performance Assessment which was developed to assess the long-term fate and transport of residual contamination in the environment resulting from the operational closures.

INTRODUCTION

Cementitious grout will be used to close Tanks 18-F and 19-F. The functions of the grout are to: 1) physically stabilize the final landfill by filling the empty volume in the tanks with a non-compressible material, 2) provide a barrier for inadvertent intrusion into the tank, and 3) reduce contaminant mobility by a) limiting the hydraulic conductivity of the closed tank, b) reducing contact between the residual waste and infiltrating water, and 4) providing an alkaline, chemically reducing environment in the closed tank to control speciation and solubility of selected radionuclides.

Objective

The objective of this work was to identify a single (all-in-one) grout to stabilize and isolate the residual radionuclides in the tank, provide structural stability of the closed tank and serve as an inadvertent intruder barrier.

Background

The FTF is located in the General Separations Area (GSA) of the Savannah River Site (SRS). The FTF includes twenty-two waste tanks constructed between 1951 and 1976. The layout of the SRS F-Area high level waste tank farm is provided in Figure 1. Waste removal operations are currently in progress in F Tank Farm to support closure of the non-compliant tanks in accordance with the Federal Facility Agreement (FFA) closure schedule. Heel removal and characterization in Tanks 18-F and 19-F are complete.

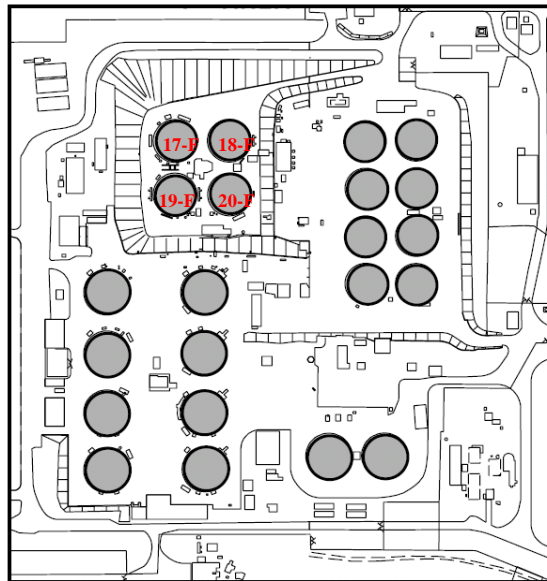


Figure 1. General Layout of the SRS FTF.

Previous SRS Tank Grout Mix Designs

In 1997, two single-shell carbon steel tanks (17-F and 20-F) in the FTF were emptied and filled with grout. Both tanks had a capacity of 1.3 million gallons and were originally used to store low-heat waste. The original concept was to use three different grouts in the closure concept: a high strength reducing grout to encapsulate the residual waste at the bottom of the tank, a Controlled Low-Strength Material (CLSM)¹ for filling the bulk of the tank and, a 2000 psi grout as an intruder barrier in the top of the tank. The high strength reducing grout was designed at the Construction Technology Laboratory, Skokie, IL.

¹ 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.

The common CLSM and 2000 psi grout mixes were modified at SRNL to eliminate bleed water.² Ingredients in the grouts used to fill Tanks 17-F and 18-F are listed in Table 1 [1]. In 2007, 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 [2].

Table 1. SRS Tank Closure Grout Mix Designs from the 1990's [2].

Ingredients		Tanks 17-F and 20-F 1997			1998 All-In-One (modification of 1997 flowable fill)	2007 Alternative All-In-One Study
		SRS Reducing Grout	SRS Zero- Bleed Flowable Fill	SRS Zero- Bleed 2000 psi Grout	SRS All-In One Zero Bleed Reducing Fill/Grout [#] OPCEXE-X-P-0-BS	All-In-One Mix 070070 [2]
Portland Cement Type I/II	lbs/cyd kg/m ³	1353 803	150 89	550 326	75 44	185 110
Slag Grade 100 (lbs / cu yd)	lbs/cyd kg/m ³	209 124	---	---	210 125	260 154
Fly Ash, Class F (lbs / cu yd)	lbs/cyd kg/m ³	---	500 297	---	375 222	850 504
Silica Fume (lbs / cu yd)	lbs/cyd kg/m ³	90 53	---	---	---	---
Quartz Sand ASTM C-33	lbs/cyd kg/m ³	1625 964 (masonry sand)	2300 1365 (concrete sand)	2285 1356 (concrete sand)	2300 1365 (concrete sand)	942 559 (concrete sand)
ASTM C-33 No. Stone 3/8 inch Crushed Granite	lbs/cyd kg/m ³	---	---	---	---	946 561
Water	gal/cyd (lbs/cyd) (kg/m ³)	86.4 (721) (428)	63 (526) (312)	65 (542) (322)	60 (500) (297)	61 (506) (300)
HRWR	(fl oz./ cyd)	250	90* Adva Flow	140 Adva Flow	90* Adva Flow	54 Adva Flex
Viscosifier Kelco-crete [®]	grams/cu yd	---	275	275	275	216
Set Retarder (Hydration Stabilizer)	fl oz./ cyd	150	---	---	---	Up to 4 Recover As required
Sodium Thiosulfate	Lbs/cyd	2.1	---	---	2.1 (optional)	2.1 (optional)

* Advaflow and Kelco-crete[®] were premixed prior to incorporation in the zero-bleed mixes rather than adding as individual components.

Mix was adopted for the Reducing CLSM, Mix No OPCEXE-X-P-0-BS, listed in the SRS Concrete Specification.

This report summarizes testing performed to design new grout formulations and incorporates lessons learned during the SRS reactor facility In-Situ Decommissioning. The new grouts combine features of the flowable, zero bleed structural fill mix that was used in the successful SRS reactor closure projects with chemical features (stabilizing grout) and strength requirements (capping grout) of the All-In-One tank closure grout concept.

² Eliminating bleed water resulted in eliminating the need for removing and disposing of radioactively contaminated liquid from the tanks. It also reduced settling and stratification which resulted in improved cured properties. Bleed water is not a problem when these materials are used in conventional soil backfill applications where the water can drain off or evaporate.

TANK 18-F AND 19-F GROUT PA ATTRIBUTES AND REQUIREMENTS

The important attributes of the cured tank fill materials, with respect to properties that control leaching (permeability and chemistry), are listed below in a general order of priority:

- A. Low water infiltration (conductivity) through the in-place grout, over the long term
- B. High reducing capacity, over the long term
- C. High long term strength of in-place grout
- D. Low long term cracking
- E. Low long term degradation of the in-place grout
- F. Adequate flowability of the grout during placement.

These attributes were combined with and interpreted in terms of engineering properties to derive general engineering parameters.

Fresh Properties

Fresh property requirements are listed in Table 2. In addition to these properties, the tank fill grout must be batched using demonstrated productions techniques and equipment, delivered in 8 to 10 cubic yard concrete delivery trucks, and pumped up to 1000 feet through 4 inch lines.

Table 2. Fresh property requirements, test methods, and bases for requirements.

Property	Requirement	Test	Basis
Fresh Slurry Properties			
Slump-Flow, Laboratory (inches) (cm)	24 to 28 61-71	ASTM C1611	SRNL / SRNS Reactor Facility Closure Experience
Initial Flow (inches) (cm)	≥ 10.5 ≥ 26.7	ASTM D6103	SRNL / SRS Tank 17-F and 20-F Closure Experience
Static Flow performed after 30 minutes static conditions (inches)	≥ 8 20.3	SRNL Modified ASTM D6103	SRNL / SRNS Reactor Facility Closure Experience
Air Content (vol. %)	≤ 8	ASTM C231	SRNL / SRNS Reactor Facility Closure Experience
Set Time (hr.)	< 24	Modified ASTM C403 or Ultrasonic Pulse Velocity method	SRNL / SRNS Reactor Facility Closure Experience
Bleed water after 24 hr (vol. %)	0	ASTM C232	SRNL / SRNS Reactor Facility Closure Experience. ³
Wet Unit Weight (lbs/cu ft)	No requirement	ASTM C138	Value required for QC
Maximum temperature during curing (°C)	65	Calculated from adiabatic calorimeter data, specific heat and thermal conductivity	SRR Operations input in order to manage moisture evaporation during filling and temperature transients during curing.
Specific Heat	No requirement	SRNL Method	Values used in temperature rise calculation and thermal transient modeling
Thermal Conductivity			
Slurry pH	≥ 12.4	> 75 lbs Portland cement/cyd > 44 kgs Portland cement/m ³	2007 FTF PA* High alkalinity is consistent with the waste tank operating conditions and does not require further analysis for tank corrosion and residual solubility

* Equal to or more conservative than values in 2007 Material Property Data Package for the FTF PA [5].

³ Zero bleed eliminates the need for liquid removal. The requirement in the TTR, < 0.5 vol. %, could result in over 6,500 gallons of free liquid.

Cured Physical Properties

Cured physical property requirements for tank fill grout, test methods and the bases for these requirements are provided in Tables 3. There are no specific requirements for the values of effective porosity, dry bulk density, and particle density, because it is not clear what values would be conservative relative to PA modeling. However these properties must be measured for the cured grout in order to provide actual values as required for PA modeling of the closed tank conditions.

Chemical degradation of all of the concrete barriers considered in the SRS tank closure performance assessments was addressed elsewhere [4]. New (improved) mix designs are expected to be more durable than those evaluated provided that the chemical features (Portland cement and slag proportions) are the same or higher and the hydraulic/transport properties are better with respect to reducing moisture transport than those for the grouts used to close Tanks 17- and 20-F.

Table 3. Cured property requirements, test methods and bases for requirements.

Property	Requirement	Test	Basis
Cured Properties			
Compressive Strength (psi)	≥ 2000 at 28 days (≥ 13.8 MPa)	ASTM C39	2007 FTF PA*
	≥ 2000 at 90 days (≥ 13.8 MPa)	ASTM C39	Engineering Design and Quality Control Criteria
Effective Porosity (vol. %)	Measure for input to closure PA	Modified ASTM C642	2007 FTF PA*
Dry Bulk Density (g/cm ³)	Measure for input to closure PA	Modified ASTM C642	2007 FTF PA*
Particle Density (g/cm ³) (Averaged particle density)	Calculate for input to closure PA	Calculated from porosity and dry bulk density ⁴	2007 FTF PA*
Dimensional Stability Shrinkage	TBD	TBD	Relevant to PA
Cracks	TBD	TBD	Relevant to PA
Alkalinity of water in contact with sample cured for 90 days	pH ≥ 12.4 ≥ 75 lbs/cyd ≥ 44 kg/m ³ Portland cement	QC ≥ 75 lbs/cyd ≥ 44 kg/m ³ Portland cement	2007 FTF PA*
Reducing Capacity	Eh ~ -200 to -400 mV ≥ 210 lbs/cyd ≥ 125 kg/m ³ Slag	Quality Control ≥ 210 lbs/cyd ≥ 125 kg/m ³ Slag	2007 FTF PA*
Durability	Minimize potential for chemical degradation	Degradation rate analysis	2007 FTF PA*

Shaded parameters are used in the FTF PA model [3].

* Equal to or more conservative than values in 2007 Material Property Data Package for the FTF PA [5].

Cured Transport (Hydraulic) Properties

The properties needed to parameterize the fate and transport code used for the Performance Assessment (PORFLOW[®]) are listed in Tables 4 and 5. More than one test method is applicable to some transport

⁴ The particle density for these materials is calculated based upon the porosity and dry bulk density per the following equation:
 $\rho_p = \rho_b / (1 - (\eta / 100))$. Where η = porosity, ρ_p = particle density and ρ_b = bulk density.

(hydraulic) properties. Data and recommended values for ion (contaminant) partitioning between liquid (leachate) and solid (tank fill grout) are presented in another report [6].

Table 4. Transport properties, test methods, and basis for requirements.

Property	Requirement	Test	Basis
Transport Properties			
Effective Diffusion Coefficient (D_e) (cm^2/s)	$\leq 8.00\text{E-}07$	D_e is a representative literature value applied to all soluble ions	2007 FTF PA*
		SIMCO Migration Test to determine tortuosity which is used to calculate D_e [7]	Option to 2007 FTF PA* Material specific data
Tortuosity (τ) (-)	≤ 20	Tortuosity is calculated from a representative molecular diffusion coefficient (D_m) [5, 7]	2007 FTF PA*
		SIMCO Migration Test for determining material specific tortuosity which is used to calculate D_e [5, 7]	Option to 2007 FTF PA* Material specific data
Saturated Hydraulic Conductivity at 20°C, average ($K_{hsat@20^\circ\text{C}}$) (cm/s)	$\leq 3.6\text{E-}08$	ASTM D 5084 Method F	2007 FTF PA*
		ASTM D 5084 Method C	
		SIMCO Drying Test for intrinsic permeability used to calculate saturated hydraulic conductivity [7]	The SIMCO Drying Test has a lower detection limit than the ASTM D5084 method
K_{ds} and for selected contaminants	2007 FTF PA	Determined for select species	2007 FTF PA

* Equal to or more conservative than values in 2007 Material Property Data Package for the FTF PA [5].

Table 5. Unsaturated transport properties, test methods, and basis for requirements.

Property	Requirement	Test	Basis
Unsaturated Transport Properties			
Volumetric Moisture Content versus pressure (where pressure is capillary head.) For 0.1 (1.5) to 15 bar (218 psi)	PA model input Saturation as a function of pressure needed for at least 6 pressures and to derive coefficients for the van Genuchten Equation	ASTM D3152 Test performed by MACTEC	2007 FTF PA* Data used to calculate van Genuchten Equation coefficients ⁵ to calculate moisture transport as a function of saturation.
Volumetric Moisture Content versus pressure for 15 bar (218 psi) to 45 bar (653 psi)	Same as above	Modified ASTM D3152	Expanded data set is used to better generate material specific van Genuchten parameters or look up tables for the PORFLOW code when the pressure plate method is used.

* Equal to or more conservative than values in 2007 Material Property Data Package for the FTF PA [5].

⁵ The van Genuchten equation for soil water content as a function of pressure is :
$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha h)^n]^m} \quad h \leq 0 \quad \theta(h) = \theta_s \quad h > 0$$

where $\theta(h)$ is water content at the pressure head h , θ_r is residual water content, θ_s is the saturated water content, h is pressure head, α is a constant related to the inverse of the air-entry pressure, and n is a measure of the pore-size distribution. The constraint $m = 1 - 1/n$ was used as suggested by van Genuchten [8, 9]. Van Genuchten coefficients used in the 2007 PA are listed: θ_s (cm^3/cm^3) = 0.279; θ_r (cm^3/cm^3) = 0.234; α ($1/\text{cm}$) = 0.008; n = 1.2153; m = 0.1770 [3, 5].

EXPERIMENTAL METHODOLOGY

Ingredients

Grout mixes tested in this study were prepared with bulk materials obtained from local suppliers and chemical admixtures that are distributed nationwide. The ingredients are listed in Table 6. The aggregate properties are provided in Table 7.

Sample Preparation and Test Methods

Samples were prepared in a 3 cubic foot (~ 85 L) mixer according to ASTM C192 and cured in a constant temperature $22.8^{\circ}\text{C} \pm 1.1^{\circ}\text{C}$ ($73^{\circ}\text{F} \pm 2^{\circ}\text{F}$) curing room at 100% relative humidity. The batch size was typically 0.75 to 1.0 cubic feet (21 to 28 L). The order of addition of ingredient to the mixer was as follows: gravel, sand, a portion of the water, fly ash, slag, cement and admixtures. The remainder of the water was added in total or in parts during the addition of the fly ash, slag, and cement. The mixing time was approximately five minutes after all of the ingredients were added. A sample was collected for the slump-flow measurement (Method ASTM C1611). After the test was completed, the material was returned to the mixer and mixed for another 5 minutes. The batch was allowed to rest for another 5 minutes prior to measuring fresh properties. After the final slump-flow was measured, (See Figure 3a) the remaining material was used for unit weight, air content, set time, and bleed water determinations; evaluation of flow under static conditions (modified ASTM D6103, Figure 3b); and to cast samples for strength (7, 28, and 90 days), permeability and other hydraulic property measurements.

Table 6. Ingredients Used to Prepare Samples of the FTF Closure Grouts.

Material	Specification	Supplier / Address
Portland cement Type I/II	ASTM C150	LaFarge, Cement, Harleyville, SC obtained from Lafarge Ready Mix Augusta, GA
Slag cement (Grade 100)	ASTM C987	Holcim, Inc., 3235 Satellite Blvd., Duluth, GA 30096
Fly ash (Class F)	ASTM C618	Wateree Power Plant,* SC, SEFA, Inc.
Concrete sand	ASTM C33	SCMI, Clearwater, SC
No. 8 stone (0.98 cm) 3/8 inch gravel (granite)	ASTM C33	Martin Marietta Quarry Augusta, GA obtained from Lafarge Ready Mix, Jackson, SC
<i>HRWR</i>		
Sika ViscoCrete 2100	ASTM C494 Type F	Sika Corporation
<i>Hydration Stabilizer**</i>		
Recover	ASTM C494 Type B	W.R. Grace & Co., 62 Whittemore Ave. Cambridge, MA 02140
<i>Viscosifier</i>		
Kelco-Crete D [®] (Diutan Gum)		CP Kelco, Inc., 8355 Aero Dr. San Diego, CA 92123
SRS domestic water		SRS

* The fly ash used in the 2007 alternative all-in-one grout study came from Boral Materials technology, Inc., Atlanta, GA.

**Set Retarder and hydration stabilizers were not required for samples prepared under laboratory conditions.

Table 7. Size Distribution of the Sand and No. 8 Stone (ASTM C136).

Property	Concrete Sand		No. 8 Aggregate (3/8 inch)	
Bulk Unit Weight (lb/ft ³)	85 @ 1.6 wt. % SSD*		93 @ 0.6 wt. % SSD*	
Specific Gravity (particle)	2.65		2.56	
Composition	Quartz		Granite	
Moisture Content (as received)	0.7 - 6.5 wt. %		~ 0	
Particle size Distribution ⁺	Wt. % Passing	Cum. Wt. % Retained	Wt. % Passing	Cum. Wt. % Retained
½ inch (12.5 mm)	100	0	99.4	0.6
3/8 inch sieve	100	0	91.8	8.2
¼ inch sieve	--	--	40.0	60.0
#4 sieve (4.75mm)	99	1	14.2	85.8
#5 sieve (4.00 mm)	--	--	6.3	93.7
#8 sieve (2.36 mm)	96	4	0.6	99.4
#16 sieve (1.18 mm)	81	19	--	--
#30 sieve (600 µm)	50	50	--	--
#50 sieve (300 µm)	17	83	--	--
#100 sieve (150 µm)	2	98	--	--
Fineness Modulus	--	2.6	--	--

* Saturated Surface Dry

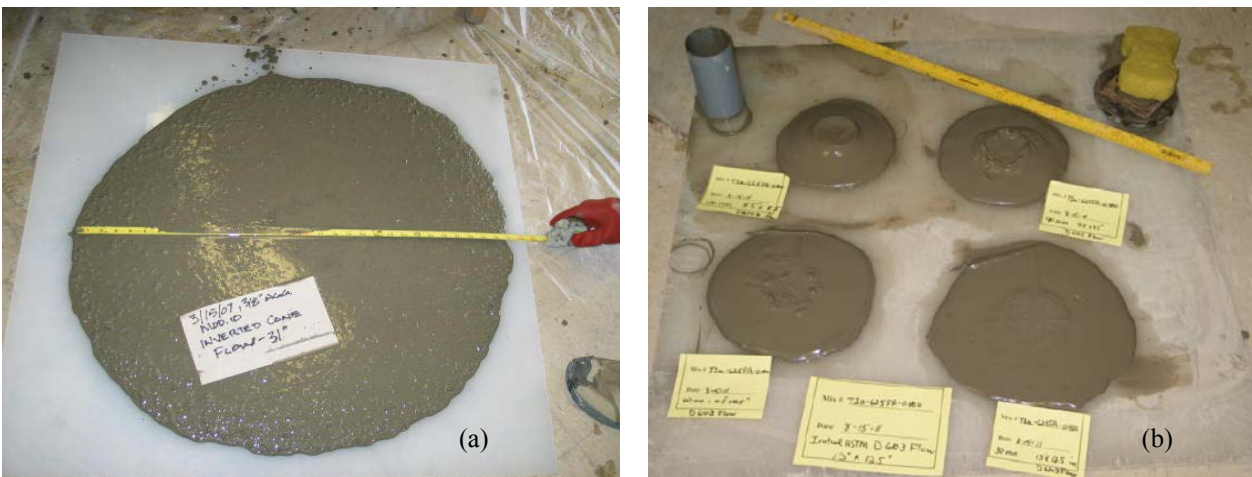


Figure 3. (a) ASTM C1611 Slump-Flow measurement of 25 inches and (b) ASTM D1603 spread evaluation at t_0 , t_{15} , t_{30} and t^{45} minutes: static conditions (12.5, 10.5, 7, and 7 inches).

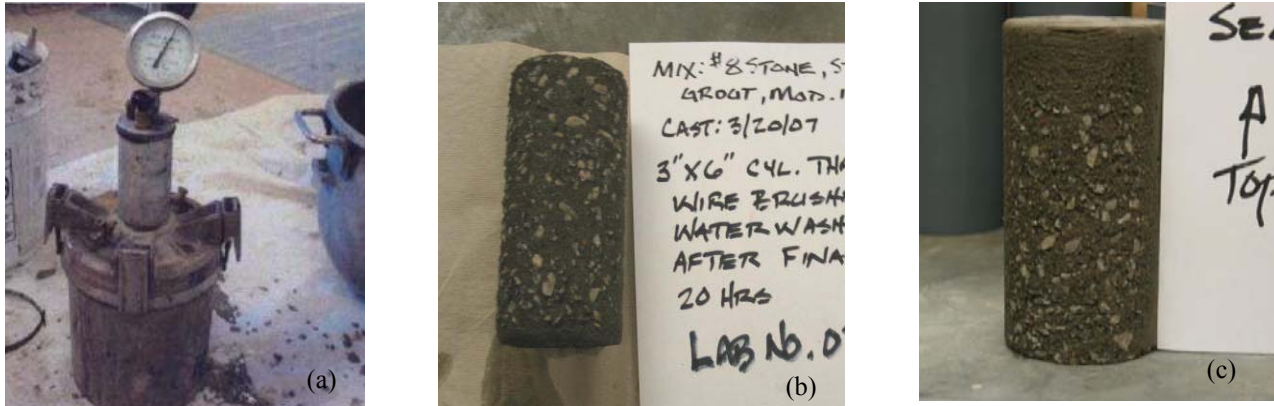


Figure 4. (a) Air content test apparatus and Visual determination of (b) unsegregated grout sample and (c) segregated grout sample.



Figure 5. Hydraulic conductivity test apparatus

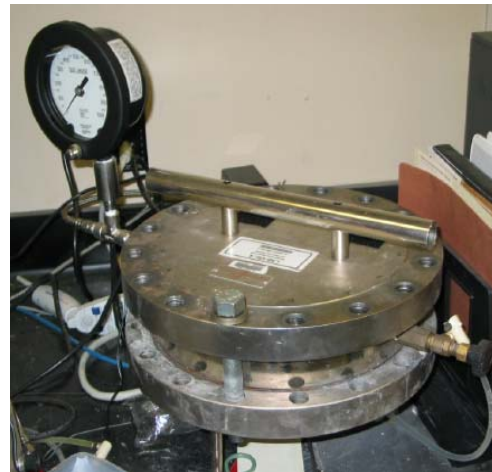


Figure 6. Pressure plate test configuration for moisture retention characterization.

RESULTS AND DISCUSSION

The LP#8 Series of trial mixes was formulated based on previous experience in developing robust self-leveling, flowable structural fills for in-situ decommissioning (ISD) of the SRS 105 P- and R-Reactor facilities during 2010 and 2011 [10]. Modification of the reactor ISD grouts was necessary because the chemical and hydraulic conductivity requirements for the tank fill grout are more restrictive. The reactor closure mix concept was modified by adding slag, adjusting the cement content, and lowering the water to cementitious materials ratios.

Proportions and properties of the LP#8 trial mixes are listed in Table 8. Trial mixes in this series with water to cementitious materials ratios between 0.610 and 0.500 met the flow requirements. Mixes with as little as 100 pounds of Portland cement plus 210 pounds of Grade 100 slag per cubic yards (59.3 and 124.6 kg/m³, respectively) met the strength requirement of 2000 psi (13.8 MPa) at 28 days and exceeded 4000 psi (27.6 MPa) after curing for 90 days. See Figures 6 and 7.

Adiabatic temperature rise data and hydraulic conductivity data were used to limit the amount of Portland cement contents to between 75 and 185 pounds per cubic yard (44.5 and 109.8 kg/m^3 , respectively) and amount of slag to 210 and 260 pounds per cubic yard (124.6 and 154.3 kg/m^3 , respectively). Fly ash was not used in the comparison because the mixes do not have enough free calcium ion, i.e., Ca(OH)_2 to react with all of the fly ash. Unreacted fly ash functioned as inert filler. A summary of the thermal properties including the adiabatic temperature rise for complete hydration are provided for selected mixes are provided in Table 9. Other thermal properties, i.e., specific heat and thermal conductivity, do not vary very much between samples.

The maximum temperature of the mix was calculated by adding the adiabatic temperature rise to the starting temperature which in the experiments ranged from 22 to 24°C . Under field conditions, the starting temperature of the grout ingredients can be 30°C or higher. For a maximum grout temperature of 65°C , the adiabatic temperature rise needs to be less than 35°C for starting materials that have an average temperature of 30°C (86°F).

All of the trial mixes tested met the saturated hydraulic conductivity requirement of $< 3.6 \text{ E-08 cm/s}$ for samples cured at least 44 days. Results are presented in Table 10. The lower limit of detection for ASTM 5084 Method C is 10^{-8} cm/s . The lower limit of detection for ASTM 5084 Method F was an order of magnitude lower, 10^{-9} cm/s . (A method for determining hydraulic conductivity specifically developed for cementitious materials by SIMCO Technologies, Inc has a lower limit of detection one to two orders of magnitude lower than ASTM Method F.)

Results for moisture retention as a function of applied pressure (pressure plate test) for the grouts recommended for closing Tanks 18-F and 19-F are summarized in Table 11 for pressures between 0 and 15 bars. The moisture retention data are reported as volumetric water content as a function of head pressure and are used as input to the RETC Code which is used to calculate relative hydraulic conductivity for input into the PORFLOW[®] code, the reactive transport code used for the SRS FTF Performance Analysis.

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Table 8. Ingredients, Proportions and Properties for Low Paste with No. 8 Stone (LP#8) Series of Tank Fill Grout Trial Mixes.

LP#8 Series	Reactor Fill w/cm = 0.641	LP#8 Series 1: w/cm _{total} = 0.610				LP#8 Series 2: w/cm _{total} = 0.580				LP#8 Series 3: w/cm _{total} = 0.550				LP#8 Series 4: w/cm _{total} = 0.500			
Ingredient (Lb/cyd)		12	14	11	13	15	16	17	18	19b	20	21	22	25	23	24	26
Portland Cement, Type I/II	150	100	125	150	185	100	125	150	185	100	125	150	185	100	125	150	185
Slag Cement Grade 100	0	210	210	210	210	210	210	210	210	210	210	210	210	260	260	260	260
Fly Ash, Class F	500	380	363	345	320	380	363	345	320	380	363	345	320	418	400	383	358
Concrete Sand, Quartz	1850	1750	1735	1750	1708	1805	1790	1778	1765	1860	1847	1837	1822	1635	1630	1621	1613
Gravel, No. 8																	
3/8 inch Crushed Granite	800	800	800	800	800	800	800	800	800	800	800	800	800	973	970	965	960
Water (lb/cyd)	416.5	420.9	425.8	430.0	436.2	400.2	404.8	408.9	414.7	379.5	383.90	387.8	393.3	387.8	392.5	396.5	401.5
(gallons/cyd)	50.0	50.5	51.1	50.5	52.4	48.0	48.6	49.1	49.8	45.6	46.1	46.5	47.2	46.5	47.1	47.6	48.2
HRWR SIKa ViscoCrete 2100 (fl oz/cyd)	79	49.5	45	36	49.5	40.5	40.5	40.5	40.5	54	54	45	54	45	45	54	45
VMA, Kelco CP, Diutan Gum (g/cyd)	205	200.16	200.16	199.8	200.16	200.16	200.16	200.16	200.16	120.24	155.16	119.16	120.24	162	162	162	162
Fresh Properties																	
Slump Flow, ASTM C1611 (in.)	24 ± 4	25.75	28.25	26	28	27.5	25.75	27	25	25	24.5	25.25	27	26	25.25	26	24
Air Content (vol. %)	< 8	1.5	1.3	1.6	1.5	1.2	2	1.5	2.2	2.8	2.5	2.1	NM	1.7	1.6	1.6	1.7
Set Time (hr.)	< 24	< 24	< 24	< 24	< 24	< 24	< 18	< 18	< 18	< 20	< 24	< 24	< 24	< 19	< 19	< 20	< 17
Bleed (ml)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Unit Weight (lbs/cft)	NA	134.94	133.9	132.86	134.94	133.33	133.67	132.26	134.27	133.67	132.86	133.67	132.86	136.68	136.68	137.89	137.89
Spread, ASTM D-6103 (in.) after static period (min)	NM	NM	NM	NM	NM	NM	t ₃₀ = 9.5 in.	NM	NM	NM	t ₃₀ = 9 in.	NM	NM	t ₀ = 12.5 t ₃₅ = 12.5	t ₀ = 11.5 t ₃₆ = 10.75	t ₀ = 11.75 t ₃₂ = 11.5	t ₀ = 10.5 t ₄₀ = 7.5
Cured Properties																	
Compressive Strength (psi)																	
7 days (1)	~250	340	190	410	280	160	370	360	490	360	360	480	590	970	970	950	1010
28 days (2)	~780	2335	2575	2500	3045	2300	2680	2495	2940	2560	2465	3090	3110	3780	4145	4585	5155
90 days	~1640	3815	4595	4185	5040	3705	4560	4530	5270	4060	4395	5205	5100	5020	5830	6855	7280
Sat. Hydraulic Conductivity k _{hsat@20} ASTM D5084 Method C, URS Data (cm/s)	1.30E-08	NM	NM	3.2E-09	NM	3.1E-09	2.1E-09 See Table 10	2.4E-09	NM	2.5E-09	See Table 10	4.2E-09	2.0E-09	2.1E-09	1.1E-09	2.0E-09	.3E-09
Shrinkage (%)	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Porosity	NM	NM	NM	NM	NM	NM	0.21	NM	NM	NM	0.21	NM	NM	NM	NM	NM	NM
Settlement/segregation	NM	NM	none	none	none	none	none	none	none	none	none	none	none	none	none	none	none
Adiabatic Temperature Rise (°C)	< 25	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	41	NM	NM	NM	37.2	NM
Maximum Temperature for starting temperature of (°C)	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	T _i = 22.0 T _f = 49.9	NM	NM	NM	T _i = 25.0 T _f = 51.5	NM
Date prepared		5/12/2011	5/12/2011	5/11/2011	5/12/2011	5/12/2011	5/16/2011	5/16/2011	5/16/2011	5/16/2011	5/17/2011	5/17/2011	5/17/2011	6/14/2011	6/9/2011	6/14/2011	6/14/2011

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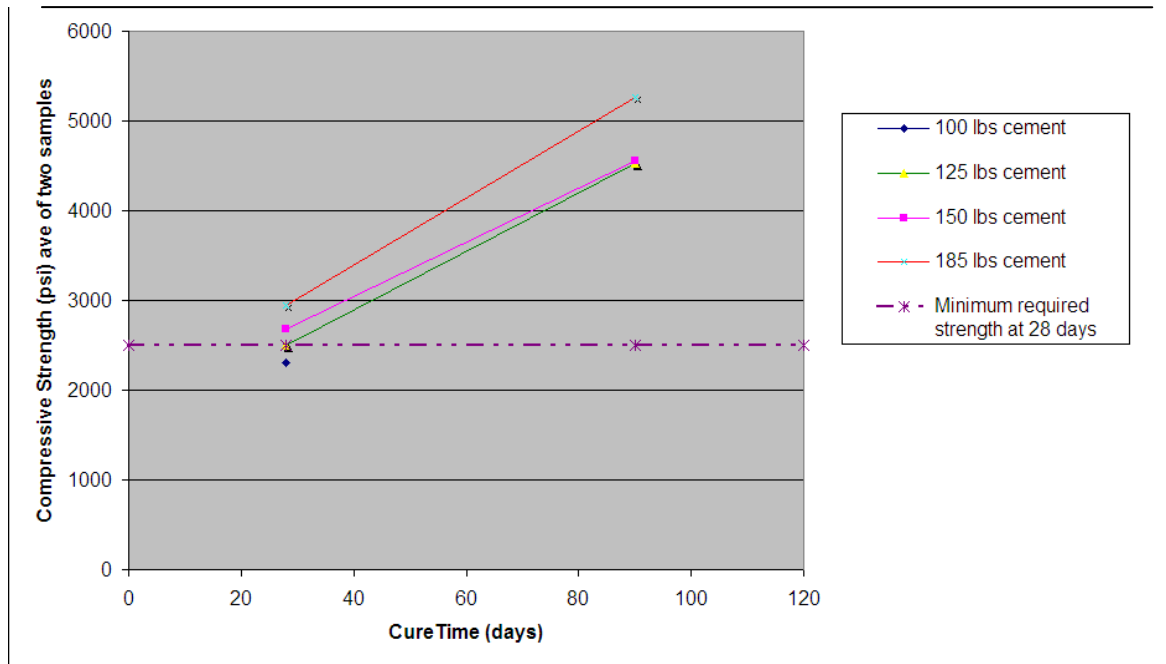


Figure 6. Compressive Strength versus cure time for LP#8 Grout Series 2 mixes with different cement contents and water to cementitious material ratio of 0.580.

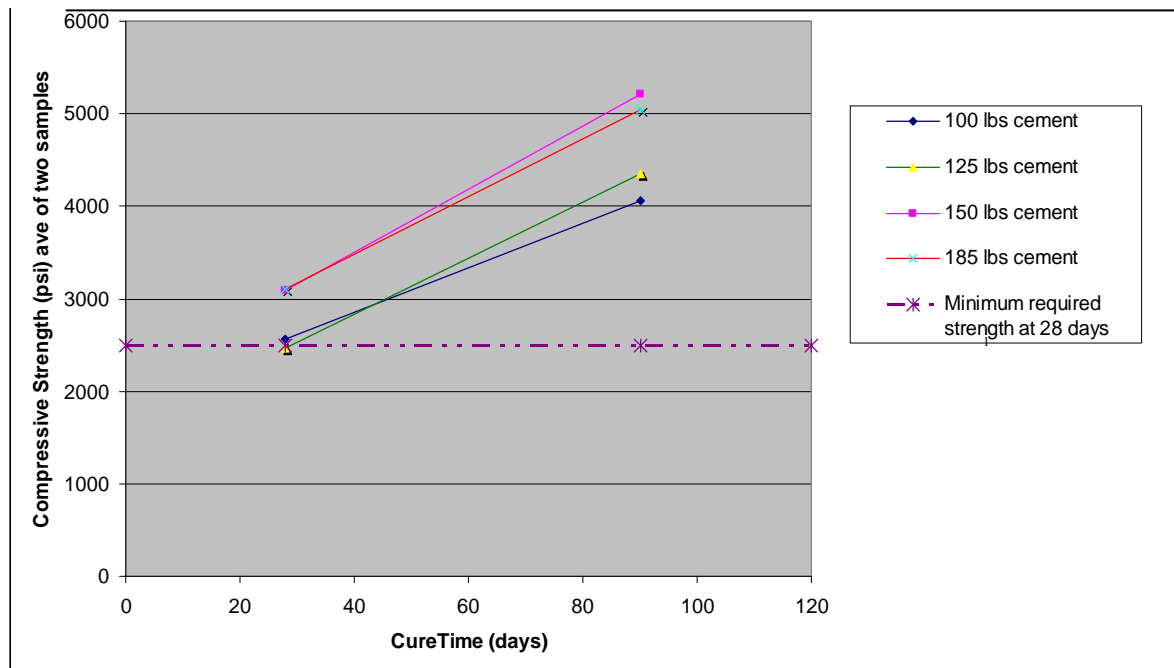


Figure 7. Compressive Strength versus cure time for LP#8 Grout Series 2 mixes with different cement contents and water to cementitious material ratio of 0.550.

[Type text]

Table 9. Summary of thermal properties for representative mixes.

Thermal Property	LP#8-016	LP#8-020	LP#8-021H	LP#8-024H
Cement (lbs/cyd)	125	125	150	150
Slag (lbs/cyd)	210	210	210	260
Adiabatic Temperature Rise: complete hydration (°C)	34	34*	41.0	37.2
Density (g/cm ³)	2.21	2.21*	2.208	2.213
Specific Heat (cal/g-K)	0.26*	0.26*	0.259	0.296
Specific Heat (J/kg-K)	1080*	1080*	1082	1240
Thermal Conductivity (W/m-K)	2.5*	2.5*	2.45	2.45
Thermal Conductivity (J/mL)	85*	85*	98	102

* Estimated

Table 10. Hydraulic properties for the grouts recommended for closing Tanks 18-F and 19-F.

	Saturated Hydraulic Conductivity K _s at 20° (cm/s)	Saturated Hydraulic Conductivity K _s at 20° (cm/s)	Saturated Hydraulic Conductivity K _s at 20° (cm/yr)	Saturated Effective Diffusion Coefficient (cm ² /s)	Saturated Effective Diffusion Coefficient, D _e (cm ² /yr)	Effective Porosity (%)	Dry Bulk Density (g/cm ³)	Average Particle Density (g/cm ³)	Moisture Content (Average) (wt %)
Material	URS Method C	MACTEC Method F	MACTEC Method F	FTF PA	FTF PA	MACTEC	MACTEC	Calculation	MACTEC
LP#8-16	2.1E-09	3.1E-10 average of 3 samples	9.78E-03	5.0E-08 literature	1.58E+00 literature	0.21	1.97	2.49	24.3
LP#8-20	Not Measured	3.5E-10 average of 3 samples	1.10E-02	5.0E-08 literature	1.58E+00 literature	0.21	1.98	2.51	21.7

Table 11. Moisture retention as a function of applied pressure for LP#8-016 and LP#8-020.

Sample No.	Initial moisture content (vol %)	Dry unit weight (lb/cft)	Applied Pressure (bars)					
			0.10	0.50	1.0	5.0	10.0	15.0
			Retained Water (volume percent)					
LP#8-016A (average of 2)	24.3	127.0	24.1	24.0	23.8	23.6	23.2	23.0
LP#8-020A (average of 2)	21.65	121.5	21.2	21.1	21.0	20.7	20.4	20.1

CONCLUSIONS AND RECOMMENDATIONS

The cement and slag contents of a mix selected for filling Tanks 18-F and 19-F should be limited to no more than 125 and 210 lbs/cyd, respectively, to limit the heat generated as the result of hydration reaction during curing and thereby enable mass pour placement. Trial mixes with water to total cementitious materials ratios of 0.550 to 0.580 and 125 lbs/cyd of cement and 210 lbs/cyd of slag met the strength and permeability requirements.

Mix LP#8-16 was selected for closing SRS Tanks 18-F and 19-F because it meets or exceeds the design requirements with the least amount of Portland cement and blast furnace slag. Ingredients and proportions for this formulation are provided in Table 12.

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This grout is expected to flow at least 45 feet. A single point of discharge should be sufficient for unrestricted flow conditions. However, additional entry points should be identified as back-up in case restrictions in the tank impede flow.

Table 12. Tanks 18 and 19-F Bulk Fill Material Recommendation.

Mix Number	Cement Type I/II	Slag Grade 100	Fly Ash Class F	Type G Shrinkage Compensating Component	Sand Quartz	Gravel No. 8 3/8 in.	Water	HRWR SIKA Visco Crete 2100	VMA Diutan Gum Kelco-Crete DG
	Lbs/cyd						Gal/cyd	Fl oz/cyd	g/cyd
LP#8-16	125	210	363	0	1790	800	48.5	41	200
	Kgs/m ³						L/m ³	L/m ³	g/m ³
LP#8-16	74	119	215	0	1062	475	239.4	1.6	261

The LP#8 series of trial mixes had surprisingly high design compressive strengths (2000 to 4000/5000 psi) which were achieved at extended curing times (28 to 90 days, respectively) given the small amount of Portland cement in the mixes (100 to 185 lbs/cyd). The grouts were flowable structural fills containing 3/8 inch gravel and concrete sand aggregate. These grouts did not segregate and require no compaction. They have low permeabilities ($\leq 10^{-9}$ cm/s) and are consequently expected to be very durable. This series of trial mixes contained by-product materials, i.e., slag and Class F fly ash, and an admixture system initially specified for the grouts used to Close Tanks 17-F and 20-F at SRS. The mix designs have low CO₂ footprints because Portland cement contents are very low and can be considered environmentally friendly.

REFERENCES

1. Langton, C. A. and N. Rajendran, 1998. "Laboratory and Field Testing of High Performance Zero Bleed CLSM Mixes for Future Tank Closure Applications (U), WSRC-TR-98-271 Revision 0, March 30, 1998, Westinghouse Savannah River Company, Aiken, SC 29808.
2. Langton, C. A., A. Ganguly, C. A. Bookhamer, M. Koval, and W. L. Mhyre, 2007. "Grout Formulations and Properties for Tank Farm Closure (U)," WSRC-STI-2007-00641 Revision 0, November 12, 2007, Washington Savannah River Company, Savannah River National Laboratory, Aiken, SC 29808.
3. SRS, 2007. Performance Assessment for F-Tank Farm at Savannah River Site, Savannah River Site, SRS-REG-2007-00002, Rev. 1, March 31, 2010, Aiken, SC, 29808.
4. Langton, C. A., 2007. "Chemical Degradation Assessment of Cementitious Materials for the HLW Tank Closure Project (U), WSRC-STI-2007-0067 Revision 0., September 14, 2007, Washington Savannah River Company, Aiken SC 29808.
5. Dixon, K. and M. Phifer, 2007. "Hydraulic and Physical Properties of Tank Grouts and Base Mat Surrogate Concrete for FTF Closure," WSRC-STI-2007-00369, Revision 0, Washington Savannah River Company, Aiken SC 29808.
6. Kaplan, D. I., 2010. Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site, SRNL-STI-2009-00473, Savannah River National Laboratory, Savannah River Site, Aiken, SC, 29808.

[Type text]

7. SIMCO 2011. "Savannah River Nuclear Solutions – Subcontract no. RA00097SE – Final Report (E-Area Vault Concrete Test Wall)," SIMCO Technologies Inc., Quebec, Canada.
8. Van Genuchten, M. T, 1980. "A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils," *Soil Science Society of America Journal*, v.44, p.892-898.
9. Van Genuchten, M. T, F. J. Leij, and S. R. Yates, 1991, "The RETC Code for Qualifying the Hydraulic Function of Unsaturated Soils, Version 1.0, EPA Report 600/2-91/065, U.S. Salinity Laboratory, USDA, ARS, Riverside, CA.
10. C. A. Langton, D. B. Stefanko, M. G. Serrato, J. K. Blankenship, W. B. Griffin, J.T. Long, J. T. Waymer D. Matheny, and D. Singh, "Use of Cementitious Materials for SRS Reactor Facility In-Situ Decommissioning", WM Symposium 2011, February 27 to March 3, 2011, Phoenix, AZ.

ACKNOWLEDGEMENTS

The authors acknowledge URS Washington Group, Quality and Testing Division management and technical personnel provided use of the SRS Civil Engineering Laboratory and test equipment, and technical expertise and input that was essential for performing the tests and obtaining the results in this report. J. L. Steimke, H. N. Guerrero, and M. L. Restivo, SRNL Engineering Development, provided the thermal properties for selected mixes. K. L. Dixon provided moisture retention data needed to calculate relative hydraulic conductivities (as a function of saturation).

This paper was prepared in conjunction with work accomplished at the Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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