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VARIABILITY STUDY FOR SALTSTONE

J. R. Harbour, T. B. Edwards, E. K. Hansen and V. J. Williams

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Immobilization Technology Section
Savannah River National Laboratory
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SRNL
SAVANNAH RIVER NATIONAL LABORATORY

REVIEWS AND APPROVALS

AUTHOR:

J.R. Harbour, SRNL, Immobilization Technology Section Date

T. B. Edwards, SRNL, Statistical Consulting Section Date

E. K. Hansen, SRNL, Immobilization Technology Section Date

V. J. Williams, SRNL, Immobilization Technology Section Date

TECHNICAL REVIEWERS:

A. D. Cozzi, SRNL, Immobilization Technology Section Date

APPROVERS

D. A. Crowley, SRNL, Manager, Immobilization Technology & Business Dev. Date

---

R. E. Edwards, SRNL, Manager, Immobilization Technology Section Date

---

R. C. Tuckfield, SRNL, Manager, Statistical Consulting Section Date

---

J. E. Occhipinti, CBU, Waste Solidification Engineering Date

EXECUTIVE SUMMARY

This report is a summary of the bench-scale experimental studies performed by the Savannah River National Laboratory (SRNL) for Waste Solidification Engineering (WSE) to establish the viability of a grout-based variability study. In order for a variability study to be useful, the property measurements of the fresh and cured Saltstone must be reproducible with an inherent variation that is small compared to the changes in the properties measured over the expected range of variability for a Salt Batch. This scoping task addressed the issue of reproducibility for Saltstone.

Measurement reproducibility was demonstrated for bleed water, grout flow, gel time, yield stress, plastic viscosity and compressive strength. The grout mixes used in this scoping study were produced using simulants that reflect current projections for the four decontaminated salt solutions that will be sent to Saltstone (Deliquification, Dissolution and Adjustment (DDA), Tank 48H, Modular Caustic Side Solvent Extraction Unit (MCU) and Salt Waste Processing Facility (SWPF)).

The inherent measurement variations of these properties in general were sufficiently small that a variability study as a function of chemical composition, water to premix ratios, and ratios of slag, fly ash, and cement in the premix, is possible. Therefore, a Saltstone variability study can be a useful part of the overall strategy for Saltstone operation.

Examples of the impact of compositional variation on the properties of Saltstone are provided in this report. An important finding of these tests was the fact that soluble phosphate and aluminate, minor species in the salt solutions, significantly affect the values of gel time, flow and rheology. Therefore, it will be important to accurately determine/estimate the concentrations of these ions in the decontaminated salt solutions and to ensure that the concentration ranges of these species are adequately covered in Saltstone variability studies.

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ACTL	Aiken County Technical Laboratory
ANSI	American National Standards Institute
ARP	Actinide Removal Process
ASTM	American Society for Testing and Materials
CSSX	Caustic Side Solvent Extraction
DDA	Deliquification, Dissolution and Adjustment
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
ES	Emission Spectroscopy
IC	Ion Chromatography
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ITP	In Tank Precipitation
MCU	Modular CSSX Unit
NRC	Nuclear Regulatory Commission
SNL	Sandia National Laboratory
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility

1.0 INTRODUCTION AND BACKGROUND

1.1 Purpose of Scoping Study

The purpose of this scoping study was to determine the feasibility of using variability studies with grout mixes (Saltstone) and to assess the usefulness of a variability study as part of the overall approach for processing Saltstone [1].

1.2 Background

A glass variability study [2] has been used for each new Sludge Batch to be processed in the Defense Waste Processing Facility (DWPF). This strategy provides greater confidence that the models developed for durability, viscosity and liquidus will successfully predict the processing and performance properties of the glass produced from the new sludge batch over a projected range of compositional variation. In a variability study, a statistically designed set of glasses is developed, glass is made for each composition, and the desired properties of each glass are measured. An evaluation of the effectiveness of the models is then made to ensure that, over this glass compositional range, DWPF operators can rely on the models to successfully process the sludge and produce a waste form that meets the Waste Acceptance Product Requirements (WAPS) [3].

Models have not been developed for the processing and performance requirements of Saltstone. This is due in part to the very low radioactivity (NRC Class A) of Saltstone, to the short term variations in the feed (not a fixed Batch), and to an uncertain dependence of the grout properties on minor constituents of the feed or premix. Therefore, operators have historically taken samples of the salt feed on a daily basis, prepared Saltstone samples from previously designed formulations, tested the samples, adjusted the formulation to address any issues if required, and then proceeded with processing of Saltstone.

Due to a change in design, the new process flow sheet for Saltstone no longer has the option for taking daily samples from a small tank as part of the operating procedure. Therefore, an alternative approach is required.

One approach is to gain understanding of the properties of Saltstone and their dependence on compositional changes through a variability study. In order for a variability study to be useful, the property measurements of the fresh and cured Saltstone must be reproducible with an inherent variation that is small relative to the changes in the measured properties due to compositional (and processing) variations. This scoping task addresses this issue of reproducibility.

A variability study may reveal regions where property acceptance criteria are not met. In these regions, adjustments to the system can be made to bring the properties back into compliance. These adjustments include the identification and inclusion of admixtures, a change to the water to premix ratio, and/or a change in the ratio of slag to fly ash to cement in the premix. A possible additional approach for remediation is to blend the decontaminated salt solutions prior to processing.

1.3 Issues

Two main issues that remain unresolved are:

- Does laboratory-scale mixing of the Saltstone mix correspond to the mixing experienced by Saltstone during production?

- Do the simulated salt streams adequately represent the actual waste streams for each batch?

2.0 EXPERIMENTAL

This section details the methods used for measurement of gel time, bleed water, grout flow, rheology, compressive strength and set time. The scope of this task was limited to testing mixes without the introduction of admixtures. Furthermore, all testing was performed under ambient conditions of ~ 25^{o}C. This Section also lists the simulants, premix materials and methods used to characterize them. Finally, the mixing method for bench-scale testing is presented.

2.1 Mixing Method

Two mixing methods were used for this testing. The first method used a Waring Blender [4] while the second method used a conventional 4-blade Rushton impeller mixing system operating in the range of approximately 500 rpm (Figure 2-4).

The Waring blender has two speeds, a lower speed of 18,000 rpm and an upper speed of 22,000 rpm. The use of the Waring blender raised the temperatures of samples up to 40^{o}C.

The method selected as most representative of the mixing at Saltstone was a conventional paddle mixing system. First the salt solution was placed into the mixing vessel and the agitator speed was set such that a vortex was generated. The premix was then added and the agitator speed increased until the premix was entrained (via the vortex) into the mix. After the premix was entrained, the agitator speed was then reduced to avoid a larger vortex and consequent air entrainment. The total mixing period was three minutes.

As previously noted, the correlation of lab mixing with plant mixing has not been determined. However, the conventional mixing system did not increase the temperature of the mix as compared to that of the Waring blender. In a reproducibility or a variability study, it is important to keep all processing parameters as consistent as possible. For the conventional mixing system, the establishment of a vortex of the right depth to exclude air entrainment was chosen as the parameter to reproduce. An alternative to this would be to choose a certain rpm value for the blade rotation and run all samples at that speed. However, this would lead to poor mixing in some cases and excessive air entrainment in others.

Figure 2-1 Paddle blade mixing system used in this study.

2.2 Gel Time

The gel time was measured by pouring the mixes from a cup into another vessel at 10 minute intervals [4]. If the grout mix shows any sign of building structure (clumping) during the very slow pour, the mix is said to have gelled. The pouring is alternated between two different cylindrical cups such that vessel 1 is used at the time intervals of 10, 30, 50, 70 minutes etc. while vessel 2 is used at the time intervals of 20, 40, 60, 80 minutes etc (Figure 2-2). The contents are poured into a weighing vessel and then returned to the original container. Each container is filled with approximately 100 mL of fresh grout. The time at which the mix has gelled is referred to as the gel time. (For example, a 40 minute gel time implies that the mix has gelled between 30 and 40 minutes.)

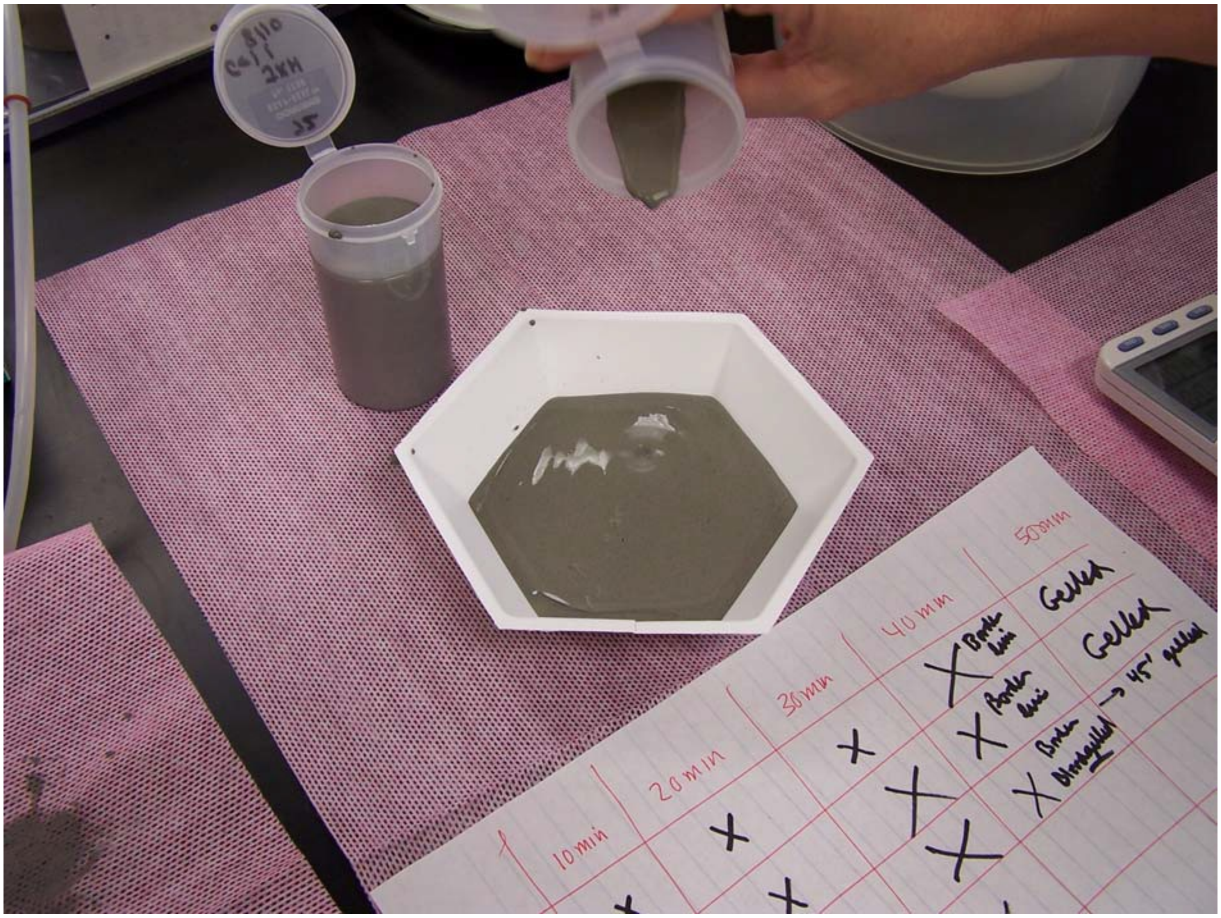

Figure 2-2 Two cylindrical cups and the weighing vessel used for determining gel times.

2.3 Bleed Water

The bleed water (also called standing water [5]) is determined in a similar but not equivalent manner to the Saltstone procedure [5]. For this testing, the bleed water (which contains a high concentration of dissolved salt) and the grout are weighed. These masses are converted to volumes by using the density values for the grout and supernate, and the volume percent of bleed water is calculated by the following equation:

Volume % Bleed Water = (Volume of Bleed Water/Volume of Grout) * 100%

The plastic vessel that is used for this measurement contains approximately 100 mL of grout.

2.4 Grout Flow

As part of this task a method was developed for the measurement of grout flow based on an ASTM procedure [6]. The approach is to fill an open-ended stainless steel cylinder to the top with the fresh grout and then lift the cylinder directly upwards (Figure 2-3). The grout flows very quickly to form a circular (pancake) shape on the Plexiglas® surface (Figure 2-4). No further spreading of the grout layer was observed in the minutes following the lift. Measurement of the diameter of this pancake provides a quantitative assessment of the ability of the grout to flow. In this task, a 110 mL stainless steel cylinder was used and the resulting diameters ranged roughly between 8 to 12 inches.

Figure 2-3 Cylinder used for the grout flow test on top of the Plexiglas® surface.

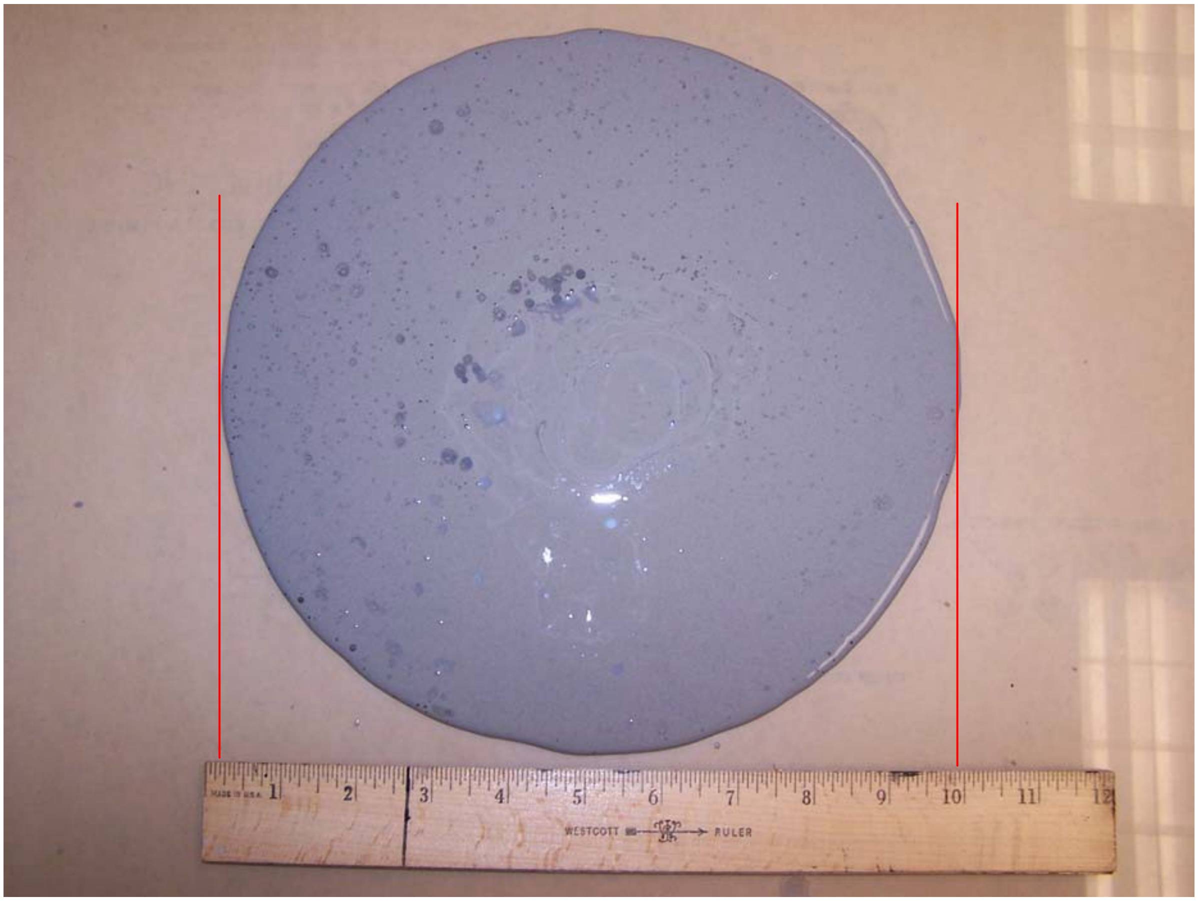

Figure 2-4 Grout flow test.

2.5 Rheological Measurements

Two rheological flow curves were obtained for the slurries. The first flow curve, which covered the shear rate range from 0 to 300 sec^{-1}, was measured at 25°C immediately after mixing was completed.   This fluid is representative of a well mixed sample, such as that leaving the discharge piping at Saltstone. A second flow curve, which covered the shear rate range from 0 to 10 sec^{-1}, was obtained 20 minutes after the mixing was completed. This measurement is more representative of the flow properties of the fluid part of the grout in the Saltstone vault.

For the first measurement, the slurry was poured directly from the mix vessel into the rheology cup. For the second measurement, the grout mix was allowed to stand in a 100 mL vessel for ~19 minutes. Any bleed water was then removed with a pipette. The top part of the mixture was then transferred to a weighing vessel and then poured into the rheology cup.

The details of the rheological measurements are provided in a report by Hansen and Langton [7].

2.6 Compressive Strength Measurements

Compressive strengths were measured by two independent methods for this task. The first method used the 100 mL plastic cups with attached lids to seal the cups after the grout mix was added. These plastic cups are 3.5 inches in height, 1.57 inches in diameter at the bottom and 1.69 inches in diameter at the top. After curing for a selected amount of time (typically 28 days or longer), the monolithic grout samples were removed from the plastic cups, leveled on the top, and then placed within the Applied Test Systems Model 900 system to measure the compressive strengths.

A second method used 2 inch cubes and complies with ASTM C-109 [8]. The Applied Test Systems Model 900 system was also used for these compressive strength measurements.

2.7 Set time

This study did not include the measurement of set times for the various grout compositions. However, a procedure [5] for measuring set times using the Vicat needle was carried out on several mixes. A grout produced using a DDA simulant set in less than two days while a grout made with the SWPF simulant set in less than one day.

2.8 Simulants

The simulants used for the four types of decontaminated salt solutions [9, 10] that will be sent to Saltstone are presented in the following table (Table 2-1). The Deliquification, Dissolution and Adjustment (DDA), Actinide Removal Process (ARP) and Modular CSSX (Caustic side solvent extraction) Unit (MCU) (hereafter referred to simply as MCU in this report) and Salt Waste Processing Facility (SWPF) simulants did not contain phosphate whereas the Tank 48H simulant did contain phosphate. Phosphate was added to the first three simulants as necessary to determine the effect of this component of the salt solution on grout properties.

Table 2-1 Chemical compositions of the DDA, Tank 48H, MCU and SWPF simulants

Compound	DDA SIMULANT			MCU SIMULANT		
	TARGET Molarity Moles/Liter	MW grams/mole	TARGET Amt/Liter grams	TARGET Molarity Moles/Liter	MW grams/mole	TARGET Amt/Liter grams
50% by Weight NaOH	0.77	40.00	61.52	1.59	40.00	127.50
$NaNO_3$	2.20	84.99	187.15	3.16	84.99	268.48
$NaNO_2$	0.11	68.99	7.56	0.37	68.99	25.39
Na_2CO_3	0.14	105.99	15.36	0.18	105.99	18.65
Na_2SO_4	0.04	142.04	6.31	0.06	142.04	8.37
$Al(NO_3)_3 9H_2O$	0.07	375.13	26.63	0.05	375.13	20.33
Total salt mass	-	-	262.27	-	-	396.20
Total Na Molarity	3.46	-	-	5.59	-	-

Compound	SWPF SIMULANT			TANK 48H SIMULANT		
	TARGET Molarity Moles/Liter	MW grams/mole	TARGET Amt/Liter grams	TARGET Molarity Moles/Liter	MW grams/mole	TARGET Amt/Liter grams
50% by Weight NaOH	2.87	40.00	229.28	1.10	40.00	88.00
$NaNO_3$	1.97	84.99	167.66	0.65	84.99	55.24
$NaNO_2$	0.48	68.99	33.43	0.10	68.99	6.90
Na_2CO_3	0.12	105.99	12.46	0.10	105.99	10.60
Na_2SO_4	0.06	142.04	7.84	0.02	142.04	2.84
$Al(NO_3)_3 9H_2O$	0.11	375.13	42.90	0.05	375.13	18.76
$Na_3(PO_4)$ 12 H_2O	-	-	360.40	0.01	380.12	3.04
Total salt mass	-	-	-	-	-	131.45
Total Na Molarity	5.67	-	-	2.11	-	-

An average simulant was used in the early stage of this work that was an overall average of the first 12 projected batches of decontaminated salt solution to Saltstone (Table 2-2). This simulant did not contain aluminum or phosphate as these components were added as necessary in the testing.

Table 2-2 Chemical composition of the simulant which is an overall average of all batches.

AVERAGE SIMULANT			
Compound	TARGET Molarity Moles/Liter	MW grams/mole	TARGET Amt/Liter grams
50% by Weight NaOH	1.22	40.00	97.60
$NaNO_3$	2.11	84.99	179.33
$NaNO_2$	0.28	68.99	19.32
Na_2CO_3	0.13	105.99	13.78
Na_2SO_4	0.05	142.04	7.10
Total Salt mass	-	-	268.33
Total Na Molarity	3.97	-	-

2.9 Characterization of the Premix and Simulants

Chemical compositions of the blast furnace slag, Class F fly ash, portland cement and simulants were determined by the Mobile Laboratory. The simulant solutions and the dissolved solids were analyzed by Inductively Coupled Plasma (ICP) Emission Spectroscopy (ES) and by Ion Chromatography (IC).

The carbon content on the fly ash was determined using Thermal Gravimetric Analysis (TGA) with an STA 409PC instrument operating over the temperature range of 27 ^{0}C to 1400 ^{0}C.

Density and wt% dissolved salts (total solids) of the simulants were measured [7]. Density measurements were obtained using an Anton Paar DMA 4500 Density Meter and the wt% dissolved solids were obtained using a Mettler Toledo HR83 Halogen moisture analyzer.

3.0 RESULTS OF THE REPRODUCIBILITY STUDY

The reproducibility study was conducted to determine the variation of the grout properties for trial run mixes that were made in an identical manner. The details of the measurement techniques for each property are provided in Section 2.

3.1 Gel Time

Five separate trial runs were used to investigate the measurement variation in gel times. The simulant used for this test was one designed to have a gel time in the region between 20 minutes and one hour. An MCU simulant was used that did not contain phosphate. The results of five replicate samples are provided in Table 3-1.

Table 3-1 Gel time measurements from five separate trial run mixes.

TRIAL RUN #	GEL TIME (minutes)
69	40 – 50
70	40 – 50
71	40 – 50
72	30 – 40
73	30 – 40

3.2 Bleed Water

The results of the volume percentage of bleed water for a DDA simulant are provided in Table 3-2. The gel time for this mix, which used the DDA simulant containing both aluminum and phosphate, was approximately 5 hours.

Table 3-2 Bleed water measurements (% by volume) from five separate trial run mixes

TRIAL RUN #	BLEED WATER (% by volume)
60	4.9
62	2.2
63	4.7
65	2.5
66	2.0
67	1.2

The very long gel times and relatively low density of the DDA simulant may have led to the higher scatter in the bleed water results shown in Table 3-2. Therefore, simulants with a higher density that produced shorter gel times were also investigated. In this case, both the SWPF and MCU simulants were used. The results of the one and three-day bleed tests are shown in Table 3-3 for bleed water from the same mix for each simulant. Additional testing will be performed to determine the variation of bleed water for samples produced in a set of trial runs.

Table 3-3 Bleed water measurements (% by volume) from two trial runs

MCU Sample			SWPF Sample		
Trial Run #	Volume % Bleed Water		Trial Run #	Volume % Bleed Water	
	1 Day	3 Days		1 Day	3 Days
MCU 108-1	0.5	0.0	SWPF 109-1	2.2	1.4
MCU 108-2	0.7	0.0	SWPF 109-2	2.0	1.4
MCU 108-3	0.4	0.0	SWPF 109-3	2.0	1.4
Average	0.5	0.0	Average	2.1	1.4
SD	0.2	0.0	SD	0.1	0.0
%RSD	29.5	0.0	%RSD	5.6	0.0

3.3 Grout Flow

The results of the reproducibility testing of grout flow are provided in Table 3-4. This testing as well as the rheological and compressive strength testing was performed with the same DDA simulant that was used for bleed water measurements (Section 3.2).

Table 3-4 Grout flow measurements from six separate trial run mixes

TRIAL RUN #	GROUT FLOW (Inches)
61	10.4
63	10.2
64	10.5
65	10.5
67	10.0
67-2	10.2

3.4 Rheology

Two separate rheological measurements were carried out on each of the six DDA trial run mixes at 0.60 water/premix ratio. The flow curves were measured over the range 0 to 300 sec^{-1}

immediately after the mixing was completed. The "down" or return part of the flow curve was fit to a Bingham Plastic model over a shear rate range of 20 to 300 sec^{-1} and the values of yield stress and plastic viscosity determined. These values are provided in Table 3-5.

Table 3-5 Initial flow curve ("down") results from six separate trial run mixes.

TRIAL RUN #	Plastic Viscosity (cP)	Yield Stress (Pa)
Trial Run 60_R1	43	3.96
Trial Run 62_R1	45	4.13
Trial Run 63_R1	45	4.02
Trial Run 65_R1	44	3.90
Trial Run 66_R1	45	4.06
Trial Run 67_R1	43	3.86

The second flow curve was measured over the range of 0 to 10 sec^{-1} at a time of 20 minutes after the mixing was completed. The yield stress and plastic viscosity values for the "down" portion of the flow curve were obtained by fitting the curve to a Bingham Plastic Model and the results are provided in Table 3-6.

Table 3-6 Flow curve ("down") results from six separate trial run mixes obtained after 20 minutes over the range of 1 to 10 sec^{-1}.

TRIAL RUN #	Plastic Viscosity (cP)	Yield Stress (Pa)
Trial Run 60_R1A	227	2.18
Trial Run 62_R1A	229	2.18
Trial Run 63_R1A	223	2.36
Trial Run 65_R1A	244	2.35
Trial Run 66_R1A	242	2.43
Trial Run 67_R1A	240	2.22

3.5 Compressive Strength

The data for the compressive strengths measured on cylinders and on two inch cubes (ASTM) are provided in Table 3-7. All 12 of these samples were obtained from four separate batches with each batch filling three cylinders or cubes. The DDA simulant was used to make these samples.

Table 3-7 Results of compressive strength measurements from samples cast both in cylinders and in 2 inch cubes after curing for 28 days.

TRIAL RUN #	COMPRESSIVE STRENGTH (PSI)	
	Cylinder	2 Inch Cube
74-1	-	904
74-1	-	910
74-1	-	882
74-2	478	-
74-2	568	-
74-2	676	-
74-3	-	1039
74-3	-	1069
74-3	-	1018
74-4	485	-
74-4	723	-
74-4	634	-

3.6 Summary of the Property Variances

The average values, the standard deviations and the percent Relative Standard Deviations (%RSD) for the properties measured during this reproducibility study are provided in Table 3-8.

Table 3-8 Summary statistics for the grout properties

PROPERTY	Unit	Average	Standard Deviation	%RSD
Gel time	Minutes	46.0	5.5	11.9
Bleed water	% by volume	2.9	1.5	51.8
Grout flow	Inches	10.3	0.2	1.9
Yield stress	Pa	4.0	0.1	2.5
Plastic viscosity	cP	44.0	0.9	2.1
Yield stress	Pa	2.3	0.1	4.7
Plastic viscosity	cP	234.0	9.0	3.7
Compressive strength	psi	970.0	80.0	8.0

4.0 RESULTS OF COMPOSITIONAL VARIATION

4.1 Role of Minor Constituents in Salt Solution

It became evident near the beginning of this scoping study that certain minor constituents play a major role in the properties of the fresh Saltstone mix. In particular, the phosphate anion and the aluminum cation were two minor constituents that had a significant effect on gel time, flow and rheology.

4.1.1 Aluminum

Aluminum was added to the simulants as aluminum nitrate. In an alkaline environment (high pH), each aluminum ion complexes with 4 hydroxide ions to generate $Al(OH)_4^-$. The aluminum concentrations in the projected, decontaminated salt solutions range from ~ 0.01 to 0.11M.

The initial tests with the average simulant (Table 2-2) revealed that aluminum extended the gel time. This effect was confirmed using a DDA simulant. In this case the DDA simulant contained neither phosphate nor aluminate. Mixes were then made using this simulant both with and without added aluminum (when added the aluminum concentration was 0.07 M). A comparison of property values for these two mixes at a 0.60 water/premix ratio shows that aluminum impacts both the gel and rheological properties (Table 4-1).

Table 4-1 Change in gel time and rheological properties of a DDA simulant as a function of added aluminum

Aluminum Nitrate (Molarity)	Gel time (minutes)	Yield Stress (Pa)	Plastic Viscosity (cP)
0	3	9.0	62.0
0.07	20	4.1	52.8

4.1.2 Phosphate

Results from this scoping study revealed that phosphate in the simulant played an even greater role in the gel and flow properties of the mixes than aluminum. Starting with the same DDA simulant in Section 4.1.1, the gel and flow properties of the mixes were determined as a function of phosphate concentration. The concentration of phosphate ranged from 2.8 E-04 to 1.3 E-03 M (Table 4-2).

Table 4-2 Change in gel time and rheological properties of a DDA simulant as a function of added phosphate

Sodium Phosphate (Molarity)	Grout Flow (Inches)	Gel time (Minutes)	Yield Stress (Pa)	Plastic Viscosity (cP)
0.00	9.4	3	9.0	62.0
2.80E-04	-	10	6.5	49.9
1.30E-03	10.3	90	5.4	48.4

For comparison, a DDA simulant which contained both aluminum at 7.0E-02 M and phosphate at 2.6 E-03 M (projected concentration for DDA), had a gel time of ~ 5 hours, a flow of 10.3 inches, a yield stress of 4.0 Pa and a plastic viscosity of 44.0 cP.

The participation of aluminum and phosphate is further confirmed by analysis of the chemical compositions of the simulant and bleed water. The composition of the bleed water relative to the initial starting DDA simulant containing both phosphate and aluminum was measured and the results are presented in Table 4-3.

Table 4-3 Chemical composition of the DDA simulant and the bleed water resulting from grout made with the DDA simulant.

Element	DDA SIMULANT (mg/L)	BLEED WATER (mg/L)	% Change
Al	1860	141	-92.4
Ca	4	13	225
Fe	<0.100	<0.100	-
K	6.2	667	10658
Na	79700	80750	1.3
P	282	66	-76.6
S	1560	3383	116
Si	2.17	302	13817
Anion	-	-	-
NO_2	5295	5198	-1.8
NO_3	148000	147500	-0.3
PO_4	543	114	-79.0
SO_4	4100	9593	134.

The yellow highlighted areas in Table 4-3 reveal that aluminum and phosphate are significantly reduced in the bleed water relative to the simulant. This implies that aluminum and phosphate are retained within the grout, consistent with their influence on grout properties. Increases in some of the elements/anions in the bleed water relative to the simulant are consistent with their release in the early hydration reactions involving the premix materials.

4.1.3 Chloride, fluoride and oxalate

The impact of other anions at low concentrations in the waste was also tested. In this case, a DDA simulant with a 0.07 M aluminum concentration was used. Each new batch was tested with additions of chloride, fluoride or oxalate at the projected concentrations of these species in the waste.

No significant changes in gel time, rheology, and flow were observed for chloride and fluoride although the results with oxalate showed a slight increase in gel time (10 minutes) and flow. However, these tests were performed only once and have not been reproduced.

4.2 Variation in Decontaminated Salt Solution

The projected batches of decontaminated salt solution to Saltstone were divided into four separate types: DDA, Tank 48H, MCU and SWPF. The projected average compositions of these 4 types of salt solution have significant variation in overall sodium, nitrate and hydroxide molarities (See Section 2.3). Table 4-4 provides the variations in properties for mixes made with these four simulants.

Table 4-4 Fresh grout properties from mixes using DDA, Tank 48H, MCU and SWPF.

BATCH TYPE	Gel Time (minutes)	Bleed (volume %)	Compressive Strength (psi)	Grout Flow (inches)	Yield Stress (Pa)	Plastic Viscosity (cP)
DDA	~300	2.9	590 @ 28 days	10.3	4.0	44
TANK 48H	110	3.0	645 @ 28 days	9.9	4.5	50
MCU	60	0	~800 @ 60 days	10.2	2.6	50
SWPF	180	1.4	~900 @ 54 days	10.3	2.1	52

4.3 Water to Premix Ratio

It is well known that the properties for a given salt and premix composition can be varied by varying the water to premix ratio. The baseline case in this study was a water to premix ratio of 0.60. The effects of varying this ratio from 0.50 to 0.65 on the grout properties of the DDA, Tank 48H, MCU and SWPF simulants were determined.

The DDA simulant used for the water/premix ratio study contained both aluminum and phosphate. The results for flow, gel time, density and rheology (measured from 0 to 300 sec^{-1}) for premix ratios of 0.50, 0.575 and 0.65 are presented in Table 4-5.

Table 4-5 Fresh grout properties for the mix using the DDA simulant as a function of water/premix ratio.

Property	DDA Water/Premix Ratio		
	0.5	0.575	0.65
Yield Stress (Pa)	7.5	4.2	2.6
Plastic Viscosity (cP)	99.6	58.1	39.1
Flow (inches)	8.5	9.8	10.5
Density (g/mL)	1.77	1.72	1.67
Gel Time (minutes)	>180	>180	>180

The Tank 48H simulant contained both aluminum and phosphate at the projected concentrations. The results for flow, gel time, and rheology (measured from 0 to 300 sec^{-1}) for mixes made with premix ratios of 0.5, 0.58 and 0.65 are presented in Table 4-6.

Table 4-6 Fresh grout properties for the mixes made using Tank 48H simulant as a function of water/premix ratio.

Property	Tank 48H Water/Premix Ratio		
	0.5	0.575	0.66
Yield Stress (Pa)	9.7	5.6	3.6
Plastic Viscosity (cP)	96.1	63.0	42.3
Flow (inches)	8.0	9.4	10.1
Gel Time (minutes)	60	-	-

The MCU simulant contained both aluminum and phosphate at the projected concentrations. The results for flow, gel time, and rheology (measured from 0 to 300 sec^{-1}) for mixes made with premix ratios of 0.5, 0.58 and 0.65 are presented in Table 4-7.

Table 4-7 Fresh grout properties for the MCU simulant as a function of water/premix ratio.

Property	MCU Water/Premix Ratio		
	0.5	0.575	0.65
Yield Stress (Pa)	5.0	3.3	1.8
Plastic Viscosity (cP)	103.0	73.3	43.8
Flow (inches)	8.3	9.4	10.7
Gel Time (minutes)	40	50	60

Grout properties were also measured as a function of water to premix ratio for mixes made using the SWPF simulant (containing aluminum but no phosphate). The results for flow, gel time, and rheology (measured from 0 to 300 sec^{-1}) for premix ratios of 0.5, 0.58 and 0.65 are presented in Table 4-8.

Table 4-8 Fresh grout properties for the mixes made using the SWPF simulant as a function of water/premix ratio.

Property	SWPF Water/Premix Ratio		
	0.5	0.575	0.65
Yield Stress (Pa)	5.1	3.0	1.6
Plastic Viscosity (cP)	100.6	66.4	42.6
Flow (inches)	8.5	9.5	10.7
Gel Time (minutes)	70.0	90.0	>90

The general trends using a linear fit of flow, yield stress and plastic viscosity to water/premix ratio are shown graphically for the DDA, Tank 48H, MCU and SWPF simulant in Figure 4.1.

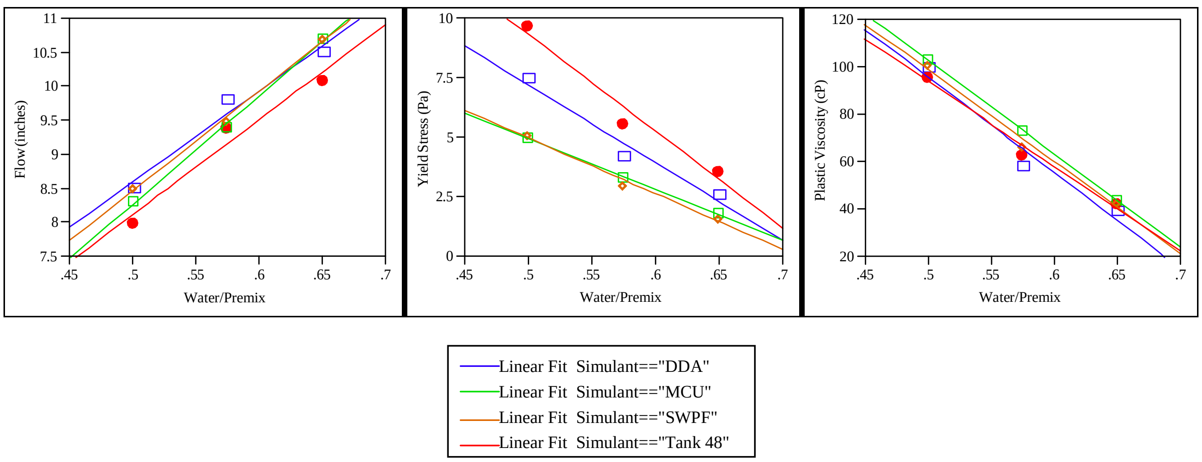

Figure 4-1 Dependence of flow, yield stress and plastic viscosity on water to premix ratio.

4.4 Composition of Premix

Several trial runs were carried out to determine the effect of a change in the relative amounts of fly ash, slag and cement in the premix. The general trend in yield stress, plastic viscosity and gel times are shown in Figure 4.2 for the simulant which is an average for all batches but without phosphate. The approximate bleed water values on a volume % for these mixes presented in Figure 4-2 were 0 % bleed water for the high portland cement mix, 1% bleed water for the high slag mix and 6 % bleed water for the high fly ash mix.

Yield Stress (Pa) Plastic Viscosity (cP) Gel Time (minutes)

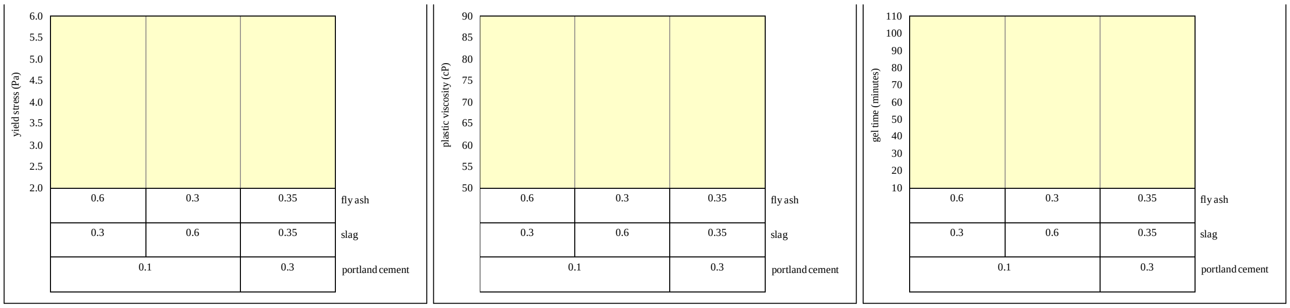

Figure 4-2 Dependence of yield stress, plastic viscosity and gel time on water to premix ratio.

Two additional mixes were prepared using the DDA simulant containing both phosphate and aluminum at a 0.60 water to premix ratio. One of the mixes was high in slag (0.60 mass fraction of the premix) and the other was high in fly ash (0.60 mass fraction of the premix) with both mixes containing the same amount of portland cement (0.1 mass fraction of the premix). The results for these two mixes are presented in Table 4-9.

Table 4-9 Fresh grout properties for the DDA simulant with high slag and high fly ash premixes.

Physical Property	**DDA grout Premix Compostion**	
	High Slag (premix fration = 0.6 slag, 0.3 fy ash, 0.1 cement)	High Fly Ash (premix fraction = 0.3 slag, 0.6 fly ash, 0.1 cement)
Yield Stress (Pa)	5	2.4
Plastic Viscosity (cP)	53.7	40.7
Bleed Water (Vol. %)	~ 5	~ 9
Gel Time (Minutes)	> 90	> 90

4.5 Premix Lot to Lot Variation

New lots of fly ash, slag and portland cement were received recently. One test was performed in which the new premix materials (Batch 2) were used in place of the original premix materials (Batch 1). These materials were obtained from the same vendor. This test used the MCU simulant containing aluminum and phosphate at a 0.60 water to premix ratio. The results are summarized in Table 4-10 and show only a slight change in properties with the new lots of materials. These results are preliminary and have not been reproduced or extended to other simulants.

Table 4-10 Fresh grout properties using the MCU simulant for different lots of fly ash, slag and portland cement.

Property	Premix Lot #	
	1	2
Yield Stress (Pa)	2.5	2.3
Plastic Viscosity (cP)	58.2	51.2
Flow (inches)	9.9	10.4
Gel Time (minutes)	60	70

In anticipation of potential changes in new lots of fly ash, slag and portland cement, the chemical compositions were determined for these materials (Table 4-11). In addition, the carbon content of the fly ash was determined by TGA to be 3.0 %. Analyses of the chemical composition of the new lots will be performed and the results compared to Table 4-11.

Table 4-11 Chemical compositions for fly ash, slag and portland cement.

FLY ASH		BLAST FURNACE SLAG		PORTLAND CEMENT	
Compound	Wt%	Compound	Wt%	Compound	Wt%
Al_2O_3	28.6	Al_2O_3	8.4	Al_2O_3	5.4
CaO	0.7	CaO	38.5	CaO	64.9
Fe_2O_3	6.0	Fe_2O_3	0.4	Fe_2O_3	3.7
K_2O	2.6	K_2O	0.3	K_2O	0.5
MgO	0.9	MgO	12.9	MgO	1.2
Na_2O	0.3	Na_2O	0.3	Na_2O	0.1
SO_4	0.1	SO_4	1.0	SO_4	3.2
SiO_2	54.2	SiO_2	37.9	SiO_2	20.5
TiO_2	1.6	TiO_2	0.4	TiO_2	0.3
Carbon	3.0	Carbon	0.0	Carbon	0.0
TOTAL	98.0	TOTAL	100.1	TOTAL	99.8

5.0 DISCUSSION

This Section discusses the results of the reproducibility study and the results of the dependence of grout properties on composition variability.

5.1 Reproducibility Study

Gel time measurements were reproducible as shown in Table 3-1. The resolution of this measurement is limited by the time interval at each pour (every 10 minutes). In addition, this method of gel time determination is limited by its subjectivity (operator dependence) and the fact that pouring the sample every 10 minutes remixes the slurry and can extend the gel time (experimentally verified in this study). An alternative method for measurement of gel time that could be refined, characterized for reproducibility, and used in a variability study is the rheological method using a vane rotating at a very low frequency (1 revolution/hr). However, the pour method developed in this study may be adequate depending upon (1) the acceptance criterion for gel time and (2) the closeness of the measured values to the acceptance criterion.

The reproducibility of bleed water (Table 3-2) showed significant variability for a mix which had a gel time on the order of 5 hours (300 minutes). The variability in bleed water was much less for samples that had shorter gel times. However, the bleed water values measured from these mixes with lower gel times were from the same trial run and therefore, did not measure the batching variability. It is proposed that the overall measurement variability of these lower gel time samples be determined. It may be that bleed water variability is dependent on the mix composition and gel time.

From an operational perspective, the time dependence of bleed water may be important. Most of the measurements of bleed water reported in this study were for samples that had cured for 3 days. An exception is the data shown in Table 3-3 where both the 1 day and 3 day bleed water measurements are presented. A decrease in bleed water is observed as the sample cures. Agreement on acceptance criteria for bleed water and other properties is required prior to the start of the variability study.

For grout flow, a method was developed that was based on ASTM measurements of flow from a cylinder for concrete mixes. The method developed as part of this study showed a 1.9% RSD for flow reproducibility. In addition the more fluid a mixture appeared visually, the greater the flow as measured by this method. The rheological measurements of yield stress and plastic viscosity from the flow curve (0 to 300 sec^{-1}) both correlated with the flow measurement. That is, the lower the viscosity or yield stress, the greater the flow (diameter of ‘pancake’).

Compressive strengths were measured by two methods. The more convenient method used the plastic cylinders as molds to produce cylindrical grout monoliths for compressive testing. However, this method had significant variability and it most likely would be necessary to measure a number of samples to get a reasonable average. On the other hand, the use of the 2 inch cube molds provided samples that gave a much tighter range of results for compressive strength. The results with the 2 inch cubes were, on average, much higher than the results using the plastic cylinders (970 vs. 590 psi). Therefore, the compressive strength results with the cylinders are conservative. The role of compressive strength measurements in a variability study will depend on the acceptance criterion, the closeness of the measured values to the acceptance criterion, and the value added to the study relative to the increase in complexity and cost of the study.

The reproducibility of set times was not measured as part of this study. However, a number of measurements of set time were made using the Vicat needle and in all cases the set times were less than 2 days.

5.2 Compositional Variability

Results from the compositional variability study revealed that minor constituents can have a major effect on the grout properties. In particular, gel time, rheology and grout flow were highly dependent on the presence of phosphate and aluminum at low concentrations in the salt solutions. The gel time of mixes was most dependent on phosphate concentration. The grout properties over the concentration range of 2.8E-04 M to 2.6E-03 M phosphate were provided in Section 4.1.2. It also appears that the sensitivity of grout properties to phosphate and aluminum depends on the waste type (sodium Molarity etc.). These data suggest that phosphate or aluminates could be, if required, added as admixtures to extend the gel times of mixes.

It is clearly important to identify those minor constituents that do have an impact on grout properties and to include their potential concentration ranges in a variability study. Other minor anions that are projected to be in the decontaminated salt solutions such as chloride, fluoride, and oxalate did not significantly affect the properties.

For this study, the impact of organics on the properties was not measured although this needs to be addressed due to the fact that Tank 48H salt solution will contain organics based on In Tank Precipitation, and MCU and SWPF will contain organics from the CSSX process.

Ultimately, the results of a variability study using a simulated salt solution will be useful only to the extent that the simulants reflect the actual waste streams. Therefore, it is important that (1) complete chemical characterization of tank samples be performed and that (2) radioactive samples be tested (i.e., made into grout samples) in such a manner that the results of the radioactive testing will provide feedback (validation) of the simulated approach.

Grout mixes made from simulants of DDA, Tank 48H, MCU and SWPF showed significant variation for the baseline 0.60 water to premix ratio. The amount of bleed water was highest for mixes made with DDA and Tank 48H (both of which had long gel times). Both of these simulants have relatively low salt concentrations and therefore lower densities. MCU and SWPF simulants have higher salt concentrations and densities. MCU had no bleed water while the SWPF mix (with a gel time of 180 minutes) had 1.4% by volume bleed water after three days. It may be that the higher densities of these two simulants retard settling and reduce bleed water. In any event, it is important to consider the acceptance criteria for bleed water in light of the other properties of the fresh and cured grout.

Water to premix ratio significantly impacted the grout properties as expected from previous studies. This parameter provides a way to adjust grout properties but must be considered in light of the impact to waste loading and volume of Saltstone produced. The results of the change in premix ratio from 0.50 to 0.65 for all four waste types demonstrated that the changes observed in properties (with the possible exception of bleed water) were much greater than the reproducibility of these properties presented in Section 3.0. This is, of course, a prerequisite to the performance of a useful variability study.

Another potential parameter in the formulation is the variation in the relative amounts of fly ash to slag to portland cement. Results are presented in Section 4.4 that demonstrate that property changes are readily observed as the premix ratio is varied.

Finally, another source of variation is the lot to lot variation in the fly ash, slag and portland cement. As new lots are received, it is proposed that the baseline mixes be prepared and properties measured to determine the variability (if any) introduced by the new lots. Both chemical and physical characterization of these materials should be measured and a data base established to track these lots and provide a resource to control and aid in the resolution of issues.

6.0 CONCLUSIONS

Measurement reproducibility was demonstrated for bleed water, grout flow, gel time, yield stress, plastic viscosity and compressive strength. The grout mixes used in this scoping study were produced using simulants that reflect current projections for the four decontaminated salt solutions that will be sent to Saltstone (DDA, Tank 48H, MCU and SWPF).

The inherent measurement variations of these properties in general were sufficiently small that a variability study as a function of chemical composition, water to premix ratios, and ratios of slag, fly ash, and cement in the premix, is possible. Therefore, a Saltstone variability study can be a useful part of the overall strategy for Saltstone operation.

Examples of the impact of compositional variation on the properties of Saltstone are provided in this report. An important finding of these tests was the fact that soluble phosphate and aluminate, minor species in the salt solutions, significantly affect the values of gel time, flow and rheology. Therefore, it will be important to accurately determine/estimate the concentrations of these ions in the decontaminated salt solutions and to ensure that the concentration ranges of these species are adequately covered in Saltstone variability studies.

7.1 RECOMMENDATIONS

The following bullets list three recommendations for the path forward on this task.

- Jointly agree on the acceptance criteria for the fresh and cured properties of Saltstone. Develop the criteria from an integrated overall approach taking into account that some of the properties are interdependent.

- As a preliminary task to the variability study, determine the effects of organics over the range of projected concentrations on the properties of Saltstone. These organics include those introduced with caustic side solvent extraction process for the MCU and SWPF waste streams, tetraphenylborate and associated breakdown products on the Tank 48H waste stream, and organics that may be present in the DDA streams (e.g., gelatin).

- After completion of the first two recommendations, perform a variability study for Saltstone to provide the baseline case for decontaminated salt solutions without admixtures.

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10. L. B. Romanoski, Personal Communication.

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