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FORMULATION DEVELOPMENT FOR PROCESSING TANK 48H IN SALTSTONE

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EXECUTIVE SUMMARY

Salt Program Engineering (SPE) requested research to help evaluate the Saltstone process as a disposition path for the contents of Tank 48H. The main objective of the task was to evaluate the processing and cured properties of Saltstone prepared with Tank 48H material aggregated with other Tank 50H inflows to determine the suitability of Saltstone as a disposition path for the contents of Tank 48H.

The Tank 48H waste was aggregated with inhibited water (IW) and a simulant of the recycle stream from the Defense Waste Processing Facility (DWPF). The aggregates targeted three tetraphenyl borate (TPB) concentrations: 1) 5500 mg/L, the aggregate determined from assumptions at the maximum reasonable limits, 2) 1500 mg/L, the aggregate containing the minimum proportion of Tank 48H material that is programmatically acceptable, and 3) 3500 mg/L, the average of the two endpoints. Saltstone prepared with Tank 48H waste aggregated with IW and a simulant of the recycle stream from the DWPF was produced in the Savannah River National Laboratory (SRNL) shielded cells. Processable Saltstone slurry formulations can be prepared with Tank 48H material and both DWPF recycle simulant and inhibited water with concentrations of 1500, 3500, and 5500 mg/L TPB. Toxic Characterization Leaching Procedure (TCLP) extractions were performed on the six aggregates. The extracts were analyzed for benzene, nitrobenzene and mercury. All of the samples passed TCLP.

Saltstone was also prepared with a Tank 48H simulant and DWPF recycle simulant. Testing of the fresh Saltstone slurry and cured Saltstone prepared with simulants indicate that neither the fresh nor cured Saltstone is hazardous for ignitability.

After transferring Tank 48H material to Tank 50H and prior to processing through the Saltstone Production Facility (SPF), Tank 50H should be sampled to verify processability.

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LIST OF ACRONYMS

ADS	Analytical Development Section
CVAA	Cold Vapor - Atomic Absorption
DWPF	Defense Waste Processing Facility
EPA	United States Environmental Protection Agency
FA	Fly Ash
GC	Gas Chromatography
GGBFS	Ground Granulated Blast Furnace Slag
ITP	In Tank Precipitation
IW	Inhibited Water
KTBP	Potassium Tetraphenylborate
MS	Mass Spectrometry
MST	Monosodium Titanate
SCS	Statistical Consulting Section
SPE	Salt Program Engineering
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
SRS	Savannah River Site
TBP	Tri-n-butyl Phosphate
TCLP	Toxic Characteristic Leaching Procedure
TPB	Tetraphenyl borate
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
ZHE	Zero-Headspace Extraction

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1.0 INTRODUCTION AND BACKGROUND

Tank 48H contains approximately 250,000 gallons of salt waste. The waste contains approximately 19,000 kg of organic material, primarily as potassium tetraphenyl borate (KTPB). The tetraphenyl borate, along with approximately 1450 kg monosodium titanate (MST), was added to Tank 48H during the demonstration and startup of the In-Tank Precipitation Facility (ITP). After the shutdown of the ITP process, no process existed for the destruction of the organic material in Tank 48H. Tank 48H is slated to serve as the feed tank for the Savannah River Site (SRS) Actinide Removal Process. Prior to this use, the current Tank 48H waste must be treated or removed.

Two options being considered for disposition of the contents of Tank 48H include[1]:

1. Aggregation of the material with DWPF recycle stream and disposal in the Saltstone Processing Facility.

2. In-Situ Thermal Decomposition using heat in combination with pH reduction and catalyst addition.

Salt Program Engineering (SPE) requested research to help evaluate the Saltstone process (option #1 above) as a disposition path for the contents of Tank 48H. The main objective of the research was to evaluate the processing (gel time, set time and bleed water) and cured (leach) properties of Saltstone prepared with Tank 48H material aggregated with recycle from the DWPF or other tank contents to determine the suitability of Saltstone as a disposition path for the contents of Tank 48H. Table 1-1 is the designation of the processing terminology used is this study.

Table 1-1. Process Terminology used in Study.

Term	Designation
Gel Time	The time at which the Saltstone slurry does not flow due to gravity, i.e. readily pour from the casting cup. For this study, acceptable gel time is 30 min < gel time < 120 min.
Set Time[*]	The elapsed time from casting the Saltstone slurry until the mixture reaches rigidity as indicated by the Set Time Determination[†] (penetrometer penetration < 2.5 mm). Preferred set time is less than three days. However, set times up to six days are acceptable[†].
Bleed Water	The autogenous emergence of water from Saltstone slurry caused by the settlement of solid materials. For this study, acceptable bleed water is 1% after 72 h.

The Savannah River National Laboratory (SRNL) was requested to 1) confirm that Saltstone prepared with actual Tank 48H material can be processed into Saltstone and pass the Toxic Characteristic Leaching Procedure (TCLP) to be considered non-hazardous and 2) confirm that Saltstone mixes prepared with a Tank 48H simulant are not considered ignitable‡.

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[*] ASTM C 125-03 “Standard Terminology Relating to Concrete and Concrete Aggregates”

[†] Manual 704-Z Procedure 4400, “Saltstone Grout Lab Analysis (U), Rev. 11 (2002).

[‡] Curing Saltstone passes the EPA manual SW-846 Methods 1010a “Pensky-Martens Closed-Cup Method for Determining Ignitability,” Revision 1 (2002) and 1030 “Ignitability of Solids” Revision 0 (1996).

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2.0 APPROACH

The Tank 48H waste was aggregated with inhibited water (IW) and a simulant of the recycle stream from the DWPF. The DWPF recycle simulant targeted the average of the Tank 23 and Tank 24 samples taken 100 inches from the tank bottom as reported by Swingle[2]. Table 2-1 is the composition of the DWPF Recycle simulant. The concentration of TPB in Tank 48H is 18,800 mg/L[3]. Table 2-2 is the components and properties of interest for the materials prior to aggregation. For the tests to determine ignitability, a simulant of the Tank 48H material was prepared to represent the material in Reference 3[4].

Table 2-1. Composition of DWPF Recycle Simulant.

Component	g/L
$NaNO_2$	21.734
$NaNO_3$	5.219
NaOH	17.399
Na_2CO_3	7.419
$Hg(NO_3)_2$	14.5 ppm
Total	51.771
Solids	5.2 wt %

Table 2-2. Concentration and Properties of Materials Used for Aggregation.

Material	TPB (mg/L)	Mercury (mg/L)	Cs activity[3] (dpm/mL) (Ci/gal)	Alpha[3] (dpm/mL)	wt % Solids		Density (g/mL)
					Undissolved	Total †	
Tank 48H	18,800	10.3	1E+09 (1.72)	2.8E+05	2.18	18.42	1.144
DWPF Recycle simulant	0	14.5‡	0	0	<1	5.2	1
Inhibited Water	0	0	0	0	0	0.1	1

†Total solids is used to determine the water:premix ratio used for Saltstone processing.
‡Value from Tank 24.

The aggregates targeted three TPB concentrations: 5500 mg/L, the aggregate determined from assumptions at the maximum reasonable limits, 1500 mg/L, the aggregate containing the minimum proportion of Tank 48H material that is programmatically acceptable, and 3500 mg/L, the average of the two endpoints. This resulted in six aggregates for testing (i.e., three TPB levels with two simulants). These aggregates span the range of potential Saltstone compositions. Table 2-3 is the calculated make up of each of the aggregates.

Table 2-3. Calculated Compositions and Properties of Aggregates.

Material	TPB (mg/L)	Solids (wt %)	Density (g/ml)	Mercury (mg/L)	Cs activity (dpm/mL) (Ci/gal)	Alpha (dpm/mL)
Tank 48H/DWPF Recycle (s)	5500	8.0	1.04	13.3	3E+08 (0.50)	8.2E+04
	3500	6.2	1.03	13.7	2E+08 (0.32)	5.2E+04
	1500	4.4	1.01	14.2	8E+07 (0.14)	2.2E+04
Tank 48H/IW	5500	6.0	1.04	3.0	3E+08 (0.50)	8.2E+04
	3500	4.1	1.03	1.9	2E+08 (0.32)	5.2E+04
	1500	1.8	1.01	0.8	8E+07 (0.14)	2.2E+04

Together, the dry materials used to make the Saltstone slurry are called premix. The ratio of the premix materials was fixed for this study. Table 2-4 is the premix composition used throughout this study.

Table 2-4. Premix Composition used in this Study.

Premix by Weight
45% Class F Fly Ash (FA)
45% GGBFS[a] (Slag)
10% Cement

[a]Ground granulated blast furnace slag.

2.1 Sample Preparation

To prepare the aggregate, a portion of the Tank 48H material was transferred from a well-mixed bottle of the material from Reference 3 into a bottle and weighed. Using the measured mass of the Tank 48H material transferred and the data in Table 2-2, the amount of IW or DWPF recycle simulant required to achieve the desired TPB concentration in the aggregate was calculated. The data in Table 2-3 then was used to calculate the amount of premix to achieve the desired water to premix ratio.

To prepare the Saltstone slurry, the aggregated liquids were added to a one liter blender carafe. At this point, set retarder or antifoam was added to the aggregate, if appropriate. The calculated amount of premix was then added to the carafe. The materials were then agitated for one minute. The contents were inspected to ensure that the premix had dispersed. Any remaining premix that had not been dispersed was reintroduced to the slurry with a spatula. The slurry was then agitated for an additional two minutes.

For each mix, five 120-mL cups were marked at 50 milliliters. Two cups were designated for gel time, one cup was designated for set time, and the remaining two cups were reserved for bleed water determination. The Saltstone slurry was then cast into the five cups and capped. For each of the six unique aggregates, Saltstone slurry was cast into two Teflon® vessels suitable for elevated temperature and pressure engraved with permanent identifications. The vessels were filled to minimize head space. One sample of each aggregate cast in Teflon® (six vessels total) was set aside to cure at ambient temperature and the remaining samples were cured for 28 days at 90 °C for TCLP extractions. After curing was complete, the heated samples were cooled to ambient and placed with the unheated samples until sampling. The TCLP samples were collected randomly being handled one sample at a time to minimize exposure to atmosphere.

2.2 Gel Time Determination

There is not a formally documented range of gel times to designate Saltstone slurry as “acceptable”. However, the range 30 min < gel time < 120 min is regarded as a conservative time frame where the formation of a gel structure in the slurry would be unlikely to cause difficulties pumping slurry to Saltstone Vaults and would not substantially increase the probability of the slurry settling. This range of gel times was applicable to the SPF prior to FY04 facility modifications and may not adequately meet the current needs of the SPF. The two samples designated for gel time determination were maintained undisturbed until a flowability test was performed. After an appropriate waiting period, the contents of one of the cups was poured into an empty cup and the flowability of the slurry was observed. Following a second waiting period, the contents of the second cup were poured into an empty cup and the flowability of the slurry was observed. This process was repeated until the slurry did not readily flow and was deemed gelled. The gel time was then recorded as the elapsed time between the casting of the sample and the unsuccessful pour that signified the conclusion of the test. For several of the aggregates it was necessary to add set retarder and antifoam to achieve an acceptable gel time. The set retarder used in these experiments was Daratard 17[§]. Two antifoams were used in these tests. The primary antifoam used in these tests was B52[**]. Previous testing indicates that B52 is effective in breaking down foam in aggregates containing TPB. An additional antifoam, tri-n-butyl phosphate (TBP), was also evaluated for effectiveness in mitigating foam formation.

2.3 Bleed Water Determination

The desired maximum bleed water is 1 vol %. The two cups designated for bleed water were inspected after 72 h. The mass of bleed water, if any, in the two cups is measured. By using 100 mL of Saltstone (two 50-mL samples), the volume percent bleed water is the mass of the water recovered from the two samples.

2.4 Set Time Determination

The desired maximum set time is three days. The time of set was determined using a Vicat needle modified for performance in shielded cells. The method of determination used instructions based on the Z-Area procedure[††]. One day after casting into the cup in Section 2.1 designated for set time determination, the cup is placed under the Vicat needle and the zero distance mark is set with the needle at the surface of the sample. The needle is raised 50 mm and released. The penetration of the penetrometer into the sample is recorded from the gauge. This process is repeated daily until the penetration is < 2.5 mm.

2.5 Toxic Characteristic Leaching Procedure

A solid waste exhibits the characteristic of toxicity if the concentration of the contaminants in the TCLP extract is greater than the regulatory levels[‡‡]. The analysis of pure, unaggregated Tank 48H contents performed in Reference 3 reported the presence of hazardous concentrations of benzene as defined by the United States Environmental Protection Agency (EPA). The nitrobenzene content was below the detection limits, but greater than the EPA regulatory limit for toxicity. The mercury content of The Tank 48H was below the limits defined by the EPA as characteristic for toxicity. However, since mercury was part of the aggregates prepared with DWPF recycle simulant, and there was a potential for the formation of benzene and nitrobenzene during curing, a modified TCLP extraction based on the EPA method was used to determine the presence of these species in the TCLP extract[5]. Table 2-5 is the regulatory limit for the contaminants of concern in this study.

Table 2-5. EPA Regulatory Limits for Contaminants in TCLP Extracts.

Contaminant	Regulatory Level (mg/L)
Benzene	0.5
Nitrobenzene	2.0
Mercury	0.2

The EPA extraction method was adhered to as closely as possible as dictated by the test conditions (i.e. radioactive materials handled with manipulators in shielded cells). For example, in Section 7.2.5 of the method, a mass of at least 100 grams is specified. This was neither practical nor possible for the samples prepared in Section 2.1, as there was not sufficient Tank 48H material available to prepare sufficient Saltstone for all of the testing and perform TCLP extractions. Table 2-6 summarizes the deviations from

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[§] W.R. Grace Daratard 17
[**] Illinois Institute of Technology (IIT) B-52
[††] Manual 704-Z Procedure 4400, “Saltstone Grout Lab Analysis (U), Rev. 11 (2002).
[‡‡] 40CFR261.24 Toxicity characteristic

the EPA method and provides explanations for the variance. To compensate for the deviation in extraction fluid to sample ratio in 7.2.11 of the EPA method, the analyses results are normalized to an extraction fluid to sample ratio of 15.

Table 2-6. Variance from EPA Method for TCLP Extraction.

Section	Action	Variance	Explanation
	Non-Volatiles		
7.2.5	Sample size Recommended > 100 g.	Used ~1 g samples.	Limited material available. Reference 6 precedence.
7.2.11	• Extraction fluid volume 20x mass of sample. • Rotate 30±2 rpm for 18±2 h @ 23±2 °C.	• Used fixed volume ~15x sample mass. • T_{cell} not controlled, exceeded 25 °C.	• Used pre-measured extract for efficiency in shielded cell. Reduced ratio introduced conservatism. • Test performed in summer. Air temperature of shielded cells not regulated.
7.2.12	Filter extract.	Settled solids and decanted extract.	During shakeout tests filters plugged, exposed extract to environment. Decant provides more conservative result.
7.2.14	Store extracts at 4 °C.	Extracts stored at ambient temperature in cells, refrigerated in ADS sample receiving.	To maintain 4 °C in shielded cells is costly. Samplers refrigerated in ADS sample receiving.
	Volatiles		
4.3.1	Use approved Zero-Headspace Extractor (ZHE) vessel.	Used glass vials with Teflon® lids filled to top.	Approved ZHE vessels for 25 g samples.
7.3.3	Sample size Recommended ~ 25 g.	Used ~1 g.	Limited material available. Reference 6 precedence.
7.3.15	Store extracts with minimal headspace at 4 °C.	Extracts stored with minimal headspace at ambient temperature. Samples refrigerated in ADS sample receiving.	To maintain 4 °C in shielded cells is costly. Samplers refrigerated in ADS sample receiving. Although samples are sealed with minimal head space, variance is non-conservative as benzene is a volatile compound.

2.5.1 Volatile Organic Compound (VOC) Extraction

After the samples prepared in Section 2.1 had cured for 28 days, samples were collected for extraction. Duplicate samples of approximately one gram each were retrieved from each vessel. The use of one gram of sample for extraction was explored previously[6]. Samples collected ranged from 0.773 to 1.015 grams. The samples were placed in 15 mL glass vials with Teflon® gaskets. To minimize exposure of the Saltstone to the environment, minimal effort was made to precisely collect one gram of material. A minimum of 0.75 grams was necessary to ensure that the extraction fluid to sample ratio was no more than 20. Extraction fluid 1[§§] was used to fill the vial to form a meniscus, and capped. The vials were

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[§§] Extraction Fluid 1is a pH 4.93 buffer made from acetic acid and sodium hydroxide.

placed in a rotator preset to 30 rpm and rotated for 18 h. After the vials were removed from the rotator, the samples were set aside to settle the solids. The extract was decanted into a sample vial and overfilled to minimize head space and limit volatility of volatile compounds. The vials then were removed from the shielded cells and submitted to the SRNL-Analytical Development Section (ADS) for volatile organic analysis (VOA) of benzene. The samples were analyzed by purge and trap Gas Chromatography / Mass Spectrometry (GC/MS). The method detection limit for this study was 0.005 mg/L for VOA. To determine the recovery of benzene during the analysis a matrix spiking experiment was performed. A 25 ppb spike of benzene was added to one of the samples and analyzed. It was determined that 83% of the benzene was recovered. This recovery rate is used to correct results for benzene losses during analysis.

2.5.2 Semi-Volatile Organic Compound (SVOC) and Metals Extraction

After the samples prepared in Section 2.1 had cured for 28 days, samples were collected for extraction. Approximately five additional grams of sample was collected to determine the appropriate extraction fluid for the TCLP*. Results determine that Extraction Fluid 2[†] be used for the SVOC and metals TCLP. Duplicate samples of approximately one gram each were retrieved from each vessel. The use of one gram of sample for extraction was explored previously[6]. Samples collected ranged from 0.967 to 1.025 grams. The samples were placed in 25 mL glass vials with Teflon® gaskets. A minimum of 0.75 grams was necessary to ensure that the extraction fluid to sample ratio was no more than 20. The vials were placed in a rotator preset to 30 rpm and rotated for 18 h. After the vials were removed from the rotator, the samples were set aside to settle the solids. The extract was decanted into two sample vials. The vials then were removed from the shielded cells and submitted to the SRNL-ADS for semi-volatile organic analysis (SVOA) of nitrobenzene and cold vapor atomic absorption (CV-AA) of mercury. The SVOC samples were extracted with methylene chloride, and the extract was analyzed by GC/MS. Gas Chromatography / Mass Spectrometry analysis was employed to identify organic compounds in the samples. The method detection limit for this study was 0.5 mg/L for nitrobenzene. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration. The method detection limit for this study was 0.11 mg/L for mercury.

2.6 Ignitability Determination of Fresh Saltstone Slurry

The presence of TPB in the Tank 48H material and the potential to form benzene in the Saltstone slurry is the basis for testing the Saltstone slurry for the characteristic of ignitability. A solid waste exhibits the characteristic of ignitability if the waste is a liquid and has a flash point of less than 60 °C (140 °F) as determined using a Pensky-Martens closed cup tester[‡]. Using a Tank 48H simulant[7], an aggregate was made with DWPF recycle simulant to target a TPB concentration of 5500 mg/L. A water to premix ratio of 0.63 was used to prepare the Saltstone slurry. Four replicate samples were submitted to SRNL-ADS for flash point testing. Samples were tested using a flash point tester similar to the Pensky-Martens tester. Dodecane (flash point 71°C/160°F) was used as the standard material.

2.7 Ignitability Determination of Cured Saltstone

The potential for the TPB present in the Tank 48H material to create benzene during curing of the Saltstone dictates testing the cured Saltstone for the characteristic of ignitability. A solid waste exhibits the characteristic of ignitability if the waste is not a liquid and is capable of causing fire and, when

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[*] ADS Manual L16.1, Procedure 2512, "Modified Toxicity Characteristic Leaching Process"

[†] Extraction Fluid 2 is a pH 2.88 solution made from acetic acid.

[‡] 40CFR261.21 Characteristic of Ignitability

ignited, burns so vigorously and persistently that is becomes a hazard. Using a Tank 48H simulant[7], an aggregate was made with DWPF recycle simulant to target a TPB concentration of 5500 mg/L. The Saltstone sample was prepared using a water to premix ratio of 0.63. Two replicate samples were cast and tested for ignitability using the EPA method 1030 “Ignitability of Solids.” A propane torch was used to produce an open flame of ~1050 °C. The flame was directed at one end of the sample for two minutes to determine if the sample was ignitable.

3.0 RESULTS

Saltstone prepared with Tank 48H waste aggregated with IW and a simulant of the recycle stream from the DWPF was produced in the SRNL shielded cells. Saltstone was also prepared with a Tank 48H simulant[7] and DWPF recycle simulant. The processing (gel time, set time and bleed water) and cured (leach) properties of the Saltstone were determined for the samples prepared with Tank 48H material. The determination of whether the Saltstone slurry or cured Saltstone were characteristic for ignitability was determined with samples prepared with the Tank 48H simulant from Reference 7 and DWPF recycle simulant.

3.1 Sample Preparation

The Saltstone samples were prepared as described in Section 2.1. After the blender had mixed the Tank 48H aggregate with the premix materials it was noted during casting that air was entrained in slurry. The quantity of air entrained increased with increasing TPB concentration. Entrained air can enhance the gelation of the slurry by producing a structure in the slurry and necessitate the use of set retarders or antifoams. Additions of antifoam reduced the quantity of entrained air and the bubbles appeared to have coalesced into larger bubbles. The coalescing of the bubbles during antifoam addition may have helped reduce the quantity of air entrained in the sample.

3.2 1500 mg/L TPB with DWPF Recycle Simulant

3.2.1 Gel Time

The Saltstone slurry was prepared as described in Section 2.1 with a water to premix ratio of 0.6. When the slurry was inspected after the first minute of mixing, it appeared thicker than desired. Additional aggregate was added to reduce the consistency of the slurry and raise the water to premix ratio to 0.68. There did not appear to be any air entrainment in the form of frothing of the slurry. The first gel time pour was after 10 minutes and it was determined that the slurry had gelled.

3.2.2 Bleed Water

After 24 hours the two bleed water cups were inspected and no bleed water was detected.

3.2.3 Set Time

Set Time was determined to be one day.

3.3 1500 mg/L TPB with Inhibited Water

3.3.1 Gel Time

Based on the results of the previous test, the Saltstone slurry was prepared with a water to premix ratio of 0.66. In addition, a set retarder (Daratard 17) was added to the aggregate prior to mixing. The amount of set retarder added was equal to 0.12 wt % of the aggregate. The slurry appeared satisfactory as it did not exhibit frothing and was thin enough to pour. The first gel time pour was after 5 minutes and it was pourable. Gel time was declared on the fourth gel time pour after 35 minutes.

3.3.2 Bleed Water

After 48 hours the two bleed water cups were inspected the bleed water was determined to be 7.2 vol %.

3.3.3 Set Time

Set Time was not measured for this aggregate.

3.4 3500 mg/L TPB with Inhibited Water

Based on the results of the previous test, the water to premix ratio was reduced and the set retarder was increased. The Saltstone slurry was prepared with a water to premix ratio of 0.60. A 0.19 wt % addition of set retarder was made to the aggregate prior to mixing. The slurry exhibited noticeable frothing but was thin enough to pour. During casting, it was noted that significant quantities of fine bubbles were entrained in the slurry. The first gel time pour was after 11 minutes. The slurry was thick but pourable. Gel time was declared on the second gel time pour after 16 minutes.

3.4.1 Bleed Water

After 24 hours the two bleed water cups were inspected and no bleed water was detected.

3.4.2 Set Time

Set Time was not measured for this aggregate.

3.5 3500 mg/L TPB with Recycle Simulant

Based on the results of the previous test, the water to premix ratio was increased and the set retarder was increased. The Saltstone slurry was prepared with a water to premix ratio of 0.63. A 0.27 wt % addition of set retarder was made to the aggregate prior to mixing. Again, the slurry exhibited noticeable frothing but was thin enough to pour. The first gel time pour was after 12 minutes. The slurry was thick but pourable. Gel time was declared on the second gel time pour after 21 minutes.

3.5.1 Bleed Water

After 24 hours the two bleed water cups were inspected and no bleed water was detected.

3.5.2 Set Time

Set Time was not measured for this aggregate.

3.6 3500 mg/L TPB with Inhibited Water (Second Iteration)

Based on the results of the two previous tests, the need for antifoam was clear. Antifoam prepared for WSRC, IIT B52 was shown to act as both a defoamer and antifoam in material similar to the contents of Tank 48H[8]. The IIT B52 was too viscous to add precisely using manipulators. A predetermined blend of Daratard 17 and B52 of 2:1 was used. The water to premix ratio was increased, the set retarder was decreased and antifoam was introduced. The Saltstone slurry was prepared with a water to premix ratio of 0.66. The admixture addition consisted of 0.20 wt % of set retarder and 0.10 wt % of B52. The slurry exhibited minor frothing. During casting, it was noted that the fine bubbles present in previous tests had coalesced into larger, less numerous bubbles. The bubbles were still entrained in the slurry. The first gel time pour was after 5 minutes. The slurry was fluid and poured easily. The second gel time pour was after 15 minutes. The slurry was thick but pourable. Gel time was declared on the fourth gel time pour after 30 minutes.

3.6.1 Bleed Water

After 24 hours the two bleed water cups were inspected and no bleed water was detected.

3.6.2 Set Time

Set Time was determined to be two days.

3.7 5500 mg/L TPB with Inhibited Water

Based on the results of the previous test, the water to premix ratio and the admixtures (set retarder + antifoam) were left unchanged. The Saltstone slurry was prepared with a water to premix ratio of 0.65. The admixture addition consisted of 0.21 wt % of set retarder and 0.10 wt % of B52. The slurry exhibited greater frothing than the 3500 mg/L TPB aggregates, but was thin enough to pour. Again, it was noted during casting that significant quantities of large bubbles were entrained in the slurry. The first gel time pour was after 7 minutes. The slurry was thick but pourable. Gel time was declared on the second gel time pour after 15 minutes.

3.7.1 Bleed Water

After 24 hours the two bleed water cups were inspected and no bleed water was detected.

3.7.2 Set Time

Set Time was not measured for this aggregate.

3.8 5500 mg/L TPB with Recycle Simulant

Based on the results of the previous test, the water to premix ratio was maintained and the admixtures were increased. The Saltstone slurry was prepared with a water to premix ratio of 0.64. The admixture addition consisted of 0.31 wt % of set retarder and 0.15 wt % of B52. The quantity of the foam noted during casting was reduced from the previous test. The first gel time pour was after 10 minutes. The slurry poured easily. The second gel time pour was after 20 minutes. During the second pour, the potential for bleed water was detected. The test was halted after the fourth gel time pour after 40 minutes when it was determined that bleed water would be present.

3.8.1 Bleed Water

After 48 hours the two bleed water cups were inspected and 9 vol % bleed water was measured.

3.8.2 Set Time

Set Time was not measured for this aggregate.

3.9 5500 mg/L TPB with Inhibited Water (Second Iteration)

Based on the results of the two previous tests, the water to premix ratio was maintained and the admixtures were decreased. The Saltstone slurry was prepared with a water to premix ratio of 0.65. The admixture addition consisted of 0.26 wt % of set retarder and 0.13 wt % of B52. The slurry exhibited minor frothing. It was noted that the amount of bubbles was similar to the previous test. Bubbles were still entrained in the slurry during casting. The first gel time pour was after 10 minutes. The slurry was fluid and poured easily. The second gel time pour was after 20 minutes. The slurry was thick but pourable. Gel time was declared on the third gel time pour after 30 minutes.

3.9.1 Bleed Water

After 24 hours the two bleed water cups were inspected and no bleed water was detected.

3.9.2 Set Time

Set Time was not measured for this aggregate.

Table 3-1 is a summary of the processing properties of the aggregates tested. The "with adjustments" term was necessary as there was not sufficient Tank 48 material available to perform the necessary test iterations to definitively determine a formulation for each of the six aggregates. Therefore, by bounding the processing requirements, it was determined that there exists an acceptable formulation that could be achieved "with adjustments".

Table 3-1. Summary of Processing Properties of Saltstone Slurries.

Aggregate	Water/ Premix	Daratard 17 Admixture (Wt %)	IIT B52 Antifoam (Wt %)	Gel Time (min)	Set Time (d)	Bleed Water (Vol %)	Processable
1500 Recycle	0.68	0.00	None	10	1	0	with adjustments
1500 IW	0.66	0.12	None	35	--	7.2	with adjustments
3500 IW	0.60	0.19	None	16	--	0	with adjustments
3500 Recycle	0.63	0.27	None	21	--	0	with adjustments
3500 IW-2	0.66	0.2	0.1	30	2	0	YES
5500 IW	0.65	0.21	0.1	15	--	0	with adjustments
5500 Recycle	0.64	0.31	0.15	> 40	--	9	with adjustments
5500 IW-2	0.65	0.26	0.125	30	--	0	Probable*

*Set time was not measured but based on gel time and bleed water results, set is expected to be acceptable.

3.10 Additional Antifoam Tests with 3500 mg/L TPB with Inhibited Water

After the initial test results were analyzed, two additional tests were performed. Aggregate made with 3500 mg/L TBP and IW was selected to represent the most likely TBP concentration. Based on previous tests the water to premix ratio was targeted as 0.65. The admixture addition consisted of 0.2 wt % set retarder and 0.15 wt % antifoam. The only variable between the two tests was the antifoam. In the first test, B52 was used and in the second test, TBP was the antifoam. In both tests, the slurries exhibited minor frothing. During casting, the larger, less numerous bubbles noted in the earlier 3500 mg/L TPB were present. The bubbles were still entrained in the slurry. The slurries were fluid and poured easily. Gel time was declared after 25 minutes.

3.10.1 Bleed Water

After 24 hours the bleed water cups were inspected and no bleed water was detected in either test.

3.10.2 Set Time

The set time was tested after one day. Neither of the mixes were set. The set time was tested again after 3 days. Again, neither of the mixes were set, although the mix made with B52 had firmed considerably. The final test was performed at six days. The mix prepared with B52 was declared set. The mix prepared with TBP as the antifoam had not yet set.

3.11 Toxic Characteristic Leaching Procedure

TCLP extractions were performed in duplicate on samples cured at ambient temperature and at 90 °C for each unique aggregate.

3.11.1 Volatile Organic Compound (VOC) Extraction

TCLP extractions were performed and extracts were analyzed as described in Sections 2.5 and 2.5.1. One of the replicated of the 1500 mg/L TPB aggregate made with IW and cured at 90 °C was compromised during handling and was not removed from the shielded cells for analysis. A statistical analysis of the benzene results performed by SRNL-Statistical Consulting Section (SRNL-SCS) determined that the TPB concentration was the only statistically significant variable affecting the benzene concentration in the TCLP extracts. The curing temperature (90 °C vs. ambient) and aggregation material (DWPF recycle vs. IW) were statistically equivalent. Table 3-2 is the results of the benzene analysis. The measured benzene is corrected for the 83% recovery described in Section 2.5.1. The corrected value is then normalized for the variations in the sample mass to a mass of one gram. Figure 3-1 is the plot of the benzene concentration in the TCLP extracts as a function of the TPB concentration in the aggregate. The benzene limit for RCRA hazardous designation from Table 2-5 is 0.5 mg/L is also displayed for reference. All of the samples passed TCLP for benzene.

Table 3-2. Benzene Concentrations in TCLP Extracts.

TPB (mg/L)	Aggregate*	Cure Temperature (°C)	replicate	Sample Mass (g)	Measured Benzene (mg/L)	Corrected Benzene (mg/L)	Normalized Benzene (mg/L)
1500	IW	27	1	0.954	0.06	0.07	0.08
1500	IW	27	2	0.949	0.06	0.07	0.07
1500	IW	95	2	0.988	0.06	0.07	0.07
1500	RC	27	1	1.000	0.02	0.02	0.02
1500	RC	27	2	1.006	0.10	0.12	0.11
1500	RC	95	1	1.051	0.06	0.07	0.07
1500	RC	95	2	1.011	0.06	0.07	0.07
3500	IW	27	1	0.821	0.12	0.14	0.18
3500	IW	27	2	0.991	0.15	0.18	0.18
3500	IW	95	1	0.911	0.09	0.11	0.12
3500	IW	95	2	1.007	0.10	0.12	0.12
3500	RC	27	1	0.895	0.10	0.12	0.13
3500	RC	27	2	0.931	0.12	0.14	0.16
3500	RC	95	1	0.934	0.14	0.17	0.18
3500	RC	95	2	0.910	0.12	0.14	0.16
5500	IW	27	1	0.804	0.14	0.17	0.21
5500	IW	27	2	1.020	0.11	0.13	0.13
5500	IW	95	1	1.000	0.08	0.10	0.10
5500	IW	95	2	0.934	0.17	0.20	0.22
5500	RC	27	1	0.980	0.10	0.12	0.12
5500	RC	27	2	0.773	0.12	0.14	0.19
5500	RC	95	1	0.856	0.13	0.16	0.18
5500	RC	95	2	0.791	0.12	0.14	0.18

*RC– DWPF Recycle Simulant; IW – Inhibited Water

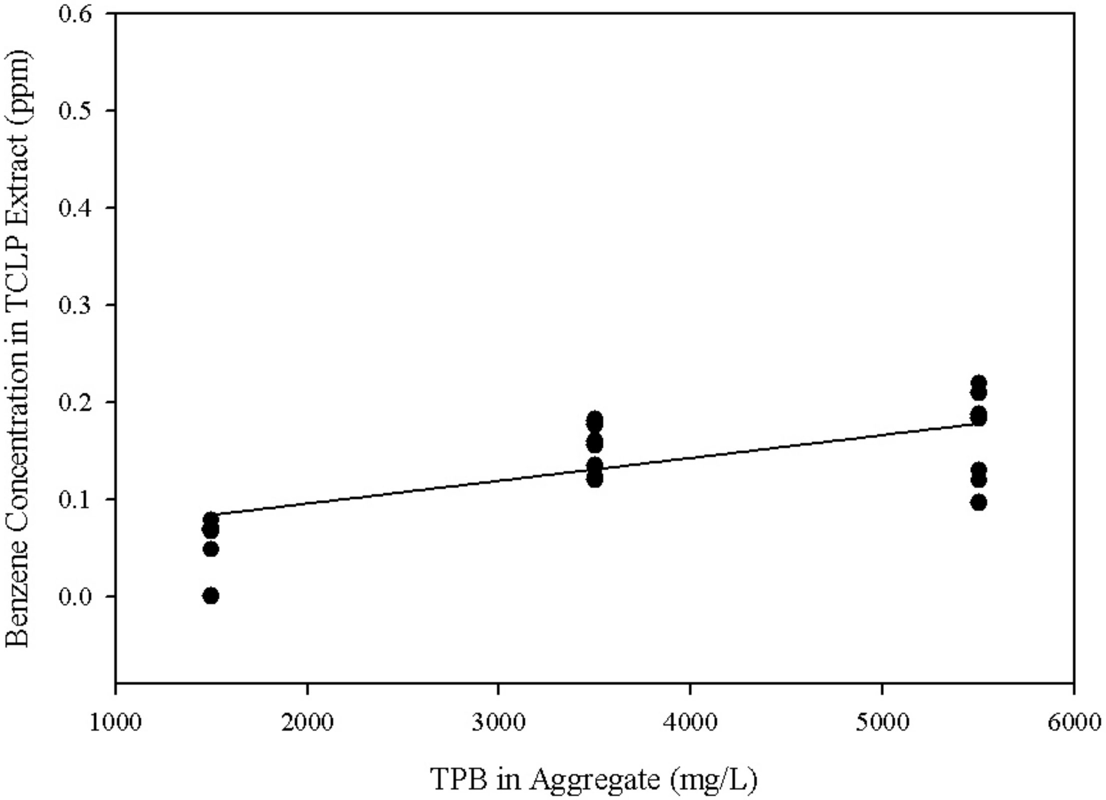

Figure 3-1. Benzene measured in the TCLP extracts for the TPB aggregates.

3.11.2 Semi-Volatile Organic Compound (SVOC) Analysis

TCLP extractions were performed and extracts were analyzed as described in Sections 2.5 and 2.5.2. The analysis for nitrobenzene for all of the samples was below the detection limits of the analytical method, 0.5 mg/L. The RCRA limit for nitrobenzene in TCLP extracts from Table 2-5 is 2.0 mg/L. Therefore all of the samples passed the TCLP for nitrobenzene.

3.11.3 Metals Analysis

TCLP extractions were performed and extracts were analyzed as described in Sections 2.5 and 2.5.2. The analysis for mercury (CV-AA) was performed only on samples that had the potential to be hazardous for mercury (i.e., Aggregates that were prepared with DWPF recycle simulant.). Results for all of the samples analyzed were below the detection limits of the analytical method, 0.11 mg/L. The RCRA limit for mercury in TCLP extracts from Table 2-5 is 0.2 mg/L. Therefore all of the samples passed the TCLP for mercury.

3.12 Ignitability Determination of Fresh Saltstone Slurry

Four replicate samples submitted to SRNL-ADS for flash point testing were analyzed using a closed cup flash point tester. The Saltstone slurry made with the 5500 mg/L aggregate of Tank 48H simulant and DWPF recycle simulant was prepared and tested as described in Section 2.6 and sampled to make the four replicates. A dodecane standard (flash point 71 °C/160 °F) was analyzed prior to the first replicate and after the final replicate. Each replicate was tested a single time. The analysis of the Saltstone slurry began approximately 20 minutes after the slurry was prepared and analysis continued for an additional 75 minutes. None of the four replicates exhibited a flash point below 100 °C, where the testing was terminated. Table 3-3 is the results of the flash point tests for the four replicates and two standards.

Table 3-3. Flash Point Results using a Closed Cup Tester.

Sample	Elapsed Time from Casting (min)	Flash Point (°C/°F)
Dodecane	10	79/174
5500 mg/L with DWPF Recycle-1	21	No Flash
5500 mg/L with DWPF Recycle-2	39	No Flash
5500 mg/L with DWPF Recycle-3	55	No Flash
5500 mg/L with DWPF Recycle-4	71	No Flash
Dodecane	86	81/178

3.13 Ignitability Determination of Cured Saltstone

The Saltstone slurry made with the 5500 mg/L aggregate of Tank 48H simulant and DWPF recycle simulant was prepared and tested as described in Section 2.7. The two replicate samples were exposed to an open flame for two minutes and it was determined that the samples were not ignitable, Figure 3-2.

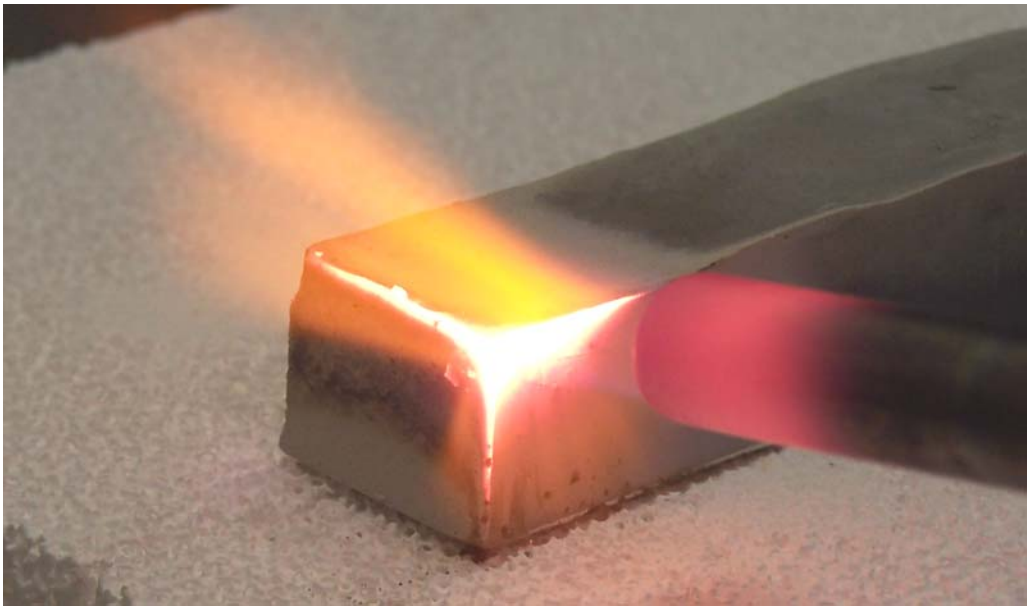

Figure 3-2. Ignitability test of cured Saltstone.

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4.0 CONCLUSIONS AND RECOMMENDATIONS

- Aggregates were prepared with Tank 48H material and either DWPF recycle simulant or inhibited water with concentrations of 1500, 3500, and 5500 mg/L TPB.
- Air entrainment caused by the mixing of the aggregate in the slurry preparation method used produced a stable structure the led to premature gelation of the slurries that required admixtures for remediation.
- Processable Saltstone slurry formulations were demonstrated with Tank 48H material and both DWPF recycle simulant and inhibited water with concentrations of 3500, and 5500 mg/L TPB. It is expected that acceptable formulation can be prepared with aggregates of 1500 mg/L TPB. Table 4-1 is the recommended initial processing parameters for the six aggregates tested.

Table 4-1. Recommended Initial Processing Parameters for Tank 48H Aggregates.

TPB (mg/L)	Water/Premix	Set Retarder (Wt %)	Antifoam (Wt %)
1500	0.60-0.63	0.1-0.2	0.1
3500	0.65	0.2	0.15
5500	0.65	0.30	0.15-0.2

- Analysis of the TCLP extracts of the Saltstone prepared from the six aggregates indicates that the resulting Saltstone is not hazardous for benzene, nitrobenzene, or mercury.
- Testing of the fresh Saltstone slurry and cured Saltstone prepared with simulants indicate that the neither the fresh nor cured Saltstone is hazardous for ignitability.
- After transferring Tank 48H material to Tank 50 and prior to processing through the SPF, Tank 50 should be sampled to verify processability with the recommended processing parameters in Table 4-1.

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