

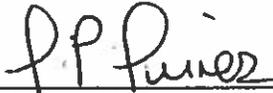
Cement-Free Formulation Down-Select Report

February 2019

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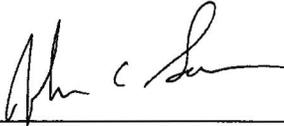
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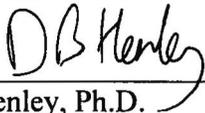
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EXECUTIVE SUMMARY

Following extensive research, it has been determined that a cement-free saltstone formulation will form a non-hazardous waste form with similar fresh and cured properties as the saltstone currently being disposed of in the Saltstone Disposal Facility (SDF) and could be a viable alternative to the current saltstone recipe. Further, based on this research, it is recommended that the down-selected composition – a 60 weight percent (wt%) Grade 120 blast furnace slag (BFS) and 40 wt% Class F fly ash (FA) dry chemical premix that is mixed with the salt solution waste at a mass ratio of 0.6 water-to-premix (w/pm) – be pursued for potential implementation at the Saltstone Production Facility (SPF).

Saltstone is a cementitious waste form utilized for the stabilization of low-level radioactive waste (LLW) at the Savannah River Site (SRS). The majority of this LLW stream is decontaminated salt solution (DSS) produced through the treatment of SRS tank waste. Significantly smaller contributing volumes originate from H-Canyon operations and the Effluent Treatment Facility (ETF) operations. The LLW exists as a highly alkaline salt solution, which is currently mixed with a combination of ordinary portland cement (OPC), BFS, and FA (termed the premix) at the SPF. The resulting grout slurry is subsequently transferred to enclosed concrete structures, termed Saltstone Disposal Units (SDUs). Once inside the SDUs, the mixture cures to form the hardened saltstone grout which exhibits low permeability and essentially encapsulates the chemical and radioactive contaminants. The constituent proportions of the premix are currently 45 wt% BFS, 45 wt% FA, and 10 wt% OPC (designated as the BFS/FA/OPC 45/45/10 premix); the premix is mixed at a w/pm mass ratio of 0.6, which corresponds to a salt solution-to-premix mass ratio of approximately 0.85.

The cement component of the current saltstone formulation is activated by water to form a calcium silicate hydrate (CSH) gel. In contrast, the BFS, though not readily activated in water, is activated in highly alkaline solutions (i.e., the SRS salt waste) to form a binding gel similar to CSH. The FA exhibits no appreciable reactivity with water or the alkaline salt solution, and essentially acts as an inert phase that is added to enhance the processing characteristics of the saltstone slurry. BFS is an essential component of saltstone since it is a reductant that serves to reduce redox-sensitive radionuclides to their low solubility and low mobility states. Cement, however, is not relied upon to chemically stabilize contaminants.

The SPF contains four large silos to store the premix materials. Each of the three premix materials is stored in its own dedicated silo and the fourth silo is currently used to store additional BFS. With the anticipated significant increase in the production of DSS from the salt treatment facilities rising to as much as 11 million gallons per year, Savannah River Remediation LLC (SRR) has been exploring and implementing opportunities to increase saltstone production efficiencies. One such efficiency would be to implement a cement-free saltstone formulation that would exclusively utilize BFS and FA in the premix. This two-component formulation would simplify the procurement, transport, off-loading, and storage of the premix materials, and increase the storage capacity for the individual components (i.e., two silos dedicated to BFS and two for FA).

Since 2012, SRR has been actively supporting applied research on the viability of a cement-free saltstone formulation. Although the initial research on a 50 wt% BFS/50 wt% FA formulation was not promising, ultimately a combination of increasing the %BFS and BFS reactivity resulted in a cement-free formulation that had similar properties when compared to the current saltstone and was relatively insensitive to changes in the hydroxide concentration of the salt solution. The down-

selected composition consists of 60 wt% Grade 120 BFS and 40 wt% Class F FA (designated as the BFS/FA 60/40 premix) and a w/pm of 0.6.

The down-selected cement-free formulation exhibits comparable fresh and cured properties to the nominal 45/45/10 formulation with one possible exception. The curing of the saltstone results from an exothermic reaction. Since the down-selected cement-free formulation contains a higher percentage of reactive material, it was expected that the heat generation in the down-selected cement-free saltstone would be higher. The heat generation in saltstone is an important property since higher reaction heats would result in higher grout temperatures within the SDU, which in turn could increase the volatilization of organic components contained in the original salt waste. Per the Documented Safety Analysis (DSA), the current grout and vapor space temperature limits to avoid vapor space gas flammability in SDU 6 are 75 and 65 °C, respectively.

As such, it was necessary to evaluate if filling an SDU with cement-free grout would challenge these temperature limits. This was achieved by developing a computational fluid dynamics (CFD) model in ANSYS® capable of predicting SDU temperatures based on variable inputs including the saltstone formulation (and associated thermal properties), grout addition rates to the SDU (or pour schedule), and the external ambient environment. Utilizing an aggressive pour schedule of 12.3 days of continuous pouring followed by 46.6 days of idling time, the partial filling of SDU 6 with the BFS/FA 60/40 formulation indicated maximum grout and vapor space temperatures of approximately 76 and 71 °C, respectively, based on one year of pouring up to a height of 22.5 ft. During a second year of pouring operations and filling of the SDU to 41 ft., the maximum grout and vapor space temperatures could be 5 °C higher. When modeling a more realistic pour schedule that results in essentially the same annual volume of saltstone produced, the maximum grout and vapor space temperatures drop to 60 and 58 °C, respectively. [SRR-CWDA-2019-00012] Although the most aggressive pour schedule results in initial modeled temperatures that are slightly higher than the current DSA limits, it is important to note that the current model is conservative for the following reasons:

1. The model-predicted grout temperatures associated with filling SDU 2A (in 2013-2014) were 5-10 °C higher than the actual measured grout temperatures;
2. The current model does not simulate heat transfer via convection in the SDU vapor space – convection was initially omitted to simplify the model and increase runtime efficiency; and
3. The model utilizes an extremely aggressive, and potentially unattainable, grout pour schedule.

Though the current SDU thermal model results conservatively predict that DSA-prescribed grout and vapor space temperatures could be exceeded under extreme pouring conditions, the cement-free formulation remains a viable alternative to the nominal BFS/FA/OPC 45/45/10 formulation. Future short-term work should predominantly focus on further optimizing the SDU thermal model with respect to reducing potential conservatisms, and further evaluating and documenting the toxic chemical and radionuclide contaminant leaching characteristics for the BFS/FA 60/40 formulation as has been done through the years for the current BFS/FA/OPC 45/45/10 saltstone formulation.

A summary of the cement-free saltstone feasibility studies is provided in Figure ES-1, which includes the objective of each phase, the variables considered, the key findings, and the subsequent cement-free evaluation.

Figure ES-1: Summary of Phased Approach for Evaluating the Viability of Cement-Free Saltstone

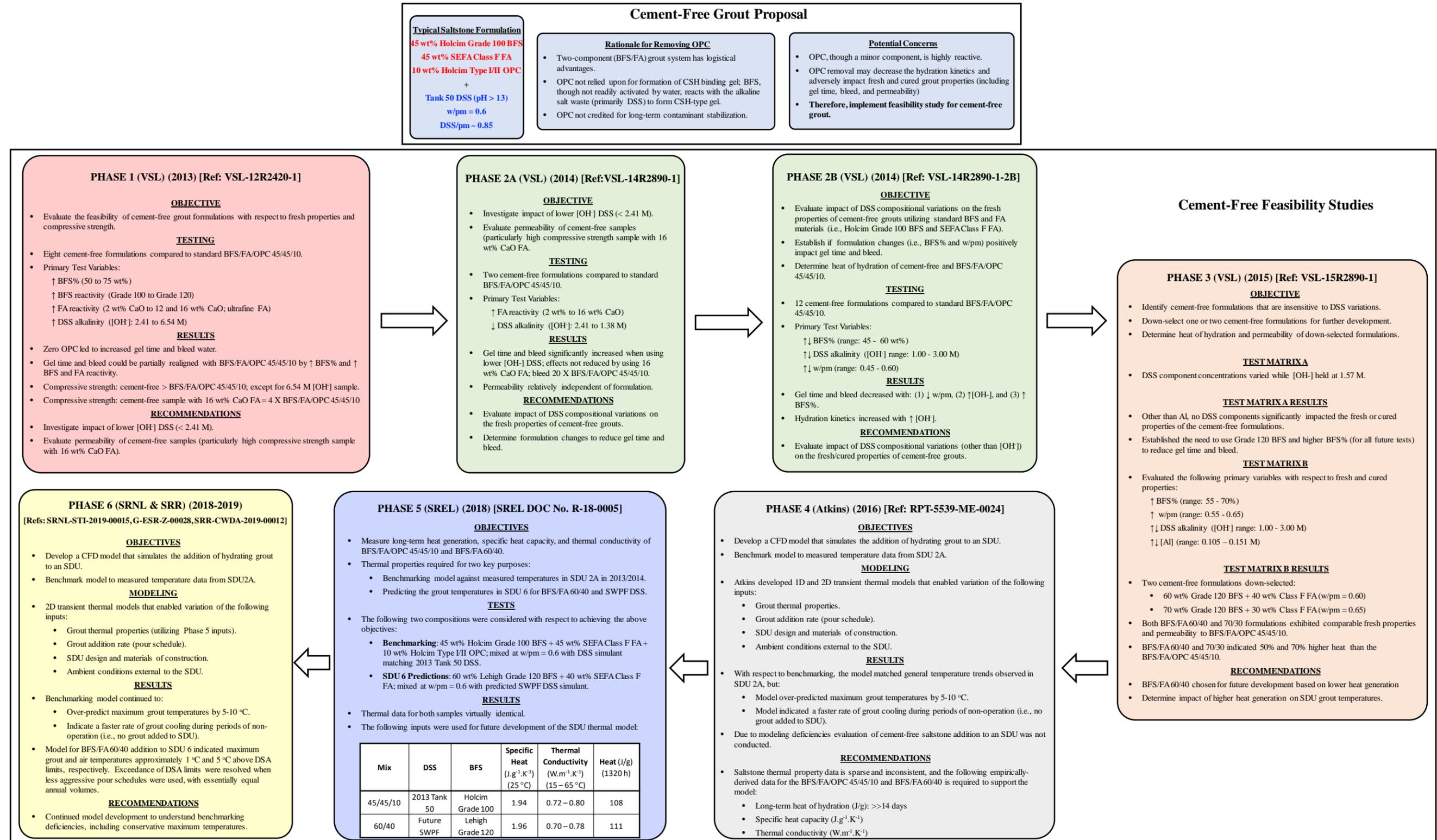


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ACRONYMNS

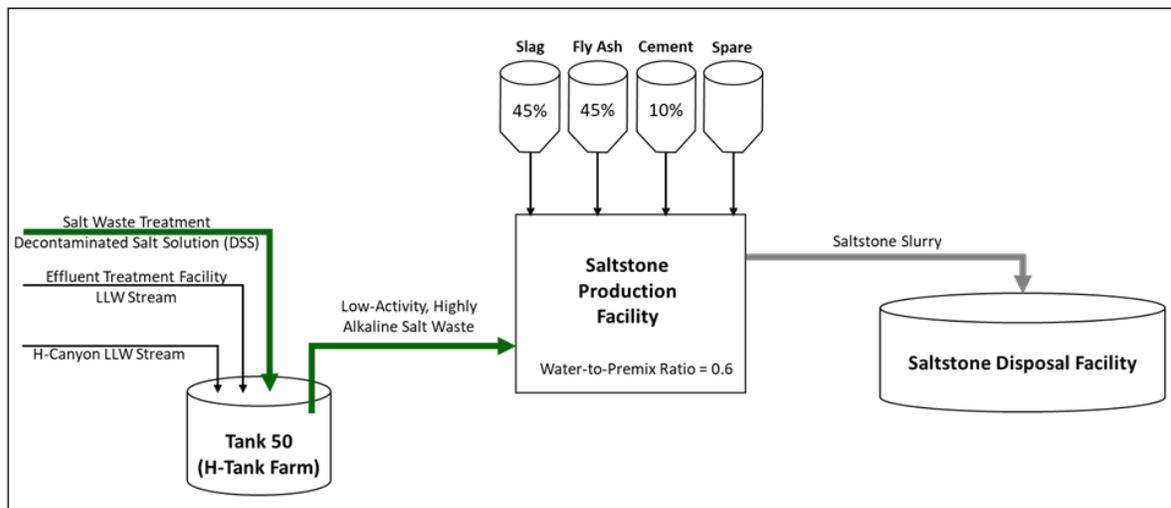
1D	One-Dimensional
2D	Two-Dimensional
ARP	Actinide Removal Process
BFS	Blast Furnace Slag
CFD	Computational Fluid Dynamics
cP	Centipoise
CSH	Calcium Silicate Hydrate
CUA	Catholic University of America
DLM	Dynamic Leaching Method
DOE	Department of Energy
DRM	Dynamic Rheological Measurement
DSA	Documented Safety Analysis
DSS	Decontaminated Salt Solution
EPA	Environmental Protection Agency
ETF	Effluent Treatment Facility
FA	Fly Ash
LLW	Low-Level (Radioactive) Waste
MCU	Modular Caustic Side Solvent Extraction Unit
MH	Moderate Heat of Hydration
OPC	Ordinary Portland Cement
Pa	Pascal
PA	Performance Assessment
psi	Pounds per Square Inch
SCDHEC	South Carolina Department of Health and Environmental Control
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SHC	Saturated Hydraulic Conductivity
SPF	Saltstone Production Facility
SREL	Savannah River Ecology Laboratory
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation LLC

SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TCCR	Tank Closure Cesium Removal
TCLP	Toxicity Characteristic Leaching Procedure
VSL	Vitreous State Laboratory
wt%	Weight Percent
w/pm	Water-to-Premix Ratio

1 INTRODUCTION

Saltstone is a cementitious waste form utilized for the stabilization of low-level (radioactive) waste (LLW) at the Savannah River Site (SRS). As shown in Figure 1-1, decontaminated salt solution (DSS) from the SRS salt treatment facilities and LLW from the Effluent Treatment Facility (ETF) and H Canyon are transferred and stored in Tank 50, the dedicated LLW storage tank in H-Tank Farm. The DSS stream currently makes up the majority of the salt waste in Tank 50 and the volume of the DSS stream will increase significantly when the Salt Waste Processing Facility (SWPF) is fully operational. The waste in Tank 50 is in the form of a highly alkaline salt solution ($\text{pH} > 13$). Saltstone slurry is formed at the Saltstone Production Facility (SPF) by combining the Tank 50 salt solution with a powder blend (termed the dry feeds or premix) of 45 weight percent (wt%) Grade 120 blast furnace slag (BFS), 45 wt% Class F fly ash (FA), and 10 wt% Type I/II ordinary portland cement (OPC). The liquid and solid components are mixed at a water-to-premix (w/pm) mass ratio of approximately 0.6 (equivalent to a salt solution-to-premix mass ratio of approximately 0.85); this formulation is designated as BFS/FA/OPC 45/45/10. The slurry is subsequently pumped to enclosed concrete structures, termed Saltstone Disposal Units (SDUs). Within the SDUs, the slurry cures to form the non-hazardous, low-permeability saltstone waste form, which is capable of encapsulating and retaining the salt waste contaminants, and thereby reducing their rate of transport to the surrounding environment.

Figure 1-1: Saltstone Production and Disposal



The use of cementitious materials for the immobilization and disposal of LLW has been extensively studied throughout the Department of Energy (DOE) complex since the 1960s, and the premix composition of BFS, FA, and cement was developed (per DPST-87-869) on the bases of SPF processability and meeting the contaminant leaching limits for non-hazardous wastes, as set forth in South Carolina Department of Health and Environmental Control (SCDHEC) Regulation R.61-79.261.24(b). Cement is considered a hydraulic material, in that it reacts with water to produce a calcium silicate hydrate (CSH) gel that binds (or cements) particulates together. Unlike cement, BFS and FA do not readily react with water and are considered pozzolans since, although not hydraulically activated, they may be activated by the calcium hydroxide ($\text{Ca}(\text{OH})_2$) formed during cement hydration (hence their use as supplementary materials together with cement in concrete). Equally, the BFS (and to a significantly lesser extent the FA) may be activated by the

alkaline salt solution ($[\text{OH}^-] > 1.0 \text{ M}$) to form a gel, which is similar to the CSH gel produced during cement hydration [Wang & Scrivener, 1995].

Since BFS activation (in this application) is not reliant on the $\text{Ca}(\text{OH})_2$ produced during cement hydration, the question arises with respect to the role of, and the need for, the minor cement component (10 wt%) in the saltstone formulation. It is also important to note that in saltstone, the BFS component is the most chemically active component with respect to the retention of key radionuclides contained in the waste (e.g., Tc-99). BFS acts as a reductant (presumed to be associated with small proportions of constituent iron and sulfur), and is capable of reducing the highly soluble and mobile Tc(VII), in the form of the pertechnetate anion (TcO_4^-), to the significantly less soluble Tc(IV) [SRNS-STI-2008-00045]. As such, the cement is not relied upon for the reduction of Tc-99, and its removal should not impact the long-term radionuclide leaching characteristics. Indeed, replacing cement with BFS, and thus increasing the percentage of BFS, would be anticipated to enhance the reduction capacity of the saltstone material.

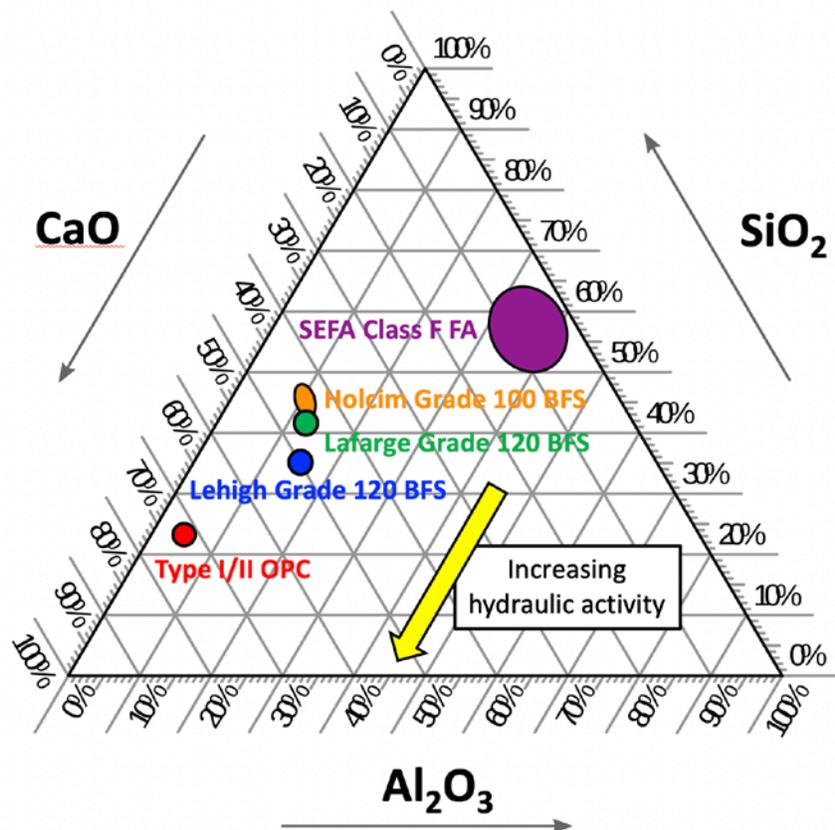
A significant advantage to eliminating the cement would be the enhanced utilization of the dry feed storage silos at SPF. There are currently four silos, three of which are used for each of the BFS, FA, and cement components, while the fourth silo serves as a spare and is currently filled with BFS. Removing the cement from the saltstone formulation would enable two silos each for BFS and FA, which in turn would enhance the material handling logistics, and support the increase in saltstone production rates following the start-up of SWPF. At present, the DSS is produced via the Actinide Removal Process / Modular Caustic Side Solvent Extraction Unit (ARP/MCU) and the Tank Closure Cesium Removal (TCCR) Unit.

A primary concern with eliminating the minor cement component is associated with decreasing the reactivity of the saltstone mixture, which in turn could adversely impact the properties of the slurry and the cured material. For example, it is assumed that decreased reactivity will prolong the time it takes for the saltstone to gel (i.e., begin to form the binding CSH-type gel structure), which in turn could lead to particulate settlement and the development of bleed water on top of the grout within the SDU. This could be problematic since the bleed water must be drained from the SDU and ultimately reprocessed through SPF. In addition, decreased reactivity might be expected to adversely impact the physical integrity of the cured saltstone, thereby reducing its capacity to retain the encapsulated contaminants. To determine the viability of removing the minor cement component, Savannah River Remediation LLC (SRR) initiated a multi-phase cement-free feasibility study in 2012 which has evaluated properties that would potentially impact the processing of the grout at SPF, the pumping of the grout to an SDU, and the long-term properties associated with contaminant retention capacity. As a result of these investigations, a single cement-free formulation has been identified that offers comparable fresh and cured characteristics to the currently utilized BFS/FA/OPC 45/45/10 formulation. This report summarizes the laboratory studies conducted between 2012 to 2018, and more recent efforts directed towards developing a computer model capable of simulating the addition of a hydrating grout to the SDUs and predicting the maximum grout temperatures attained for a given rate of saltstone addition.

2 SALTSTONE COMPONENTS

The ternary diagram in Figure 2-1 indicates the approximate compositions of Type I/II OPC and specific BFS and FA products (particularly pertinent to this report) with respect to alumina (Al_2O_3), silica (SiO_2), and calcia (CaO). Note that each oxide component is expressed as a percentage of the sum ($\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{CaO}$) (i.e., the ternary diagram does not account for other minor components in these materials). Cement is high in CaO , BFS has equivalent amounts of CaO and SiO_2 , and Class F FA is high in SiO_2 . In general, as the CaO content increases so does the hydraulic activity (i.e., the reactivity of the material with water to form a CSH-type binder phase). Vendor specification sheets for materials currently utilized in the production of saltstone are provide in Ref. SRR-CWDA-2019-00021.

Figure 2-1: Ternary Phase Diagram for Key Materials (Identified in this Report)



The major constituent compositions of each of the materials are indicated in Table 2-1. Note for some materials, the composition has been measured at different points in time and by different institutions; differences in oxide proportions are also reflected by the spot size in Figure 2-1 (i.e., large spot = discernible compositional differences measured between institutions; small spot = marginal compositional differences or measurement conducted by a single institution). In addition, the OPC manufacturer is not provided in Figure 2-1 or Table 2-1 since OPCs are manufactured products with standardized compositions and properties. In contrast, BFS and FA are by-products that may exhibit significant compositional and property variation. Relevant

information regarding the premix components, applicable standards, and measurement variations between institutions is provided in the subsequent text.

Table 2-1: Compositions of Dry Feed Components

Material	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	SiO ₂	SO ₃
Holcim Grade 100 BFS	8.4	36.8	0.3	12.0	39.6	1.9
	11.1	40.4	0.4	7.8	36.0	2.3
	7.5	36.8	0.4	13.0	39.2	1.8
Lehigh Grade 120 BFS	13.5	42.5	0.6	6.0	31.1	3.0
Lafarge Grade 120 BFS	10.0	40.9	0.5	8.3	37.3	1.1
SEFA Class F FA	24.7	12.5	11.8	0.7	37.9	1.0
	29.5	1.7	7.0	1.0	54.4	0.5
	28.6	0.7	5.8	0.9	55.5	0.2
Type I/II OPC	5.0	66.3	3.6	1.4	20.4	3.2
	4.1	62.9	3.2	3.6	18.9	5.8
	5.3	64.0	3.8	1.2	20.4	3.3

Note: **Data in red from SREL Doc. No. R-19-0001**
Data in blue from VSL-12R2420-1
Data in green from WSRC-TR-2006-00067

2.1 Blast Furnace Slag

The extraction of pig iron from iron ore and limestone (heated in a blast furnace) results in a molten by-product referred to as slag (BFS). The molten BFS is subsequently passed into a granulator and quenched with water to form a glassy particulate containing oxides (typically amorphous) of calcium, silicon, aluminum, and magnesium. The proportions of these oxides are dependent on the compositions of the raw materials (i.e., iron and limestone) and, to some degree, on the specific production process and equipment used [VSL-11S2420-1]. Following granulation, which produces sand-like particles with respect to size, the BFS can be ground into particles that have particle diameters equivalent to (or less than) cement.

BFS does not exhibit adequate hydraulic properties (i.e., it does not readily hydrate/react in the presence of water), but can be used as a partial substitute for cement since it is activated by the Ca(OH)₂ (portlandite) that is produced during the initial stages of cement hydration. As such, BFS is said to be alkali-activated and produces a binding gel similar to the CSH gel formed during cement hydration. Given its activation in the presence of OH⁻, BFS is an ideal candidate for mixing with the caustic LLW at SRS. In addition, BFS substitutions have been shown to reduce the permeability of cement-based materials, which offers additional advantages for waste retention in terms of reducing both the rate of liquid transport through the cured grout and the leaching rate of contaminants from the grout to the surrounding environment. In addition, BFS is specifically added to saltstone because it acts as a reductant with the ability to reduce Tc-99 from its highly soluble (and mobile) Tc(VII) state, in the form of the pertechnetate anion (TcO₄⁻) to its less soluble (and therefore less mobile) Tc(IV) state [SRNS-STI-2008-00045].

BFS is available in three different grades, or reactivities, namely 80, 100, and 120. The various grades are defined in ASTM C989-18a, *Standard Specification for Slag Cement for Use in Concrete and Mortars*. Grading is based on a “slag activity index,” which is defined as the 28-day compressive strength ratio of samples produced with a 50/50 wt% OPC-BFS blend to samples produced with 100 wt% OPC. For Grades 80 and 100, this ratio is less than one, indicating a lower attained compressive strength with BFS substitution. For Grade 120 BFS, the ratio is greater than one, indicating enhanced compressive strength in comparison to the 100% OPC sample. The strength differential when using Grades 80/100 or 120 is associated with finer particulates and compositional variations that serve to enhance the reactivity of the higher-grade BFS.

Figure 2-1 indicates three different BFS materials that are pertinent to this report. Holcim Grade 100 BFS was used in the production of BFS/FA/OPC 45/45/10 saltstone until 2016, at which point the facility producing the BFS closed and an alternate BFS source was sought. Lehigh Grade 120 BFS was chosen to replace the Holcim Grade 100 BFS based on a study conducted by the Vitreous State Laboratory (VSL) of the Catholic University of America (CUA) [VSL-15R3740-1] and will likely be the BSF component used if cement-free saltstone is implemented at SRS. Lafarge Grade 120 BFS was the material used by VSL in their cement-free viability testing (Sections 3.1 to 3.5). Though the compositions of the Lafarge and Lehigh Grade 120 BFS materials are slightly different (per Figure 2-1 and Table 2-1), the impact to fresh and cured properties is anticipated to be minimal and will be discussed further in Future Work (Section 4).

2.2 Class F Fly Ash

Class F FA is produced during the combustion of pulverized coal and consists of the mineral impurities transported within the flue gases. FA is essentially a silicate glass containing oxides of silicon, aluminum, iron, and calcium. According to ASTM C618-19, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, Class F FA contains ≥ 50 wt% ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$); per the ASTM Class F FA may also contain up to 18% CaO. Table 2-1 indicates that the CaO contents of SEFA Class F FA measured in 2006 [WSRC-TR-2006-00067] and 2013 [VSL-12R2420-1] were less than 2 wt%. However, compositional measurements of more recent FA batches conducted in 2019 [SREL Doc. No. R-19-0001] indicate approximately 12 wt% CaO. The aforementioned increase in CaO is not anticipated to have any significant impact on fresh or cured saltstone properties. Indeed, Class F FA does not exhibit significant hydraulic behavior and essentially serves as a reactively inert component in the saltstone formulation. However, it can enhance the processing-related properties of the freshly mixed saltstone slurry by increasing the time for the saltstone to gel (stiffen) and set (harden). It also serves to reduce the viscosity of the fresh slurry thereby improving its pumpability, and since it is a non-reactive substitute for cement, the FA will also reduce the heat generated during hydration [VSL-11S2420-1].

2.3 Ordinary Portland Cement

OPC is the product of finely ground portland clinker (formed by heating a mixture of limestone and clay in the presence of fluxes) and gypsum. Types of portland cement and their respective compositions are described in ASTM C150-18, *Standard Specification for Portland Cement*. Saltstone production currently utilizes a Type I-II (MH) cement. Type I-II is a general-use cement with moderate sulfate resistance; the MH refers to a moderate heat of hydration. The approximate composition of the Type I-II (MH) cement currently used in saltstone is 66% CaO, 20% SiO_2 , and 5% Al_2O_3 (with small proportions of MgO, Fe_2O_3 , and SO_3) (Table 2-1). Cement exhibits

hydraulic activity and reacts rapidly with water to form a product typically composed of 60-70 wt% CSH gel, 20-25 wt% portlandite, and 5-15 wt% other complex mineral phases [VSL-11S2420-1].

3 CEMENT-FREE SALTSTONE

Given the reactivity of BFS with the caustic salt solution, the benefit of the minor cement component (10% by mass) is uncertain and a saltstone composition without cement (i.e., cement-free) has been proposed since its removal is expected to offer significant advantages in terms of:

- Material procurement and handling logistics,
- Storage silo utilization,
- Process control, and
- Overall process simplification.

It is envisaged that a two-component grout will offer logistical processing advantages with respect to enhanced utilization of the four dry feed silos at the SPF. Currently, three silos are filled with one of either BFS, FA, or cement and the fourth silo remains as a spare and is currently filled with BFS. For a two-component system, two of the four silos could each be filled with BFS or FA, thereby reducing the dry feeds delivery frequency and supporting the predicted increase in saltstone processing rates following the start of SWPF operations.

The primary concern with eliminating the highly reactive cement component is related to the potential impacts of a lower reactivity grout mixture on the fresh and cured properties of the resulting saltstone product, which in turn may impact: (1) the ability to process the grout in the SPF and pump it to the SDU, and (2) the capacity of the cured saltstone to resist water ingress and subsequent contaminant leaching to the surrounding environment. Thus, to determine the viability of cement-free saltstone, it is necessary to evaluate the following key fresh and cured properties and compare them to the currently utilized saltstone formulation:

- *Gelation (Gel) Time* – the time at which the CSH-type gel structure begins to form. For saltstone, the onset of gelation should ideally occur after the material has been emplaced into the SDU. However, excessive gel times can result in enhanced bleed water generation (see description below).
- *Yield Stress* – freshly prepared saltstone behaves like a Bingham plastic in that it acts as a rigid body at low stresses but flows as a viscous fluid once a finite yield stress has been reached. Higher yield stresses may adversely impact operation of the grout pump.
- *Plastic Viscosity* – plastic viscosity is a measure of the resistance to fluid flow once the yield stress has been exceeded. Higher viscosities may adversely impact operation of the grout pump.
- *Set Time* – setting is the stage at which the grout changes from a slurry to a hardened solid and is no longer flowable. The grout must be emplaced in the SDU prior to setting.
- *Bleed Water* – bleeding is caused by the settlement of solid particles and the simultaneous upward migration of water. Excessive bleeding increases the contaminated water that must be drained from the SDU and reprocessed through SPF.
- *Heat of Hydration* – hydration reactions are exothermic and generate heat within the emplaced saltstone. Higher hydration heats result in higher grout temperatures that may impact the grout quality, the volatilization of flammable components in the material, and the feasible range of grout pouring rates.

- *Saturated Hydraulic Conductivity (SHC)* – the material property that defines how easily a specific fluid may flow through saturated porous media. Higher hydraulic conductivities will result in faster water transport into the saltstone monolith, and faster contaminant transport from the monolith to the surrounding environment.

A phased research and development approach was undertaken to establish the viability of a cement-free saltstone formulation. Six phases of development have been conducted and these include:

- **Phases 1-3:** Preparation of various cement-free compositions and comparative testing of key fresh and cured properties with the standard BFS/FA/OPC 45/45/10 formulation. The ultimate goal was to select a single cement-free saltstone formulation for continued development and potential implementation at SRS. This work was conducted at VSL between 2012 through 2015.
- **Phase 4:** Development of a two-dimensional (2D) transient thermal model to simulate the addition of hydrating grout to an SDU, and to determine the maximum grout temperatures attained for the standard BFS/FA/OPC 45/45/10 and the alternate cement-free saltstone formulations. An initial model was developed by Atkins in 2017.
- **Phase 5:** Empirical measurement of key thermal properties (for the BFS/FA/OPC 45/45/10 saltstone and alternate cement-free formulation) required as inputs for the SDU thermal model. Measured properties included long-term (>14-day) heat of hydration, specific heat capacity (C_p), and thermal conductivity (λ). This work was conducted by the Savannah River Ecology Laboratory (SREL) in 2018.
- **Phase 6:** Utilization of the thermal parameters measured in Phase 5 within an updated SDU thermal model. The computer modeling work was conducted by the Savannah River National Laboratory (SRNL) and SRR.

3.1 Phase 1 – VSL Preliminary Testing of Cement-Free Saltstone Formulations

[Primary Reference: VSL-12R2420-1]

3.1.1 Objectives

Phase 1 was conducted by VSL in 2012 and was treated as an initial feasibility study to determine the effects of removing the cement from the standard saltstone formulation (BFS/FA/OPC 45/45/10; w/pm = 0.6) with specific emphasis on evaluating the potential impacts to processing the grout in SPF. Factors controlling the performance of cement-free formulations were investigated by varying the %BFS, the OH⁻ concentration of the simulat salt solution, the w/pm ratio, and the reactivity of BFS and FA components. The reactivity of the BFS was increased by using a Grade 120 BFS in place of the Grade 100, and the reactivity of the Class F FA was altered by increasing the CaO content or using finer (higher surface area) powders.

3.1.2 Testing and Results

The first phase of testing provided general insight into compositional variables that had significant impact on the fresh and cured properties of the cement-free saltstone formulations. Phase 1 considered the nine grout formulations shown in Table 3-1, one of which represented the current BFS/FA/OPC 45/45/10 formulation (GF-1). Each of the

nine dry feed formulations were combined with a simulation salt solution consistent with that anticipated during operation of SWPF determined at the time of testing (approximately 2.87 M NaOH), except for GF-7, which utilized a simulant salt solution concentration of 7.0 M NaOH (this concentration will bound any salt solution produced at SWPF) (see Table 3-2). Freshly prepared simulant grouts were tested with respect to gel time, bleed water generation, heat of hydration, rheology (viscosity and yield stress), and initial and final setting times, while cured grouts were tested with respect to compressive strength.

Table 3-1: Phase 1 Test Matrix

Grout ID	Premix Proportions (wt%)							Salt Solution		w/pm	Testing Variable
	OPC	Type of BFS		Type of Class F FA / CaO wt%				NaOH (M)	Free OH- (M)		
		Grade 100 Holcim	Grade 120 Lafarge	SEFA	Jewett	Boral PV14	Boral UFA				
GF-1	10	45	-	45	-	-	-	2.866	2.41	0.6	None
GF-2	-	50	-	50	-	-	-	2.866	2.41	0.6	Eliminate Cement
GF-3	-	75	-	25	-	-	-	2.866	2.41	0.6	↑ %BFS
GF-4	-	-	50	50	-	-	-	2.866	2.41	0.6	↑ BFS Reactivity
GF-5	-	50	-	-	50	-	-	2.866	2.41	0.6	↑ FA Reactivity
GF-6	-	50	-	-	-	50	-	2.866	2.41	0.6	↑ FA Reactivity
GF-7	-	50	-	50	-	-	-	7.0	6.54	0.6	↑ Salt Solution Alkalinity
GF-8	-	50	-	50	-	-	-	2.866	2.41	0.45	↓ w/pm Ratio
GF-9	-	50	-	-	-	-	50	2.866	2.41	0.6	↑ FA Reactivity

Ref. VSL-12R2420-1, Table 2.1

Note: Unless a specific variable was being tested, all saltstone samples were fabricated using SRS material grade and vendor, specifically Grade 100 BFS from Holcim and Class F FA from The SEFA Group. Grouts associated with testing a particular variable used additional material grades and vendors, including Grade 120 BFS from Lafarge, Jewett Class F FA containing 12 wt% CaO, PV14A Class F FA from Boral Material Technologies containing 16 wt% CaO, and UFA (ultra-fine FA), also from Boral Material Technologies. The nominal BFS/FA/OPC 45/45/10 blend additionally utilized ASTM C150-18 Type I/II cement.

Table 3-2: Waste Simulant Formulation for the Fabrication of Grouts used in Phase 1

Ingredient	SWPF1X Waste Simulant Conc. (All samples except GF-7) (M)	SWPF7M Waste Simulant Conc. (M)
Sodium Hydroxide (NaOH) (50 wt%)	2.866	7.0
Free Hydroxide (OH ⁻)	2.41	6.54
Sodium Nitrate (NaNO ₃)	1.973	1.973
Sodium Nitrite (NaNO ₂)	0.485	0.485
Sodium Carbonate (Na ₂ CO ₃)	0.118	0.118
Sodium Sulfate (Na ₂ SO ₄)	0.055	0.055
Aluminum Nitrate (Al(NO ₃) ₃ ·9H ₂ O)	0.114	0.114
Sodium Phosphate (Na ₃ PO ₄ ·12H ₂ O)	0.007	0.007

Ref. VSL-12R2420-1, Tables 3.1 and 3.2]

With respect to Table 3-2, it is important to differentiate between NaOH and free hydroxide concentrations for salt solutions that also contain aluminum (Al). In alkaline solutions, Al (from Al(NO₃)₃·9H₂O) will form a stable Al(OH)₄⁻ complex which serves to reduce the alkalinity of the solution; one Al cation essentially removes four hydroxide anions. Therefore, for the 2.866 M NaOH, the free hydroxide concentration is actually 2.866 M – (4 x 0.114 M) (i.e., 4 x the Al concentration) = 2.41 M. Likewise, the free hydroxide concentration for the 7.0 M NaOH solution is actually 7.0 M – (4 x 0.114 M) = 6.54 M. Henceforth, text references to OH⁻ concentrations are associated with free hydroxide concentrations.

A summary of the fresh and cured properties of the saltstone simulant grouts (fabricated with the formulations of Table 3-1 and waste simulant compositions of Table 3-2) are provided in Table 3-3.

Table 3-3: Summary of Fresh and Cured Grout Properties for Formulations Tested in Phase 1

Sample ID	Gel Time (min)	Set Time (h)		Bleed Water (wt%) ^a	Yield Stress (Pa)	Viscosity (cP)	Hydration		Compressive Strength (psi)	
		Initial	Final				Peak Time (h) ^b	Normalized Heat at 48 h (J/g)	7 days	28 days
GF-1	200	8	11	0.53	18.4	162	3	56	648	1260
GF-2	>480	15	25	2.29	11.9	120	7	53	845	1707
GF-3	150	8	9	0	15.1	131	3	71	1365	1858
GF-4	>480	16	24	3.76	7.6	180	14	65	1354	2065
GF-5	290	18	28	2.40	7.6	108	8	59	1198	2058
GF-6	140	33	>49	1.30	13.7	150	15	62	1952	4338
GF-7	120	8	12	0	22.4	220	2	42	168	203
GF-8	130	9	14	0	41.8	425	6	57	1631	2625
GF-9	320	>45 ^c	>45 ^c	1.80	26.6	242	24.5	60	1056	2936

Ref VSL-12R2420-1, Table 6.1

^a Expressed as wt% of the water mass present in the freshly prepared paste.^b Average value from independent experiments.^c Formulation failed to set within the experimental time.

A primary concern with the cement-free formulations is that removal of the reactive cement component could result in reduced reactivity and enhanced bleed water generation. Indeed, simply removing the cement component with no other modifications to the base formulation (Sample GF-2: BFS/FA 50/50) caused at least a two-fold increase in gel time, a two-fold increase in set time, and a four-fold increase in bleed water generation (in comparison to the standard saltstone: GF-1). In some instances, the bleed water generation could be decreased by using more reactive FA components (i.e., finer FA: GF-9 or FA with higher CaO content: GF-6), increasing the proportion of the reactive BFS (i.e., higher %BFS: GF-3), or decreasing the w/pm ratio (i.e., lower water content: GF-8). When considering grout processability in the SPF, longer gel and set times, as well as lower grout viscosity and yield stress, could be considered positive property changes since they potentially increase the window of saltstone processability and the opportunity for recovery in case of process upsets. However, the lengthening of gel time in cement-free formulations raises concerns of particle settling in the slurry, and additionally, the associated presence of increased amounts of bleed water may lead to operational problems when managing potentially greater volumes of drain water within the facility. With respect to cured properties, all cement-free samples, other than that produced with the 6.54 M OH⁻ simulant salt solution (GF-7), indicated enhanced compressive strength and similar hydration heats in comparison to the BFS/FA/OPC 45/45/10 saltstone formulation. Indeed, the compressive strength of the BFS/FA 50/50 sample prepared with 16 wt% CaO-containing FA (GF-6) demonstrated a near four-fold increase in compressive strength compared to the standard BFS/FA/OPC 45/45/10 material (GF-1). Compressive strength is not a critical property for saltstone and the requirement is that it merely exceeds 500 psi [T-CLC-Z-00006]; however, compressive strength often correlates inversely with SHC

(i.e., as the compressive strength increases so the SHC decreases). Saltstone SHC determines the rate of fluid transport through the cured saltstone, which in turn influences the leaching rate of contaminants from the grout monolith to the surrounding environment.

Despite some property differences in comparison to the BFS/FA/OPC 45/45/10 formulation, the Phase 1 data ultimately indicated that removal of cement was a potentially viable option, though continued development and evaluation efforts were required to better optimize the cement-free formulations, particularly with respect to reducing the bleed water generation. In addition, it was considered critical to: (1) measure the SHC of cement-free formulations to compare the hydraulic transport properties with the standard BFS/FA/OPC 45/45/10, and (2) determine if the enhanced compressive strength for samples prepared using the 16 wt% CaO-containing FA translated to a lower SHC.

3.2 Phase 2A – Optimization of Viable Cement-Free Saltstone Formulations

[Primary Reference: VSL-14R2890-1]

3.2.1 Objectives

Based on the empirical fresh and cured property data derived from Phase 1, Phase 2 (later to be termed Phase 2A) efforts were initiated in 2014 with the primary objectives of decreasing the bleed water generation and evaluating the hydraulic properties of cement-free compositions utilizing the 16 wt% CaO-containing FA. In addition, Phase 2A further considered the role of the salt solution waste simulant composition (in particular OH⁻ concentration) on saltstone performance.

3.2.2 Testing and Results

The test matrix for Phase 2A is indicated in Table 3-4. Three sample formulations were considered, and these were identical with respect to the raw materials and w/pm ratios used in Phase 1 for samples GF-1 (BFS/FA/OPC 45/45/10), GF-2 (BFS/FA 50/50), and GF-6 (BFS/FA 50/50 with 16 wt% CaO-containing FA). The difference between these samples and their Phase 1 counterparts was that Phase 2A samples were prepared with an ARP/MCU simulated salt solution, as indicated in Table 3-5; as such Phase 2A samples were designated with an M to differentiate them from the Phase 1 samples. The ARP/MCU simulant had a lower OH⁻ concentration than the SWPF salt solution simulant used in Phase 1 (approximately 1.38 M compared to 2.41 M, respectively); as such, decreased reaction (hydration) rates were anticipated.

Table 3-4: Phase 2A Test Matrix

Sample ID	Premix (wt%)			
	Cement	Holcim Grade 100 BFS	SEFA Class F FA	Boral PV14A Class F FA
GF-1M	10	45	45	0
GF-2M	0	50	50	0
GF-6M	0	50	0	50

Ref. VSL-14R2890-1, Table 2.1

Note: All samples were prepared at a w/pm of 0.6.

Table 3-5: ARP/MCU Salt Solution Simulant used for Fabrication of Grouts used in Phase 2A Testing

Ingredient	ARP/MCU Simulant Concentration (M)
Sodium Hydroxide (NaOH) (50 wt%)	1.594
Free Hydroxide (OH ⁻)	1.38
Sodium Nitrate (NaNO ₃)	3.159
Sodium Nitrite (NaNO ₂)	0.368
Sodium Carbonate (Na ₂ CO ₃)	0.176
Sodium Sulfate (Na ₂ SO ₄)	0.059
Aluminum Nitrate (Al(NO ₃) ₃ ·9H ₂ O)	0.054
Sodium Phosphate (Na ₃ PO ₄ ·12H ₂ O)	0.012

Ref. VSL-14R2890-1, Table 3.1

The fresh and cured grout properties for the Phase 2A formulations are summarized in Table 3-6 and discussed in the subsequent text.

Table 3-6: Summary of Fresh and Cured Grout Properties for the Down-Selected Formulations Tested in Phase 2A and Compared with Grout Tested in Phase 1

Grout ID	Gel Time (min)	Final Set Time (h)	Bleed Water (wt%)	Yield Stress [Pa]	Viscosity [cP]	Peak Hydration Time (h)	28-Day Compressive Strength (psi)	28-Day SHC (cm/sec)
GF-1	200	11	0.5	18.4	162	3	1260	-
GF-1M	65	11	0.0	13.8	78	3	761	3E-09
GF-2	>480	25	2.3	11.9	120	7	1707	-
GF-2M	>480	36	10.6	4.5	52	55	2236	1E-09
GF-6	140	>49	1.3	13.7	150	15	4338	-
GF-6M	330	>48	11.2	6.9	51	117	3161	7E-10

Ref. VSL-12R2420-1, Table 6.1, and VSL-14R2890-1, Tables 6.1 and 6.2

Fresh Grout Properties

Cement-free samples prepared with the lower [OH⁻] ARP/MCU salt solution (1.38 M compared to 2.41 M used in Phase 1) indicated lower yield stress and viscosity, and for a given [OH⁻], both the yield stress and viscosity were higher for the BFS/FA/OPC 45/45/10 in comparison to either of the cement-free formulations. For both OH⁻ concentrations, the cement-free gel times exceeded two hours and the set times exceeded one day; in general, these times were longer than those measured for the BFS/FA/OPC 45/45/10 formulation. However, perhaps the most significant fresh property data from Phase 2A was the five to ten-fold increase in cement-free bleed water content when using the lower [OH⁻] salt solution (GF-2 → GF-2M: 2.3 → 10.6 wt%; GF-6 → GF-6M: 1.3 → 11.2 wt%). This result is of some concern since it places undesirable strain on the SDU drainage systems and requires reprocessing of the drain water through SPF. Of potentially greater concern

is the fact that the cement-free formulations studied thus far indicate a significant sensitivity to changes in the salt solution composition (specifically OH^- concentration).

Cured Grout Properties

The 28-day compressive strengths for the Phase 2A samples prepared with ARP/MCU salt solution all decreased, which was expected based on the reduced hydration rate associated with the lower OH^- concentration. However, as with Phase 1, the cement-free composition utilizing 16 wt% CaO-containing FA (GF-6M) again indicated significantly higher compressive strength in comparison to the other Phase 2A samples. It was anticipated that the enhanced strength might also correlate with a decrease in SHC, though improvement was marginal. The SHC for GF-6M was only 1.5 times lower than GF-2M (BFS/FA 50/50 with SEFA Class F FA) and approximately 4 times lower than GF-1M (the standard BFS/FA/OPC 45/45/10). Since the potential benefits of incorporating a higher CaO-containing FA were marginal, especially when using a salt solution with a lower OH^- concentration, future work would only consider the traditionally used SEFA Class F FA.

Per the Phase 2A data, VSL concluded that the study needed to be extended based on the following observation:

- Given the adverse impact of a lower OH^- concentration on the hydration rate of the cement-free compositions, it was necessary to examine the effect of the waste composition variations on the processability of the cement-free formulations.

3.3 Phase 2B – Optimization of Viable Cement-Free Saltstone Formulations

[Primary Reference: VSL-14R2890-1-2B]

3.3.1 Objectives

Phase 2B was primarily designed to investigate the effect of salt solution alkalinity on the fresh and cured properties of cement-free formulations. In addition, since Phase 2A had already highlighted decreased hydration kinetics in salt solutions with lower OH^- concentrations, Phase 2B was also used to examine formulation changes, namely %BFS and w/pm, that might decrease the adverse impact of reduced OH^- concentrations on the cement-free properties. Property testing for Phase 2B was limited to fresh property evaluation (gel/set times, bleed water generation, viscosity, and yield stress), and heat of hydration since it was anticipated that the planned changes to both dry feed constituents and the salt solution composition would result in varied rates of hydration.

3.3.2 Testing and Results

To develop a salt solution compositional test matrix, data from quarterly analysis of actual salt solution waste samples from 2009 to 2013 was statistically evaluated to provide the mean, standard deviation, maximum, and minimum concentrations for the major salt solution components, as shown in Table 3-7.

Table 3-7: Statistics for Quarterly Sample Analysis Data for Salt Waste Compositions from 2009-2013 Converted to Molar Values

Species	Mean (M)	St. Deviation (M)	Minimum (M)	Maximum (M)
Carbonate (CO_3^{2-})	0.163	0.028	0.131	0.233
Free Hydroxide (OH^-)	1.569	0.332	1.029	1.988
Nitrate (NO_3^-)	1.967	0.222	1.677	2.452
Nitrite (NO_2^-)	0.273	0.135	0.128	0.511
Oxalate ($\text{C}_2\text{O}_4^{2-}$)	0.009	0.003	0.005	0.015
Phosphate (PO_4^{3-})	0.007	0.002	0.004	0.011
Sulfate (SO_4^{2-})	0.053	0.013	0.034	0.074
Aluminum (Al)	0.124	0.014	0.105	0.151

Ref. VSL-142890-1-2B, Table 2.1

Mean concentrations and the likely range of variation (in combination with the expectations of significance of these variations on grout properties) for each salt solution waste chemical component were considered for Phase 2B testing. Through this assessment, VSL placed primary significance on the concentrations of free hydroxide, nitrate, and nitrite, and secondary significance on the concentrations of phosphate, sulfate and aluminate. However, it was anticipated that of all the salt solution components, the free hydroxide concentration would have the most significant effect on the fresh grout properties, and thus a key objective of the Phase 2B testing was to determine the effects of waste free hydroxide concentration on the fresh grout properties. Based on the compositional data in Table 3-7, the following five OH^- concentrations were considered: 1.0, 1.67, 2.0, 2.33, and 3.0 M. The concentrations of the other salt solution constituents were held constant and are detailed in Table 3-8.

Table 3-8: Salt Solution Simulant used for Fabrication of Grouts used in Phase 2B Testing

Ingredient	Concentration (M)
Sodium Hydroxide (NaOH) (50 wt%)	Variable
Free Hydroxide (OH^-)	Variable
Sodium Nitrate (NaNO_3)	1.967
Sodium Nitrite (NaNO_2)	0.273
Sodium Carbonate (Na_2CO_3)	0.163
Sodium Sulfate (Na_2SO_4)	0.053
Aluminum Nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)	0.124
Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$)	0.009
Sodium Phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	0.007

Ref. VSL-14R2890-1, Table 3.2

Based on the results from Phases 1 and 2A, it was determined that for this stage of development, the BFS and FA sources should remain constant, and Phase 2B would utilize only the BFS and FA materials that had been traditionally used in the production of saltstone (i.e., Holcim Grade 100 BFS and SEFA Class F FA). Thus, only the w/pm and the %BFS were considered formulation variables for this test matrix. The w/pm ratio was varied between 0.45 and 0.6 and the %BFS from 45 to 60%.

Specific grout formulations (in terms of OH⁻ concentration, w/pm, and %BFS) considered in this study are detailed in Table 3-9, together with the respective fresh grout properties and heat of hydration data.

Table 3-9: Summary of Phase 2B Test Data

Grout Formulation ^a				Gel Time (min) ^b		Fresh Density (g/cm ³)	Set Time (h)	Bleed Water (wt%) ^c	Yield Stress (Pa)	Viscosity (cP)	Hydration		
Mix	[OH ⁻] (M)	w/pm	%BFS	Onset	Finish						Main Peak Time (h)	Normalized Heat at 48 h (J/g)	Normalized Heat at 28 days (J/g)
1.67M1	1.67	0.50	50	150	240	1.80	11.2	3.17	10.7	125	100.9	2.9	115.9
1.67M2	1.67	0.55	55	130	220	1.75	16.8	3.79	17.0	168	76.8	3.5	122.6
2.33M1	2.33	0.55	50	110	230	1.77	12.6	3.45	5.0	96	6.5	67.1	111.6
2.33M2	2.33	0.55	50	120	250	1.77	13.3	3.02	5.3	90	7.2	69.1	100.4
2.33M3	2.33	0.50	55	80	120	1.80	6.6	1.98	10.5	123	5.2	78.4	118.4
1.00M1	1	0.45	45	32	88	1.81	46.2	1.55	16.4	216	198.6	2.5	94.6
1.00M2	1	0.45	60	12	42	1.80	7.1	1.12	37.6	316	146.9	2.6	109.2
1.00M3	1	0.60	60	62	96	1.69	18.7	2.89	12.2	93	170.7	3.0	114.9
3.00M1	3	0.45	45	50	80	1.84	7.6	1.06	15.0	247	5.0	62.2	100.8
3.00M2	3	0.60	45	100	190	1.73	10.0	2.52	2.6	65	5.5	58.0	105.9
3.00M3	3	0.45	60	44	99	1.84	5.3	0.36	21.4	286	3.1	75.7	119.7
2.00M2	2	0.525	52.5	180	270	1.77	8.1	3.41	8.0	108	7.4	65.0	110.8
2.00M1 ^d	2	0.60	45	90	135	1.73	15.6	1.38	6.5	82	3.2	57.3	100.0

Ref. VSL-14R2890-1-2B, Table 5.1

^a A grout formulation is determined by the concentration of free [OH⁻] in simulant, w/pm ratio, and wt% BFS in the binder premix.

^b Gel time was determined by Dynamic Rheological Measurement (DRM).

^c % of the water mass present in the freshly prepared paste according to ASTM C232-14, *Standard Test Method for Bleeding of Concrete*.

^d Reference formulation BFS/FA/OPC 45/45/10.

From the data presented in Table 3-9, it was determined that, in general, bleed water content and gel/set times decreased with: (1) decreasing w/pm, (2) increasing [OH⁻], and (3) increasing %BFS. Yield stress and plastic viscosity decreased with: (1) increasing w/pm, (2) decreasing [OH⁻], and (3) decreasing %BFS. Though all the observed trends were consistent with expectations, the property of primary concern, as highlighted in Phases 1 and 2A, was bleed water generation and its dependence on OH⁻ concentration. The bleed water content for the BFS/FA/OPC 45/45/10 mix was measured at approximately 1% irrespective of OH⁻ concentration but increased from 2 to 10% for the BFS/FA 50/50 composition when the OH⁻ concentration was decreased from approximately 2.41 to 1.38 M (see Table 3-6). There are two formulations to note in Table 3-9 with respect to the impact of w/pm and %BFS on bleed water content for low OH⁻ concentrations. The first formulation is 1.00M1 with a w/pm of 0.45 and 45% BFS (hence a BFS/FA 45/55 mix) in which the reactive %BFS is equivalent to that in the standard BFS/FA/OPC 45/45/10 mix

but the w/pm has been lowered. With an OH^- concentration of 1.0 M, this sample indicated a bleed water content of approximately 1.6%. The second is formulation 1.00M3 with a w/pm of 0.6 and 60% BFS (hence a BFS/FA 60/40 mix) in which the w/pm is equivalent to that of the standard BFS/FA/OPC 45/45/10 mix but the reactive %BFS has been increased. For this sample, when using an OH^- concentration of 1.0 M, a bleed water content of approximately 2.9% was measured. Thus, these data points confirm the positive impact of lower w/pm (i.e., mixes with less water and therefore less salt solution) or higher %BFS (i.e., more reactive phase) with respect to reducing the bleed water content for the cement-free formulations. However, even though for these particular samples the bleed water content of the 1.00M3 sample (higher %BFS) was greater than that of 1.00M1 (lower w/pm), for future cement-free formulations it is preferable to increase %BFS to decrease the bleed water content, since decreasing the w/pm will decrease the salt solution loading per unit mass of dry feeds (higher mass of dry feeds required to disposition a unit volume of salt solution) and likely increase the SDU space required to disposition the entire salt solution inventory at SRS.

With respect to the heat of hydration for the formulations investigated in Phase 2B, the main peak times (indicative of the hydration initiation) were influenced by the OH^- concentrations, as peaks for the eight grout mixes with higher OH^- concentrations (i.e., 2.00M, 2.33M and 3.00M) appeared much earlier than those formulations with lower concentrations. This indicates, as anticipated, that the kinetics of hydration are highly dependent on the alkalinity of the simulant used for preparing grout samples, and that $[\text{OH}^-]$ plays a dominant role in determining the peak time of hydration. However, while $[\text{OH}^-]$ had a strong effect on early heat release, it did not play a significant role with respect to the 28-day normalized heat released. In general, higher OH^- concentrations resulted in increased maximum heat flow, decreased hydration peak time and increased heat release at 2 days of curing. After 28 days of curing, the %BFS appeared to be somewhat more influential than $[\text{OH}^-]$ as shown in Table 3-9.

Overall, the data collected in Phase 2B indicated that changes to w/pm, %BFS, and $[\text{OH}^-]$ resulted in predictable behaviors with respect to fresh properties and hydration kinetics. This data again supported the viability of cement-free saltstone formulations, particularly with respect to the observation that increasing the %BFS decreased the fresh property sensitivity of the cement-free mix with respect to changes in $[\text{OH}^-]$. A third and final phase of testing was developed in order to identify cement-free formulations that were relatively insensitive to changes in all major salt solution constituents.

3.4 Phase 3 – Down-Select of Cement-Free Formulations

[Primary Reference: VSL-15R2890-1]

3.4.1 Objectives

The primary objective of Phase 3 (initiated in 2015) was to identify one or two cement-free saltstone formulations whose fresh and cured properties were equivalent to the standard saltstone formulation and relatively insensitive to the anticipated range of salt waste compositions. To accomplish this objective, Phase 3 consisted of two stages of salt solution variability testing, which ultimately led to the identification of two viable cement-free candidates. These down-selected cement-free formulations were subsequently

evaluated with respect to elevated temperature curing (indicative of the SDUs) to determine if the cured properties were adversely impacted by above-ambient curing temperatures.

3.4.2 Testing and Results

Variability Test Matrix A

The first stage of Phase 3 testing evaluated the effects of varying salt waste components (other than $[\text{OH}^-]$ which was held at 1.57 M) including nitrate, nitrite, phosphate, sulfate, aluminum, and carbonate. Each constituent was evaluated at its minimum and maximum concentration (per Table 3-7), while holding all other waste components at their mean concentrations. Table 3-10 provides an example composition in which all components are held at their mean values (according to Table 3-7) except for nitrate which was set to its maximum concentration.

**Table 3-10: Example Salt Solution Recipe with High Nitrate Concentration
(Corresponding to Sample NO3HL in Table 3-11)**

Ingredient	Concentration (M)
Sodium Hydroxide (NaOH) (50 wt%)	2.065
Free Hydroxide (OH^-)	1.570
Sodium Nitrate (NaNO_3)	2.452
Sodium Nitrite (NaNO_2)	0.273
Sodium Carbonate (Na_2CO_3)	0.163
Sodium Sulfate (Na_2SO_4)	0.053
Aluminum Nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)	0.124
Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$)	0.009
Sodium Phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	0.007

Ref. VSL-15R2890-1, Table 3.3

As shown in Table 3-11, the dry mix compositions and w/pm were fixed at values (i.e., 50 wt% Holcim Grade 100 BFS and 50 wt% SEFA Class F FA and w/pm = 0.55) based on the results of the Phase 2B work to obtain fresh properties that are reasonably close to those of the standard BFS/FA/OPC 45/45/10 formulation.

Table 3-11: Composition of Grout Mixes for Test Matrix A of Phase 3 Testing

Test Matrix				Formulation Parameters
Test	Species	Value	Molarity (moles/L)	
NO3LL	Nitrate (NO ₃ ⁻)	LOW	1.677	All samples prepared with: 50 wt% Holcim Grade 100 BFS + 50 wt% SEFA Class F FA w/pm = 0.55
NO3HL		HIGH	2.452	
NO2LL	Nitrite (NO ₂ ⁻)	LOW	0.128	
NO2HL		HIGH	0.511	
Al-LL	Aluminum (Al)	LOW	0.105	
Al-HL		HIGH	0.151	
SO4LL	Sulfate (SO ₄ ²⁻)	LOW	0.034	
SO4HL		HIGH	0.074	
CO3LL	Carbonate (CO ₃ ²⁻)	LOW	0.131	
CO3HL		HIGH	0.233	
OX-LL	Oxalate (C ₂ O ₄ ²⁻)	LOW	0.005	
OX-HL		HIGH	0.015	
PO4LL	Phosphate (PO ₄ ³⁻)	LOW	0.004	
PO4HL		HIGH	0.011	

Ref. VSL-15R2890-1, Table 2.1

Notes: In each test, the concentrations of all species are held at their mean values listed in Table 6-1; sodium concentration is determined by the charge balance.

As with Phase 2B testing, Phase 3 grouts were tested with respect to fresh grout properties, including viscosity, yield stress, gel/set times, and bleed water generation, and the 12-day cumulative heat of hydration. Phase 3 also included SHC and compressive strength evaluation. The test results of Matrix A grouts are provided in Table 3-12 and indicate that only variations in aluminum content significantly impacted the fresh grout properties. Higher aluminum concentrations retarded hydration kinetics which in turn increased gel time and bleed water generation. For all compositions indicated in Table 3-12, the high limit Al sample (Al-HL) had the highest bleed water content (7.9%), while the low limit Al sample (Al-LL) had the lowest bleed water content (3.83%) of all samples. Variations in aluminate concentrations had been shown to impact the fresh properties of saltstone in a previous study [SRNL-STI-2009-00184].

Table 3-12: Summary of Test Results from Variability Testing – Test Matrix A

Composition	Gel Time (by DRM) (min)		Set Time (h)	Bleed Water (wt%)	Yield Stress (Pa)	Viscosity (cP)	28-Day Compressive Strength (psi)	28-Day SHC (cm/sec)
	Onset	Finish						
NO3LL	140	250	35.0	5.74	4.31	53.85	1931	2.10E-09
NO3HL	125	250	35.3	4.97	4.30	60.91	2057	2.20E-09
NO2LL	100	220	34.3	4.99	4.05	59.60	1658	2.80E-09
NO2HL	90	210	37.2	5.68	4.44	60.69	1679	2.20E-09
AI-LL	60	140	45.6	3.83	4.22	59.77	2357	2.43E-09
AI-HL	110	250	16.6	7.92	4.46	64.96	1465	2.20E-09
SO4LL	110	220	33.8	6.07	3.29	59.69	2014	3.20E-09
SO4HL	105	220	29.9	5.95	3.86	56.89	2065	2.63E-09
CO3LL	90	210	24.1	4.97	3.68	61.89	2216	2.20E-09
CO3HL	110	210	37.6	5.35	4.21	58.77	2094	2.27E-09
OX-LL	120	250	28.9	6.48	5.49	68.28	1564	1.60E-09
OX-HL	120	230	26.5	5.52	5.26	67.94	1641	1.77E-09
PO4LL	130	230	23.0	5.30	5.50	70.76	1632	2.27E-09
PO4HL	100	240	32.4	6.14	4.32	66.48	1719	1.97E-09

Ref. VSL-15R2890-1, Table 5.1

Note: In Ref. VSL-15R2890-1, Table 5.1 the composition suffixes of “LL” (low limit) and “HL” (high limit) have been erroneously interchanged; the correct suffixes are used in Table 3-12 of this document.

Variability Test Matrix B

Based on the high bleed water generated by all samples in Test Matrix A, scoping studies were conducted prior to development of Test Matrix B to evaluate variables that could be adjusted to reduce the bleed water content. In addition, adjustment of the identified variables should allow the w/pm ratio to be adjusted back to 0.6 or higher (note that for the Phase 3 Test Matrix A, a w/pm = 0.55 was used). The scoping studies determined that increasing the %BFS and the BFS reactivity (i.e., replacing Grade 100 with Grade 120 BFS) reduced bleed water, and thus should be considered in Test Matrix B. As such, ten cement-free grout compositions, all utilizing Grade 120 BFS, and a BFS/FA/OPC 45/45/10 reference sample (utilizing Grade 100 BFS) were included in the second stage of variability testing. This stage of testing examined the effects of varying the following parameters on the fresh and cured grout properties:

- %BFS (at constant w/pm),
- w/pm (at constant %BFS),
- OH⁻ concentration, and
- Aluminum concentration.

Formulations investigated in Phase 3 Test Matrix B are indicated in Table 3-13.

Table 3-13: Composition of Grout Mixes for Test Matrix B of Phase 3 Testing

Composition	Variant	OPC (wt%)	BFS (wt%)	BFS Grade	FA (wt%)	w/pm	[OH ⁻] (M)
60FS0.60	Nominal	0	60	120	40	0.60	1.57
70FS0.65	High (BFS + w/pm)	0	70	120	30	0.65	1.57
60FS0.65	High w/pm	0	60	120	40	0.65	1.57
60FS0.55	Low w/pm	0	60	120	40	0.55	1.57
55FS0.60	Low BFS	0	55	120	45	0.60	1.57
65FS0.60	High BFS	0	65	120	35	0.60	1.57
LL-OH	Low OH (1 M)	0	60	120	40	0.60	1.00
HL-OH	High OH (3 M)	0	60	120	40	0.60	3.00
LL-Al	Low Al (0.105 M)	0	60	120	40	0.60	1.57
HL-Al	High Al (0.151 M)	0	60	120	40	0.60	1.57
Ref-ST	Control	10	45	100	45	0.60	1.57

Ref. VLS-15R2890-1, Table 2.3

Note: The concentration of aluminum used in the salt solution is 0.124 M except for the LL-Al and HL-Al compositions.

The data derived from conducting Test Matrix B (shown in Table 3-14) identified viable cement-free formulations that exhibited comparable or enhanced performance in comparison to the BFS/FA/OPC 45/45/10 reference sample with respect to bleed water generation, gel time, set time, plastic viscosity, yield stress, SHC, and compressive strength. However, the 12-day heat of hydrations were higher for all cement-free compositions.

Table 3-14: Summary of Phase 3 Test Matrix B Variability Testing

Composition	Variant	Gel Time (min)		Set Time (h)	Yield Stress (Pa)	Viscosity (cP)	Bleed Water (wt%)	12-Day Cumulative Heat (J/g)	28-Day SHC (cm/sec)
		Onset	Finish						
60FS0.60	Nominal	36	60	20	7.3	58.1	1.2	125.4	2.0E-09
70FS0.65	High (BFS + w/pm)	48	56	18	6.3	50.8	0.7	139.7	2.0E-09
60FS0.65	High w/pm	UC	UC	23	5.0	45.9	1.0	125.9	1.3E-09
60FS0.55	Low w/pm	UC	54	24	10.7	80.3	1.0	125.2	1.4E-09
55FS0.60	Low BFS	UC	60	24	6.8	51.5	0.9	118.8	1.7E-09
65FS0.60	High BFS	UC	56	21	11.2	62.6	1.1	136.8	2.4E-09
LL-OH	Low OH (1 M)	30	90	72	5.2	48.1	1.7	113.5	1.3E-09
HL-OH	High OH (3 M)	44	154	8	8.6	77.3	1.0	121.6	1.4E-09
LL-AI	Low AI (0.105 M)	44	84	15	8.8	59.4	1.6	126.7	1.2E-09
HL-AI	High AI (0.151 M)	18	60	28	10.6	58.7	0.4	129.8	1.5E-09
Ref-ST	Control	56	96	13	9.5	86.5	0.7	83.0	2.0E-09

Ref. VSL-15R2890-1, Tables 5.5 and 5.7

Note: UC = value uncertain

After reviewing the results, the following two cement-free grout formulations were down-selected for curing profile testing based on their comparable, or enhanced properties, with respect to the BFS/FA/OPC 45/45/10 reference:

1. BFS/FA 70/30 (w/pm = 0.65) and
2. BFS/FA 60/40 (w/pm = 0.6).

Both selected compositions are potentially viable with respect to fresh properties and would not adversely impact grout processing and placement. Lower viscosity and yield stress, as well as notably higher compressive strengths and shorter gel times, were observed in both cement-free samples when compared to the BFS/FA/OPC 45/45/10 reference sample. Set times were only a few hours longer than that of the reference saltstone and SHC values were essentially the same. The BFS/FA 70/30 exhibited almost identical bleed to the BFS/FA/OPC 45/45/10 reference, but a 70% higher 12-day heat of hydration. The BFS/FA 60/40 sample indicated slightly higher bleed water and approximately 50% higher hydration heat than BFS/FA/OPC 45/45/10 reference.

Two separate curing profile tests were performed on the down-selected cement-free grouts and the BFS/FA/OPC 45/45/10 reference to determine the potential cured-property impacts of elevated temperature curing in the SDUs. The results indicated that curing to temperatures of 50 and 75 °C had no significant impacts on the cured properties of either the cement-free formulations or the standard saltstone reference.

3.5 Cement-Free Down-Selection

Based on the data provided by Test Phases 1-3, two compositions were down-selected as potential cement-free saltstone candidates. These were a BFS/FA 60/40 (Grade 120 BFS) at w/pm = 0.6 and a BFS/FA 70/30 (Grade 120 BFS) at w/pm = 0.65. While either formulation is conceivably viable in terms of exhibiting similar fresh properties and SHC to the base BFS/FA/OPC 45/45/10 formulation, both indicate significantly higher heats of hydration (see Table 3-15). The increases in heat generated over a 12-day period for the BFS/FA 60/40 and 70/30 formulations were approximately 50% and 70%, respectively. It is worth noting, if implemented, cement-free saltstone would be emplaced in the “mega vaults” (SDU 6 and beyond), and the thinner pours (and the larger surface area-to-volume ratio associated with saltstone pours into the larger SDUs) are expected to enhance the dissipation of heat from the hydrating grout.

Table 3-15: Property Comparison for BFS/FA/OPC 45/45/10 and BFS/FA 60/40 and 70/30

Formulation Variables				Fresh Properties					Cured Properties	
Mix	BFS Grade	w/pm	[OH] ⁻ M	Gel Time (min)	Set Time (hr)	Yield Stress (Pa)	Viscosity (cP)	Bleed (%)	12-Day Heat of Hydration (J/g)	28-Day SHC (cm/sec)
45/45/10	100	0.60	1.57	56	13	9.5	86.5	0.7	83.0	2.0E-09
60/40	120	0.60		36	20	7.3	58.1	1.2	125.4	2.0E-09
70/30	120	0.65		48	18	6.3	50.8	0.7	139.7	2.0E-09

Other factors that may influence the choice of cement-free formulations include the cost of raw materials and saltstone processing duration and storage (i.e., SDU construction costs). With respect to raw materials (currently utilized for saltstone production), the estimated costs for Lehigh Grade 120 BFS, SEFA Class F FA, and Holcim OPC are \$170, \$69, and \$154 per ton, respectively [SRR-CWDA-2019-00021]. Based on those costs, the cost per ton for each dry feed formulation would be as follows:

- BFS/FA/OPC 45/45/10: \$123,
- BFS/FA 60/40: \$129, and
- BFS/FA 70/30: \$140.

However, it should be noted the BFS/FA 70/30 formulation has a higher w/pm (0.65), which should be factored into the dry feed cost. The corrected cost associated with the increased salt solution processed per unit mass of dry feeds results is a true cost of \$129 per ton (i.e., \$140 x 0.6/0.65) since fewer dry feeds will ultimately be required to disposition the entire salt solution inventory when using a higher w/pm. As such, there is no cost differential between the raw materials for the two cement-free formulations. In addition, as indicated by VSL [VSL-15R2890-1], the volume of fresh grout produced from a unit volume of salt solution is approximately 3 to 4% less for the BFS/FA 70/30 (w/pm = 0.65) formulation in comparison to the BFS/FA 60/40 (w/pm = 0.6). While a 3-4% decrease in total volume of grout processed is unlikely to result in reduction of the number of SDUs that require construction, it should yield a 3-4% decrease in total SPF operating time (i.e., the time associated with dispositioning the entire salt solution inventory produced at SRS).

Relevant to the ultimate choice of a cement-free formulation is the robustness of the material properties (fresh and cured) to variations around its base composition. It is important to note that investigations with respect to the sensitivities of a formulation to processing variations were only conducted for the BFS/FA 60/40 material; this was predominantly based on the higher heat generated by the BFS/FA 70/30 formulation, which was considered a significant impediment to its potential implementation.

According to data from VSL (Table 3-16 through Table 3-18), the BFS/FA 60/40 formulation appears robust with respect to changes in $[\text{OH}^-]$, w/pm ratio, and BFS/FA ratio. Changes to the latter two formulation parameters may result from SPF processing inconsistencies associated with slight variations around the target masses and volumes for the premix components and salt solution, respectively. However, SPF processing variations with respect to premix composition and w/pm will not approach the upper and lower limits investigated in the VSL study. With respect to the hydroxide concentration (Table 3-16), higher concentrations resulted in similar gel times, yield stress, and viscosity, shorter set times, marginally lower bleed water generation, and marginally higher heat of hydration. SHC was unaffected with all samples indicating values from $1\text{-}2\text{E-}09$ cm/sec, which is equivalent to the SHC measured for the standard BFS/FA/OPC 45/45/10 formulation (see Table 3-15). Table 3-17 indicates that varying the w/pm from 0.55 to 0.65 has no significant effect on any of measured fresh or cured properties. While the yield stress and viscosity do marginally increase with lower w/pm ratios, the observed differences in these properties from those of the baseline material are unlikely to be large enough to result in any significant differences in the ability to process the grout. Table 3-18 indicates fresh and cured property data for BFS proportions of 55, 60, and 65 wt%. Other than the expected increase in heat of hydration with an increased proportion of BFS, no other changes appeared significant.

Table 3-16: Properties for BFS/FA 60/40 Composition with Varied OH⁻ Concentrations

Formulation Variables				Fresh Properties					Cured Properties	
Mix (BFS/FA)	BFS Grade	w/pm	$[\text{OH}^-]$ (M)	Gel Time (min)	Set Time (h)	Yield Stress (Pa)	Viscosity (cP)	Bleed (wt%)	12-Day Heat of Hydration (J/g)	28-day SHC (cm/sec)
60/40	120	0.6	1.00	90	72-90	5.2	48.1	1.7	113.5	1.3E-09
			1.57	60	20	7.3	58.1	1.2	125.4	2.0E-09
			3.00	154	8	8.6	77.3	1.0	121.6	1.4E-09

Table 3-17: Properties for BFS/FA 60/40 Composition with Varied w/pm

Formulation Variables				Fresh Properties					Cured Properties	
Mix (BFS/FA)	BFS Grade	w/pm	$[\text{OH}^-]$ (M)	Gel Time (min)	Set Time (h)	Yield Stress (Pa)	Viscosity (cP)	Bleed (wt%)	12-Day Heat of Hydration (J/g)	28-day SHC (cm/sec)
60/40	120	0.55	1.57	54	23.7	10.7	80.3	1.0	125.2	1.4E-09
		0.6		60	20	7.3	58.1	1.2	125.4	2.0E-09
		0.65		UC	23	5.0	45.9	1.0	125.9	1.3E-09

Note: UC = value uncertain

Table 3-18: Properties for Varied BFS/FA Ratio Compositions

Formulation Variables				Fresh Properties					Cured Properties	
Mix (BFS/FA)	BFS Grade	w/pm	[OH] (M)	Gel Time (min)	Set Time (h)	Yield Stress (Pa)	Viscosity (cP)	Bleed (wt%)	12-Day Heat of Hydration (J/g)	28-day SHC (cm/sec)
55/45	120	0.6	1.57	60	24.0	6.8	51.5	0.9	118.8	1.7E-09
60/40				60	20	7.3	58.1	1.2	125.4	2.0E-09
65/35				56	21.4	11.2	62.6	1.1	136.8	2.4E-09

In summary, the three phases of development at VSL confirmed that cement-free saltstone is a viable alternative to the current cement-containing mix with respect to short-term fresh properties that have the potential to impact processing in SPF, and subsequent transfer to and placement in the SDU, and also with respect to post-cured properties, such as hydraulic conductivity, that influence the long-term performance of the grout in relation to radionuclide retention. The only potential deficiency of the cement-free formulations is the higher heat generated during curing which would be expected to impact the grout temperature in the SDU and conceivably restrict the feasibility of more aggressive grout pour schedules. However, the impact level of higher hydration heats would require evaluation by thermal modeling similar to that previously employed for the SDUs [SRNL-STI-2008-00410]; the models developed for investigating the viability of cement-free saltstone are described in Sections 3.6 and 3.8. With respect to recommending a single cement-free formulation to replace the BFS/FA/OPC 45/45/10 formulation, the BFS/FA 60/40 (w/pm = 0.6) is the most promising formulation since its properties are not significantly influenced by variations to the base composition, and it generates less heat during curing than the BFS/FA 70/30 (w/pm = 0.65) formulation. Ultimately, any additional heat generated by the 70/30 composition is undesirable from the standpoints of: (1) restricting the use of more aggressive pour schedules and (2) limiting the allowable concentration of organics in the grout to protect the Saltstone Disposal Facility (SDF) Documented Safety Analysis (DSA). For SDU 6, the maximum allowable grout temperature is currently set at 75 °C [WSRC-SA-2003-00001]. As such, it was determined that all future cement-free development efforts should be directed towards the BFS/FA 60/40 (w/pm = 0.6) formulation [SRR-CWDA-2017-00055]. The next step in the development process was to evaluate the impact of the increased heat generation of the BFS/FA 60/40 formulation on grout temperatures attained within an SDU.

3.6 Phase 4 – Initial SDU Thermal Model Development

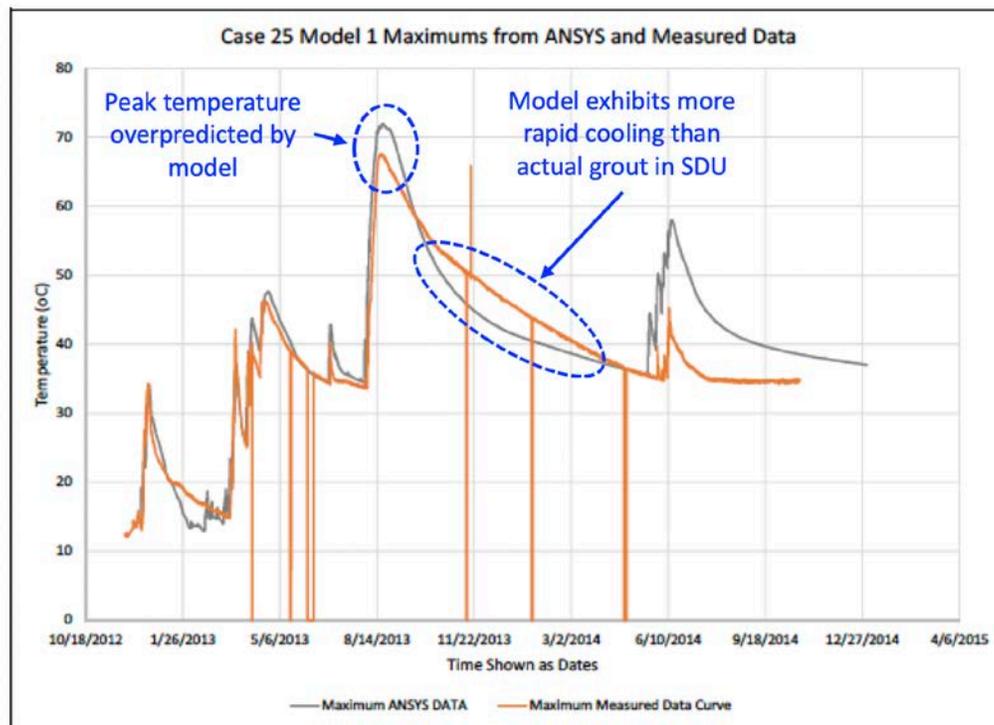
[Primary Reference: RPT-5539-ME-0024]

Phase 4 of the cement-free validation effort was directed towards evaluating the comparative temperatures attained in the SDU for the BFS/FA 60/40 and BFS/FA/OPC 45/45/10 saltstone formulations given the higher hydration heat of the cement-free material. It was envisaged that such an evaluation could be conducted by developing a computer model that simulated the addition of hydrating grouts to an SDU. In 2016, Atkins was tasked with developing a 2D SDU transient thermal model capable of simulating the pouring of hydrating grout into an SDU, and subsequently predicting the time-dependent grout temperatures attained throughout the grout monolith [G-SOW-Z-00023]. The model was designed to account for the following major input variables:

- Grout pour rate, pour schedule (periods of active grout addition and intermittent idling), and the dates on which grout is poured (this latter variable is relevant due to seasonal changes in the environment external to the SDU).
- Changes in grout formulation and associated changes in heat of hydration, specific heat capacity, and thermal conductivity (note these values exhibit dependency on the grout formulation).
- SDU dimensions (should be capable of simulating grout addition to current and future SDU designs).
- Thermal properties of SDU and soil materials (including specific heat capacity and thermal conductivity).
- Ambient conditions exterior to the SDU.

The model was developed using ANSYS® Mechanical, a finite element analysis package. The data associated with the aforementioned input variables were provided to Atkins by SRR and are detailed in RPT-5539-ME-0024. The first step in the development process was to construct the model and then benchmark it against actual temperature data recorded during the filling of SDU 2A (2.9 million-gallon capacity) with the standard BFS/FA/OPC 45/45/10 mixture between April 2013 and August 2014. Atkins initially developed a simplified one-dimensional (1D) model to predict temperatures vertically through the SDU. The 1D model was easier to manipulate and had a faster run-time, which enabled the effects of model modifications to be more rapidly discerned. Once the 1D model was deemed acceptable in terms of correlation with the measured grout temperatures within SDU 2A, the 2D model was developed using the lessons learned, parameters, and inputs from the 1D model. In general, both the 1D and 2D models performed well with respect to matching general trends of increasing and decreasing temperatures, but in many cases the maximum grout temperatures attained in the SDU were overpredicted by 5 to 10 °C and the models also exhibited more rapid cooling during periods of idling (i.e., no grout addition to the SDU) (see Figure 3-1).

Figure 3-1: Example of Comparative Data Between SDU 2A Measured Data and the Thermal Simulation



In part, the observed inconsistencies were believed to be associated with the lack of available and consistent thermal property data for saltstone, such as heat of hydration, specific heat capacity, and thermal conductivity. These are all critical parameters associated with the amount of heat generated in the SDUs, the influence of that heat on the grout temperature, and the ability of the grout to dissipate the heat via conduction to the floors, wall, and vapor space of the SDU. In addition, the heat of hydration data that had been available was typically restricted to 14-day measurements. Though much of the hydration heat for saltstone, and any cementitious material, will be generated within the first 14 days, these materials continue to hydrate for months and sometimes years [WSRC-TR-97-00357], and that heat will impact the ultimate temperatures attained in the SDUs. As such, thermal model development was halted until the aforementioned thermal properties could be empirically derived.

3.7 Phase 5 – Extended Thermal Properties Testing

[Primary Reference: SREL Doc. No. R-18-0005]

3.7.1 Objectives

Per the initial SDU thermal modeling efforts, described in Section 3.6, the disparity between the measured data and the model-predicted data (for maximum grout temperatures and rate of grout cooling during periods of non-operation) was thought to be potentially connected to a lack of the following key saltstone thermal property data:

- **Time dependent heat generation** – though much of the heat from the hydration is generated within two weeks of mixing, these reactions may continue (albeit at a

much slower rate) for months and even years. Empirical measurements of saltstone heats of hydration have typically been limited to approximately 14 days, since the purpose of the data was for comparative evaluation of varied saltstone formulations. As such, longer term hydration measurements were required for both BFS/FA/OPC 45/45/10 and BFS/FA 60/40 formulations, to better inform the cumulative heat derived from saltstone many weeks and months after it has been added to an SDU.

- **Consistent specific heat capacity (C_p) and thermal conductivity (λ) data** – the specific heat capacity and thermal conductivity of saltstone are critical parameters in determining the temperature attained in the SDUs during saltstone addition, and the subsequent transfer of heat from the hydrating material to the SDU floor, walls, and vapor space. Empirical data (for the BFS/FA/OPC 45/45/10 formulation) that can be used as model inputs for benchmarking are scarce, and the data that does exist is ambiguous. As such, specific heat capacity and thermal conductivity data is required for the BFS/FA/OPC 45/45/10 formulation (to facilitate the model benchmarking process), but also for the BFS/FA 60/40 composition in order to evaluate its impact on temperatures attained in the SDUs.

SREL was contracted in 2017 for Phase 5 of the cement-free feasibility program to provide long-term hydration data, specific heat capacity, and thermal conductivity for both the BFS/FA/OPC 45/45/10 and BFS/FA 60/40 saltstone formulations.

3.7.2 Testing and Results

Long-Term Heat of Hydration

Heat of hydration measurements were conducted at SREL using an 8-channel TAM Air Calorimeter (TA Instruments) according to ASTM C1702-17, *Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Material Using Isothermal Calorimetry*. Four samples of each formulation were evaluated; the hydration data presented in this section is equivalent to average taken from 4 samples. Tests were conducted at ambient temperature for 1320 hours (55 days). Long-term hydration evaluation considered the sample types indicated in Table 3-19 (note all samples were prepared with a w/pm = 0.6); the compositions of salt solutions identified in Table 3-19 are provided in Table 3-20.

Table 3-19: Sample Types Investigated with Respect to Long-Term Heat of Hydration

Formulation	Salt Solution	BFS Type	Rationale
H45-45-10	Tank 50 CY2013 Q1-Q3	Holcim Grade 100	Required for benchmarking SDU thermal model against the measured temperature data when pouring saltstone into SDU 2A during 2013. The CY2013 salt simulant is based on quarterly analysis of the Tank 50 contents in 2013.
L60-40	New SWPF	Lehigh Grade 120	Required for evaluating the heat generated in SDU 6 when pouring the BFS/FA 60/40 formulation prepared with Tank 50's anticipated salt solution composition once SWPF operations startup.

Note: For formulation designators, L = Lehigh Grade 120 BFS and H = Holcim Grade 100 BFS.

Table 3-20: Salt Solution Simulants used for the Fabrication of Grouts in Phase 5 Testing

Material	New SWPF ^a (M)	Tank 50 CY2013 Q1-Q3 ^b (M)
Sodium Hydroxide (50 wt% NaOH)	2.391	2.514
Free Hydroxide (OH ⁻)	1.823	1.918
Sodium Nitrate (NaNO ₃)	1.475	1.592
Sodium Nitrite (NaNO ₂)	0.583	0.403
Sodium Carbonate (Na ₂ CO ₃)	0.262	0.204
Sodium Sulfate (Na ₂ SO ₄)	0.055	0.048
Aluminum Nitrate (Al(NO ₃) ₃ ·9H ₂ O)	0.142	0.149
Sodium Phosphate (Na ₃ PO ₄ ·12H ₂ O)	0.004	0.005

Ref. SREL Doc. No. R-18-0005, Table 3

Note: The simulant salt solutions were chemically designed to represent the average salt solution present in Tank 50: a) after being treated via the SWPF and b) during quarters Q1-Q3 of CY2013.

Figure 3-2 shows the cumulative heat generated by the two sample types relevant to Phase 5, and Table 3-21 indicates the cumulative heats at 336 hours (14 days) and 1320 hours (55 days).

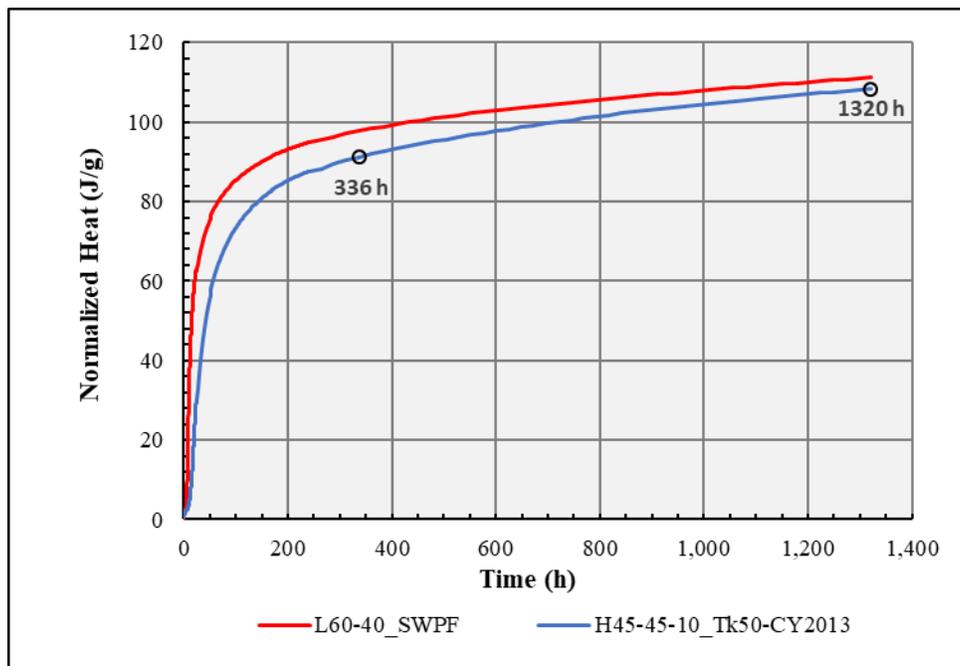
Figure 3-2: Cumulative Heat for Phase 5 Saltstone Simulants

Table 3-21: Time Dependent Cumulative Heat for Phase 5 Saltstone Simulants

Sample	Time Dependent Cumulative Heat (J/g)	
	336 h	1320 h
L60-40_SWPF	98	111
H45-45-10_Tk50-CY2013	91	108

As shown in Figure 3-2 and Table 3-21, both samples continue to generate heat after the typical evaluation period of 336 h (14 days). For example, in the case of the cement-free composition (L60-40_SWPF) mixed with the predicted SWPF salt solution, an additional 10% heat is generated between 336 and 1320 hours. In addition, the shape of the curve indicates that the samples will continue to generate heat beyond the 1320-hour testing endpoint. Based on this, future modeling efforts (Phase 6 – Section 3.8) incorporated an extrapolation function (produced via curve fitting the empirical data) to predict the heat generated beyond 1320 hours [SRNL-STI-2019-00015, Appendix A].

The formulations considered in Phase 5 were not specifically measured to facilitate sample-to-sample comparison, but it is noteworthy that for the H45-45-10 and L60-40 samples the cumulative heats generated at 1320 hours were 108 and 111 J/g, respectively. This is in contrast to the VSL Phase 3 data (Table 3-15) that indicated a 50% higher heat of hydration for the cement-free BFS/FA 60/40 formulation in comparison to the BFS/FA/OPC 45/45/10 formulation. However, it is important to note that the BFS/FA 60/40 formulation incorporated a more reactive Lafarge Grade 120 BFS in the VSL study [VSL-15R2890-1]. The assertion that the Lafarge Grade 120 BFS is more reactive than its Lehigh counterpart is based on another VSL study associated with determining a viable BFS alternative for the Holcim Grade 100 BFS, which had gone out of production. BFS/FA/OPC 45/45/10 samples produced with the Lafarge Grade 120 BFS indicated a 12-day cumulative heat release of 80 J/g compared to 65 J/g for those produced with Lehigh Grade 120 BFS. [VSL-15R3740-1]

Based on the newly-derived data from SREL the following heat generation inputs were used for continued development of the thermal model [SRR-CWDA-2018-00074]:

- For SDU 2A benchmarking, the H45-45-10 (with CY2013 salt solution) cumulative heat depicted in Figure 3-2 was used; i.e., 108 J/g generated over a period of 1320 h.
- For the filling of SDU 6 with cement-free grout, the L60-40 (with new SWPF salt solution) cumulative heat depicted in Figure 3-2 was used; i.e., 111 J/g generated over a period of 1320 h.

Specific Heat Capacity and Thermal Conductivity

The specific heat capacities and thermal conductivities of the various mixtures is provided in Table 3-22.

Table 3-22: Thermal Properties of Saltstone Formulations

Composition	Salt Solution	BFS	Thermal Conductivity (λ) ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	Specific Heat Capacity (C_p) ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$) (25 °C)
H45-45-10	CY2103	Holcim	0.72 (15 °C) – 0.80 (65 °C)	1.94
L60-40	New SWPF	Lehigh	0.70 (15 °C) – 0.78 (65 °C)	1.96

There appears to be little influence of BFS source, salt solution chemistry (including $[\text{OH}^-]$), or formulation (standard versus cement-free) on either the thermal conductivity or the specific heat capacity. However, in comparison to historical data the thermal conductivity measured by SREL (approximately $0.7\text{--}0.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ between $15\text{--}65 \text{ °C}$) is lower than the $1.06 \pm 0.06 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [WSRC-TR-97-00357] though the SREL data is consistent with the thermal conductivity of mortars in which the cement component has been partially replaced with BFS and FA [Asadi et al., 2018]. Comparing the specific heat capacity data from SREL with historical data, it is apparent that the newly derived empirical data is well matched to the $1.95 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ (25 °C) reported in SRNS-STI-2008-00102, though both are much higher than the $1.25 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ reported in WSRC-TR-97-00357. Based on the newly-derived data from SREL and its general agreement with thermal data measured in SRNS-STI-2008-00102, the following thermal property inputs were used for continued development of the SDU thermal model [SRR-CWDA-2018-00074].

- For SDU 2A benchmarking, the specific heat capacity (C_p) and thermal conductivity (λ) for the H45-45-10 (with CY2103 salt solution) in Table 3-22 were used; i.e., $C_p = 1.94 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, $\lambda = 0.72\text{--}0.80 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (15-65°C).
- For the filling of SDU 6 with cement-free grout, the specific heat capacity (C_p) and thermal conductivity (λ) for the L60-40 (with new SWPF salt solution) in Table 3-22 were used; i.e., $C_p = 1.96 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, $\lambda = 0.70\text{--}0.78 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (15-65°C).

3.8 Phase 6 – Continued Thermal Model Development

[Primary References: SRNL-STI-2019-00015, G-ESR-Z-00028, SRR-CWDA-2019-00012]

In 2018, SRNL was contracted to evaluate the finite element thermal model constructed by Atkins (per Section 3.6), and to subsequently develop their own alternate 2D model with the following key objectives (G-TTR-Z-00013):

- Develop a computational model to predict temperatures reached in SDU 2A during saltstone grout addition and its subsequent disposal period.
- Benchmark the modeling predictions against grout temperature data measured in SDU 2A.
- Manage input variables such as saltstone pour schedules, SDU designs, saltstone compositions, saltstone thermal properties, and seasonal ambient conditions.
- Utilize recently derived empirical data from Phase 5 experiments (Section 3.7); the input parameters used for model development are summarized in SRR-CWDA-2018-00074.
- Perform a sensitivity analysis with respect to the baseline design and operating conditions, such as grout pour schedule and seasonal ambient conditions.

- Create a large-scale model of SDU 6 based on the modeling parameters (established by the SDU 2A benchmarking test results) that could be used to predict the temperatures associated with using the BFS/FA 60/40 cement-free grout.

SRNL opted for a computational fluid dynamics (CFD) modeling approach and developed their model using ANSYS® FLUENT®. The CFD modeling approach in terms of modeling geometry and solution methodology is described in SRNL-STI-2019-00015. With respect to benchmarking, Figure 3-3 and Figure 3-4 compare measured and modeled data for SDU 2A at heights of 2.5 and 10.5 ft., respectively. The general trends of the modeled curves match those of the measured data though the modeled data is conservative in that it over-predicts the temperature by approximately 5-10 °C.

Figure 3-3: Comparison of the Modeling Predictions and SDU 2A Thermocouple Data at the Thermocouple Position 2.5 ft for Train A/B

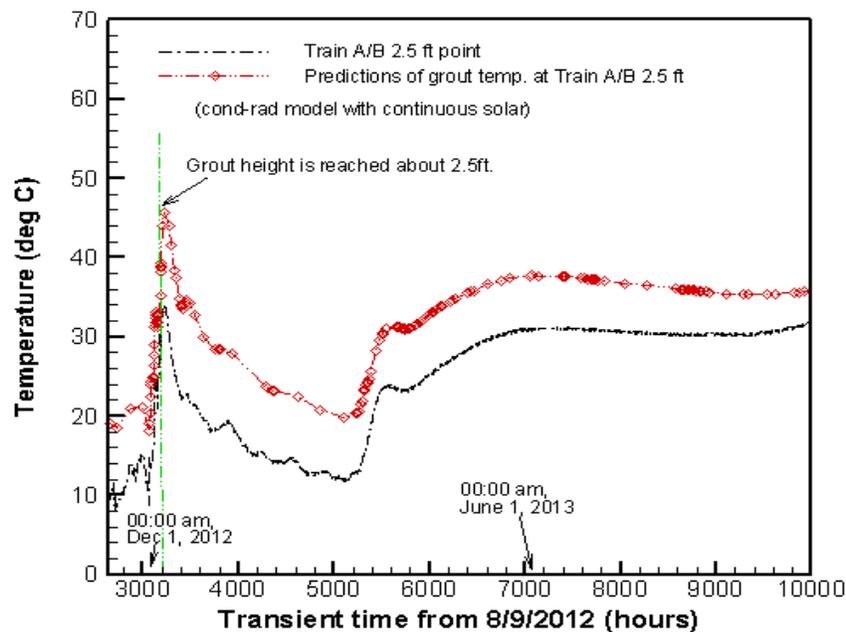


Figure 3-4: Comparison of the Modeling Predictions and SDU 2A Thermocouple Data at the Thermocouple Position 10.5 ft for Train A/B

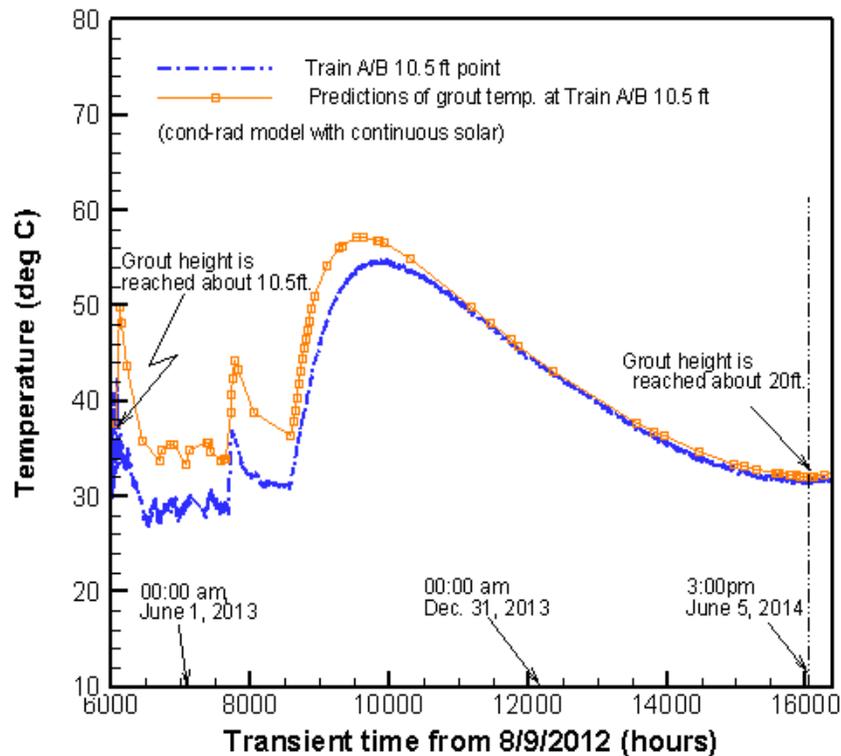
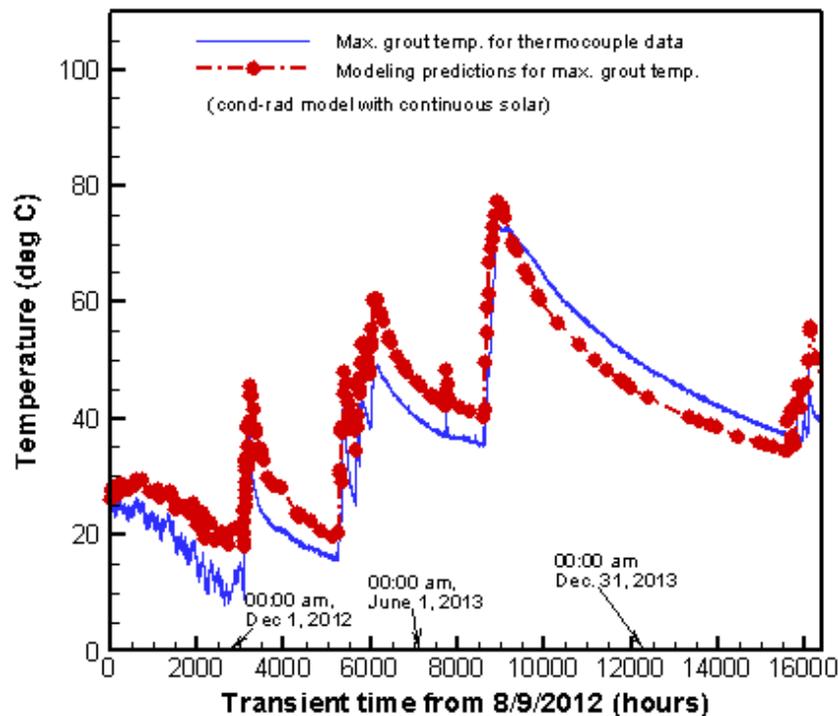


Figure 3-5 compares the measured maximum temperature (irrespective of height) in SDU 2A at any given time; it is compared to the maximum modeled temperature. For the most part, the model indicates conservative behavior in particular with respect to maximum peak temperatures which are 5-10 °C above the measured peak temperatures. However, similar to the Atkins thermal model described in Section 3.6, the SRNL model also indicates a more rapid cooling of the grout in comparison to the measured data, particularly following the concentrated pour regime that occurred around 9000 hours.

Figure 3-5: Comparison of Maximum Grout Temperatures Between the Modeling Predictions and SDU 2A Thermocouple Data

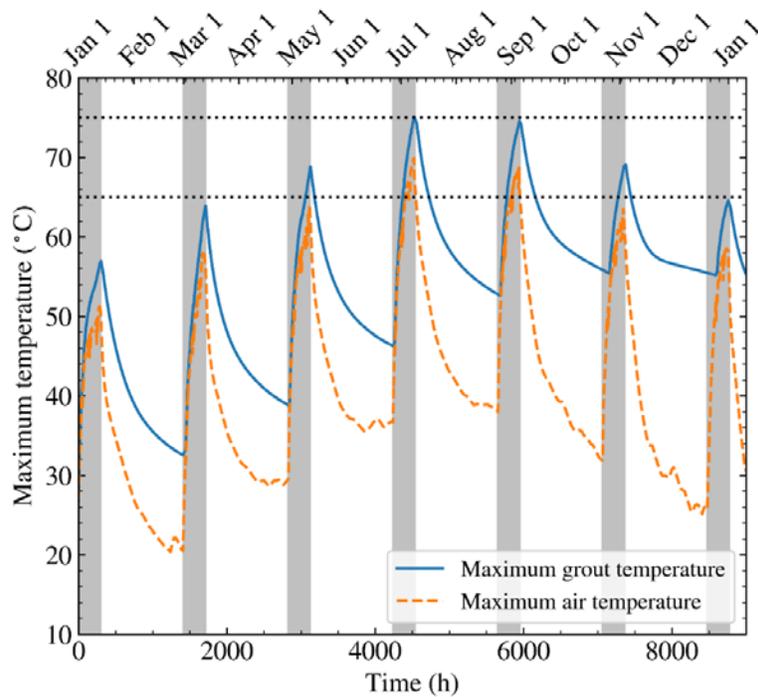


Thus, it appears that despite the use of newly derived thermal property data from Phase 5, the disparities between measured and predicted SDU grout temperatures remain. However, the model efficacy with respect to predicting conservative maximum temperatures was sufficient grounds for it to be applied to simulating the filling of SDU 6 with the BFS/FA 60/40 grout formulation.

Model development has now been handed off to SRR and efforts continue with respect to understanding the disparities between the modeled and measured data and improving the modeling efficiency in terms of enhanced automation and run-time [G-ESR-Z-00028]. With respect to run-time, the previous model was capable of simulating 8 months of real time per month of computer time. In comparison, for the SRR-updated model, 1.3 years of SDU 2A time can be simulated in 5-6 hours of computer time, and 1 year of SDU 6 time can be simulated in 3-4 days of computer time. This model has been used to simulate one year of filling SDU 6 with cement-free grout using a pour schedule of 12.3-day continuous pouring separated by 46.6-day idle periods [SRR-CWDA-2019-00012]. Details regarding the pour schedule rationale are provided in Ref. SRR-SDU-2016-00021.

After one year of pouring the grout fill height in SDU 6 is 22.5 ft.; the maximum fill height is 41 ft. Figure 3-6 and Figure 3-7 indicate the maximum grout and air temperatures when pouring the BFS/FA 60/40 grout (with new SWPF salt solution per Table 3-19 and Table 3-20) into SDU 6; for Figure 3-6 pouring began on January 1 and for Figure 3-7 pouring began on July 1 to evaluate potential impacts of ambient temperature.

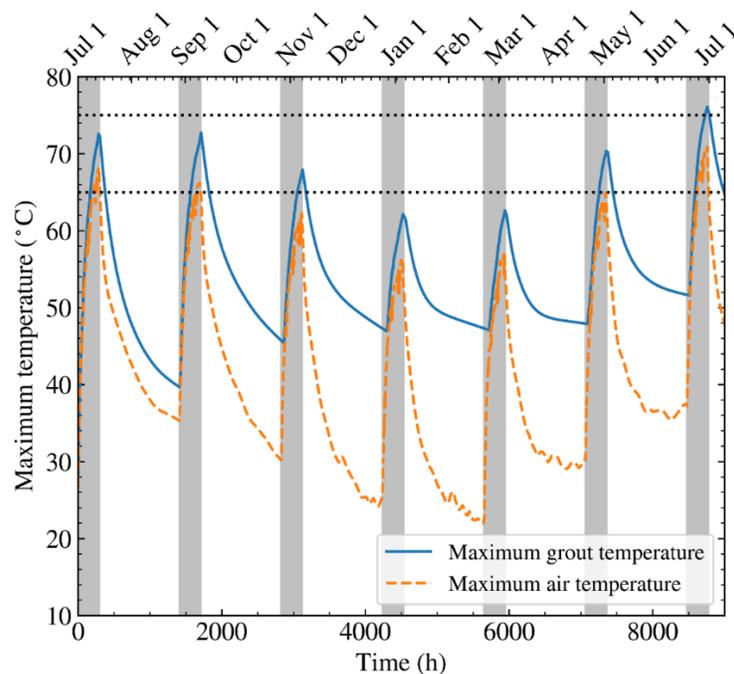
Figure 3-6: Maximum Grout Temperature and Maximum Air Temperature in SDU 6 During One Year of Pouring BFS/FA 60/40 Grout – Start of January 1



Solid Blue Curve – Maximum Grout Temperature
Dashed Orange Curve – Maximum Air Temperature

Note: The gray bands indicated the timings of the pours. The horizontal dashed lines indicated the maximum DSA-prescribed grout and air temperatures (75 °C and 65 °C, respectively).

Figure 3-7: Maximum Grout Temperature and Maximum Air Temperature in SDU 6 During One Year of Pouring BFS/FA 60/40 Grout – Start of July 1



Solid Blue Curve – Maximum Grout Temperature
Dashed Orange Curve – Maximum Air Temperature

Note: The gray bands indicated the timings of the pours. The horizontal dashed lines indicated the maximum DSA-prescribed grout and air temperatures (75 °C and 65 °C, respectively).

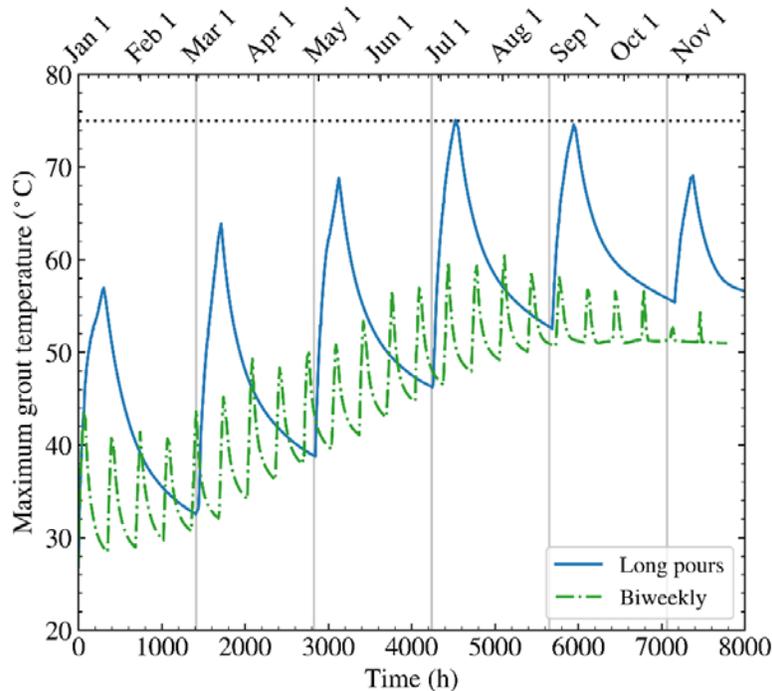
For a run starting on January 1 (Figure 3-6), the maximum temperatures occur at the end of the fourth pour in July. The maximum grout and air temperatures are 75.1 and 69.9 °C, respectively. For a run starting on July 1 (Figure 3-7), the maximum temperatures occur at the end of the seventh pour in June. The maximum grout and air temperatures are 76.1 and 70.9 °C, respectively. The maximum temperatures for the second year of pouring are estimated to be ~5 °C higher. Though these modeled temperatures would exceed the DSA limits of 75 and 65 °C for grout and air, respectively, it is important to note that the current model is considered conservative for the following reasons:

- The model-predicted grout temperatures associated with the filling of SDU 2A (in 2013/2014) were approximately 10 °C higher than the actual measured grout temperatures.
- The current model does not simulate heat transfer via convection in the SDU vapor space; convection was omitted in order to simplify the model and increase run-time efficiency.
- The model utilizes an extremely aggressive, and potentially unattainable, grout pour schedule.

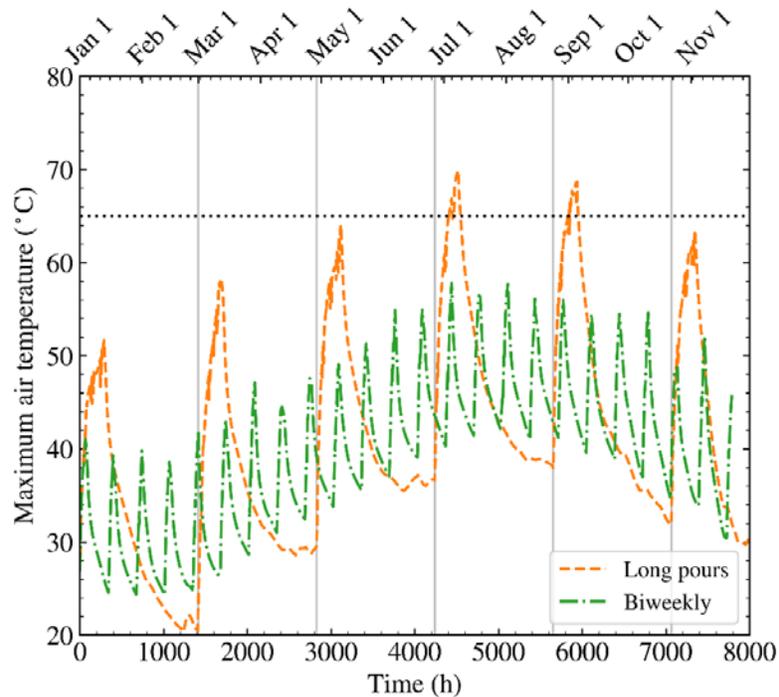
With respect to pour schedule, an alternate and less aggressive schedule of approximately 3 days pouring and 11 days idling was also considered (refer to SRR-SDU-2016-00021 regarding the rationale for this alternate pour schedule). Per Figure 3-8 and Figure 3-9, this schedule results in

lower SDU temperatures while maintaining the same annual grout pouring rate as the initially simulated aggressive pour schedule. The predicted maximum grout and air temperatures are 60.4 (Figure 3-8) and 58.0 °C (Figure 3-9), respectively, which are within the DSA-prescribed SDU temperature limits.

Figure 3-8: Comparison of the Maximum Grout Temperatures in SDU 6 Predicted for Long Pours (12.3 days Pouring + 46.6 days Idling) and for Biweekly Pour Schedule (~3 days Pouring + 11 days Idling)



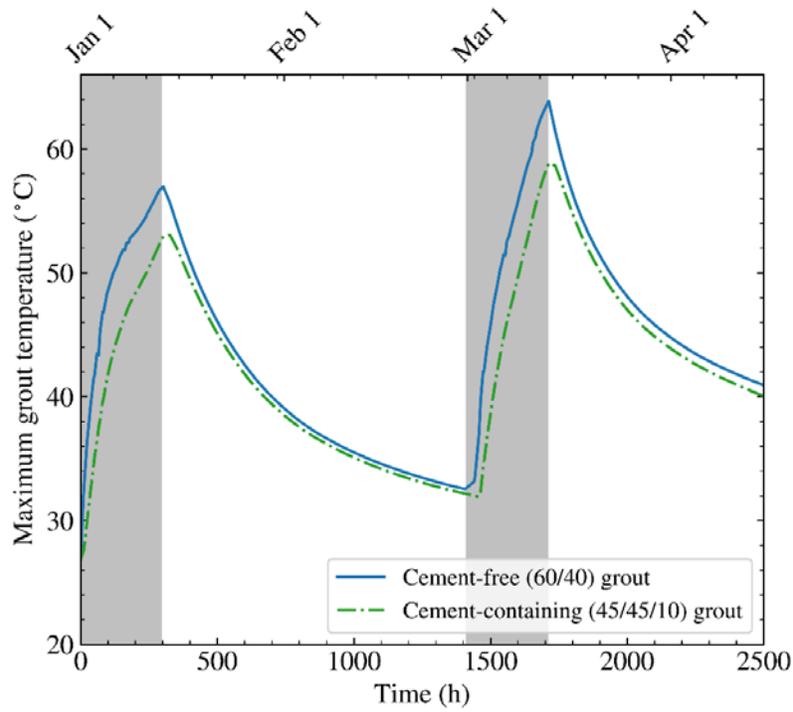
The vertical gray lines indicate the starts of the long pours. The horizontal dotted line indicates the DSA limit (75 °C).

Figure 3-9: Same as Figure 3-8 but Showing the Maximum Air Temperatures

The horizontal dotted line indicates the DSA limit (65 °C).

Comparative simulations were also conducted for the BFS/FA 60/40 and BFS/FA/OPC 45/45/10 formulations using the new SWPF and CY2013 salt solutions, respectively, per Table 3-20. Figure 3-10 provides a comparison of grout temperatures for the BFS/FA/OPC 45/45/10 and BFS/FA 60/40 during the first two pours (starting January 1st). The peak temperatures for the cement-free grout are approximately 5 °C higher than for the standard saltstone; higher temperatures for the cement-free grout are anticipated based on its higher heat of hydration (Table 3-21).

Figure 3-10: Comparison of the Maximum Grout Temperatures in SDU 6 Predicted for BFS/FA 60/40 and BFS/FA/OPC 45/45/10 Grouts



4 FUTURE WORK

Based on the six phases of investigation detailed in this report, the BFS/FA 60/40 (w/pm = 0.6) formulation was chosen for potential implementation. The primary argument for the BFS/FA 60/40 formulation over the BFS/FA 70/30 formulation was the higher reaction heat generated by the latter, which has the potential to limit grout production rates and further challenge DSA-prescribed SDU temperature limits. The following activities are recommended with respect to future work associated with the implementation of the BFS/FA 60/40 (w/pm = 0.6):

- Thermal Model Development

Continued development of the SDU transient thermal model by SRR is recommended with respect to:

1. Further increasing the run-time efficiency, and
2. Identifying factors that account for conservative maximum grout temperatures and accelerated grout cooling in the model compared to the actual SDU. It is necessary to ensure that the model, to the maximum extent possible, accurately represents the heat production and transfer mechanisms in the SDU, which in turn should reduce the currently observed over-prediction of maximum grout and vapor space temperatures.

- Fresh Property Analysis

The BFS/FA 60/40 cement-free composition identified by VSL incorporated Lafarge Grade 120 BFS, whereas the SPF currently utilizes a Lehigh Grade 120 BFS; it is the Lehigh BFS that has been used for determining the hydration heat generated by the cement-free grout. To date, therefore, the fresh properties of a BFS/FA 60/40 formulation incorporating Lehigh Grade 120 BFS have not been measured. Another study by VSL compared Lehigh and Lafarge BFS in the BFS/FA/OPC 45/45/10 formulation and indicated increased reactivity for the Lafarge-containing formulation. As such, the use of Lehigh BFS in the cement-free formulation would be expected to decrease reactivity. Potential adverse effects associated with decreased reactivity would be longer gel times and higher bleed water contents. As such, it is recommended that the fresh property testing be confined to evaluating these two aforementioned properties, which can be achieved with relatively simple testing methods (refer to VSL studies).

- Contaminant Leaching Behavior

It is recommended that the cement-free saltstone be evaluated with respect to the leaching behavior of radioactive and chemically toxic contaminants contained in the salt solution. Key radionuclides of concern associated with the SDF Performance Assessment (PA) include Tc-99 and I-129 [SRR-CWDA-2009-00017]. The ability of the BFS/FA/OPC 45/45/10 formulation to retain these radionuclides has been evaluated via conventional determination of their adsorption coefficients (K_d) in the presence of granulated BFS/FA/OPC 45/45/10 materials and also via Environmental Protection Agency (EPA) Method 1315, *Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure*, which assesses the time-dependent diffusivity of the radionuclides from intact saltstone samples. Tc-99 and I-129 K_d and EPA Method 1315 data for BFS/FA/OPC 45/45/10 are available in SREL

documents [SREL DOC No. R-14-0005, SREL DOC No. R-18-0006]. In addition to the above two methods, a third method, co-developed by SREL and SRR (termed the Dynamic Leaching Method (DLM)), has been successfully utilized to evaluate the leaching rates of Tc-99 and I-129 from intact monolithic samples (both laboratory prepared saltstone samples and actuals samples retrieved from SDU 2A) [SREL DOC No. R-18-0006]. The DLM uses a flexible-wall permeameter to force leachate through the interior of the saltstone monolith to mimic the eventual ingress of water into saltstone and subsequent pore volume exchange to establish the dynamic leaching behavior of saltstone contaminants. The leaching characteristics of Tc-99 and I-129 from BFS/FA 60/40 samples should be evaluated to provide input values for PA modeling, and also to provide a direct comparison with the currently utilized BFS/FA/OPC 45/45/10 saltstone formulation. This testing is already planned and will commence soon at SREL.

In addition, the ability of cement-free saltstone to retain toxic contaminants, including mercury, must be determined since this data impacts facility compliance with SCDHEC hazardous waste regulations. Salt solution samples are retrieved every quarter from Tank 50, mixed with the BFS/FA/OPC 45/45/10 premix, and evaluated with respect to toxic chemical leaching according to the EPA SW-846 Test Method 1311, *Toxicity Characteristic Leaching Procedure (TCLP)*. This test was recently conducted using the BFS/FA 60/40 premix, and the data suggests slightly enhanced Hg retention for the cement-free formulation in comparison to the standard saltstone formulation [SRNL-L3300-2018-00067]. It is anticipated that future quarterly samples retrieved from Tank 50 (and mixed with the BFS/FA 60/40 premix) will continue to be evaluated via TCLP and compared to their BFS/FA/OPC 45/45/10 counterparts.

5 CONCLUSIONS

Six phases of property testing and SDU thermal modeling have been conducted to determine the viability of replacing the standard BFS/FA/OPC 45/45/10 saltstone with a cement-free, BFS/FA-only formulation. As anticipated, removal of the minor cement component (10%) did result in reduced reactivity but this could be compensated by increasing both the proportion and reactivity of BFS in the mixture. These studies have led to the down-selection of a BFS/FA 60/40 formulation with a 0.6 w/pm ratio. Both the fresh (relevant to processing) and the cured (relevant to long-term contaminant retention) properties of the cement-free saltstone are similar to those of the currently used standard saltstone formulation. The only significant difference between the two formulations is a higher heat of hydration for the cement-free saltstone. This differential was originally thought to be as high as 50% (VSL Phase 3), but more recent data suggests that the heat generated by the BFS/FA 60/40 formulation is less than 10% (SREL Phase 5) higher than that for the BFS/FA/OPC 45/45/10 formulation. The latter heat data would appear to be more realistic given that the proportion of reactive phase in the premix has only increased from 55% (i.e., 10 wt% cement + 45 wt% BFS) to 60% (i.e., 60 wt% BFS).

A transient thermal model has been developed to predict the maximum SDU temperatures attained when filling future SDUs with the BFS/FA 60/40 formulation. Per the DSA, the current grout and vapor space temperature limits to avoid vapor space gas flammability are 75 and 65 °C, respectively. Utilizing an aggressive pour schedule of 12.3 days of continuous pouring followed by 46.6 days of idling time, the partial filling of SDU 6 with the BFS/FA 60/40 formulation indicated maximum grout and vapor space temperatures of approximately 76 and 71 °C, respectively, based on one year of pouring up to a height of 22.5 ft. It is envisaged, however, that during a second year of pouring (and complete filling of the SDU to 41 ft.) the maximum grout and vapor space temperatures may be 5 °C higher. When modeling a more realistic pour schedule that results in essentially the same annual volume of saltstone produced, the maximum grout and vapor space temperatures drop to 60 and 58 °C, respectively.

Although the most aggressive pour schedule results in initial modeled temperatures that are slightly higher than the current DSA limits, it is important to note that the current model is conservative for the following reasons:

1. The model-predicted grout temperatures associated with the filling of SDU 2A (in 2013/2014) were 5-10 °C higher than the actual measured grout temperatures;
2. The current model does not simulate heat transfer via convection in the SDU vapor space; convection was omitted in order to simplify the model and increase run-time efficiency; and
3. The model utilizes an extremely aggressive, and potentially unattainable, grout pour schedule.

With respect to future short-term work, the following efforts should be considered:

- Continued development of the SDU thermal model to enhance the runtime efficiency and ease of use, and to evaluate the sensitivity of input parameters and heat transfer modes (i.e., convection) in determining the cause of conservative maximum grout temperatures, and faster rates of grout cooling compared to grout in the SDU.

- A limited fresh property assessment (per Section 4) of BFS/FA 60/40 prepared with Lehigh Grade 120 BFS since the VSL studies utilized a Lafarge Grade 120 BFS.
- Continued documentation of leaching characteristics of toxic chemical (e.g., Hg) and radioactive (e.g., Tc-99 and I-129) contaminants from intact monolithic and granulated cement-free samples similar to recent studies on the current saltstone waste form.

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