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PROPERTIES OF SALTSTONE PREPARED CONTAINING H-CANYON WASTE

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April 2005

Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

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EXECUTIVE SUMMARY

Saltstone slurries were prepared from solutions made from H-Canyon waste and evaluated for processing properties. Salt solutions prepared with a 1:1 ratio of Tank 50H simulant and H-Canyon blended waste produced slurries that met the processing requirements in Table 2 of the Task Technical and Quality Assurance Plan (TTQAP)[1]. Additions of set retarder and antifoam were necessary to meet these processing requirements. The water to premix ratio used to achieve acceptable processing properties was 0.63. Slurries prepared solely with H-Canyon blended waste as the salt solution met the gel time and bleed water requirements, but did not set in the allotted time. Compressive strength samples prepared from the mix with acceptable processing properties had an average compressive strength of 814 psi (Samples with a compressive strength value of >200 psi are acceptable[2].). Analysis for mercury of the leachate of samples analyzed by the Toxic Characteristic Leaching Procedure (TCLP) indicated a concentration of mercury in the leachate <0.11 mg/L (The limit set by the Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) for mercury to require treatment is 0.2 mg/L.). It is recommended that without further testing; Tank 50H be limited to no more than 50 wt% H-Canyon material. It is also recommended that prior to the transfer of Tank 50H to the Saltstone Processing Facility; a sample of the Tank 50H waste be evaluated for processing properties.

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LIST OF ACRONYMS

ADS	Analytical Development Section
dpm	Disintegrations per minute
EPA	Environmental Protection Agency
ETP	Effluent Treatment Project
GPE	General Purpose Evaporator
IW	Inhibited Water
RCRA	Resource Conservation and Recovery Act
SPF	Saltstone Processing Facility
SRNL	Savannah River National Laboratory
TCLP	Toxic Characteristic Leaching Procedure
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WCT	Waste Collection Tank

1.0 INTRODUCTION AND BACKGROUND

Unirradiated nuclear materials containing enriched uranium clad in aluminum are currently being processed in H-Canyon facilities. Normally the 1AW high activity waste stream that is generated from First Uranium Cycle solvent extraction operations would be neutralized with excess 50 wt% NaOH and transferred to the Tank Farm. However, the radionuclide content associated with unirradiated fuel is such that stabilization in Saltstone is a viable option. Bottoms from the General Purpose Evaporator (GPE) require no further processing or additions prior to transfer to the Tank Farm. The H-Canyon material identified for transfer to Tank 50 will consist of 75% of the neutralized 1AW stream and 25% of the GPE stream.

The Savannah River National Laboratory (SRNL) was requested to develop a formulation for processing H-Canyon material from Tank 8.4 and the GPE in Saltstone[3]. Samples were obtained of unneutralized Tank 8.4, Tank 710 and the Effluent Treatment Project - Waste Collection Tank (ETP-WCT). A second Technical Task Request (TTR)[4] requested that the consolidation and neutralization of the H-Canyon samples be performed at SRNL. Processability of the slurry through the Saltstone Processing Facility (SPF) and product quality were used to determine the acceptability of the formulation. Processing properties: 1) gel time, 2) set time and 3) standing (bleed) water were measured. The cured properties of compressive strength and mercury leachability (via a modified Toxic Characteristic Leaching Procedure (TCLP[5])) were measured.

2.0 APPROACH

The H-Canyon 1AW material is acidic and is neutralized prior to transfer to the Tank Farm. Sampling of the neutralized material can lead to inhomogeneous samples. Solid Waste personnel[4] requested that the consolidation and neutralization of the H-Canyon samples be performed at SRNL. The sample taken for SRNL had not been neutralized and therefore, prior to preparing Saltstone from the H-Canyon material, the 1AW material was neutralized using written instructions based on Section 5.5 "Neutralizing Waste" of the H-Canyon procedure[6].

2.1 Salt Solution Preparation and Analysis

The Tank 8.4 material was neutralized and blended with the GPE in a 3:1 ratio by volume. For this work, the resulting blend was designated as HC. Parallel work performed in the Actinide Technology Section[7] provided the necessary data to perform the neutralizations. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Ion Chromatography (IC) were used to analyze the as-received Tank 8.4 and GPE wastes). Cold Vapor Atomic Absorption (CVAA-Hg) and Gamma Scan were used to analyze the Tank 8.4 material. Table 2-1 provides the results for the two wastes.

Table 2-1. Analysis of As-Received Tank 8.4 and GPE.

ANALYTE	TANK 8.4	GPE
Cations	**Wt%**	**Wt%**
Al	3.1	1.4E-3
Mn	0.26	< 4E-7
Na	0.58	12.6
Hg	375 mg/L	NM
Anions	**Wt%**	**Wt%**
NO_3^-	30.4*	16.2*
SO_4^{2-}	< 5E-3	2.2
$COOH^-$	< 1E-2	9.0
$C_2O_4^-$	0.02	2.1
Nuclides	**dpm/mL**	
Sb-125	2.6E6	NM
Sb-126	1.8E3	NM
Cs-137	2.9E5	NM
Tl-208	1.1E3	NM
Am-241	6.4E3	NM
Density		
g/cm^3	1.25[7]	1.23

*Calculated
NM – Not measured

A simulant was prepared for the Tank 50H portion of the testing because no Tank 50H material was available at the time of the testing. The Tank 50H heel simulant was prepared from a sample from the ETP-WCT and inhibited water. The Tank 50H simulant was determined by assuming that the heel after the last transfer from Tank 50H to Z-Area on 5/29/2003 was essentially inhibited water (IW), and any additions to Tank 50H since then were from the ETP. This resulted in a blend of 69 % ETP-WCT and 31% IW by volume. A blend of equal volumes of the HC and Tank 50 was prepared as a salt solution to

make Saltstone. Table 2-2 is the weight percent solids and density of the neat materials and subsequent blends. The high solids content of the neutralized, concentrated solutions resulted in dissolved solids analyses that were not reproducible. Reference 7 discusses the physical and radiological aspects of the neutralized 1AW material.

Table 2-2. Weight Percent Solids and Density of Salt Solutions.

MATERIAL	WEIGHT PERCENT SOLIDS		DENSITY (g/cm^3)
	Total	Dissolved*	
1AW (neutralized)	40.42%	Not measured	Not measured
GPE	28.83%	Not measured	1.25
HC	38.14%	Not measured	1.35
ETP	34.90%	Not measured	1.29
IW	0.11%	Not measured	1.00
Tank 50	26.12%	25.34%	1.24
HC/50	32.22%	Not measured	1.27
HC 11/04	41.00%	Not measured	Not measured
1AW 11/04	41.64%	Not measured	Not measured
GPE 11/04	35.29%	Not measured	Not measured
NaCl Standard (15%)	15.00%	15.00%	Not measured
*Filtration of neutralized concentrated salt solutions did not provide reproducible results.			

2.2 Saltstone Mixes

Throughout the testing the premix ratios were maintained as shown in Table 2-3. The water to premix ratio was initially set at 0.60 and was adjusted as necessary to achieve acceptable processing properties. Admixtures were introduced as necessary to meet the acceptable processing criteria. Formulation tests were initiated using an iterative strategy of changing water/premix ratios and admixture additions in sequential tests. Mixes that resulted in acceptable processing properties were repeated to prepare samples for compressive strength testing and TCLP. Samples for compressive strength were cast in triplicate in 2-inch by 4-inch cylinders. The cylinders were cured for 27 days. The cured samples were transferred to the Z-Area laboratory for compressive strength testing. Mercury was the only hazardous metal present in quantities sufficient enough to require TCLP analysis for disposal. The crushed samples were screened and submitted to the SRNL-Analytical Development Section (SRNL-ADS) for a modified TCLP analysis.

Table 2-3. Initial Conditions for Processing Properties Formulations.

PREMIX	WEIGHT PERCENT	WATER/PREMIX (W/P)
Cement	10	0.60
Slag	45	
Fly Ash	45	

3.0 RESULTS

3.1 Phase I Processing Formulation

Formulation tests were initiated using an iterative strategy of changing water/premix ratios and admixture additions in sequential tests. Saltstone slurry prepared with H-Canyon blended waste did not perform like slurries made with salt solutions tested previously. The slurry gelled earlier than expected. The quantity of set retarder added to improve the gel time resulted in excessive bleed water. Similar behavior was noted in mixes prepared with the H-Canyon waste/Tank 50 blend.

3.2 Phase II Processing Formulation

Additional Tank 8.4 waste and GPE material were sampled 11/4/04. The H-Canyon blend and the H-Canyon waste/Tank 50 blend were prepared as before. Two antifoams and a water reducing admixture were tested individually and in conjunction with the set retarder. H-Canyon blended waste that contained an addition of antifoam (Dow Corning, Q2 3183A1) and reduced amounts of the set retarder (W.R. Grace, Daratard 17) resulted in a grout slurry that was very thick but did not gel after 20 minutes. After three days no bleed water was detected. However, the sample had not set when tested after six days. Saltstone prepared with H-Canyon waste/Tank 50 blend and similar additions of antifoam and set retarder did not thicken until after 40 minutes. After three days of curing, the sample exhibited no bleed water and was set.

3.3 Compressive Strength

A batch of the H-Canyon waste/Tank 50 blend formulation (with admixtures) was prepared and three 2-in x 4-in cylinders were cast for compressive strength testing. Table 3-1 contains the formulation that met the processing properties and was used to prepare the compressive strength samples. Compressive strength samples were not prepared for the H-Canyon blend formulation because it did not meet the processing requirement of set time. The samples were cured for 27 days and transferred to the Z-Area Laboratory for compression testing. All of the samples had compressive strengths >600 psi and the average of the three replicates was 814 psi. Table 3-2 contains the results of the compression testing for the individual samples.

3.4 TCLP

Two TCLP replicates from the compressive strength samples were submitted to SRNL-ADS for TCLP extraction and analysis for mercury. The 375 mg/L mercury in the unneutralized Tank 8.4 material translates to 36.4 ppm mercury in the Saltstone slurry. SRNL-ADS used a modified TCLP procedure to minimize the amount of radioactive material handled and waste generated (one gram used versus 100 grams in procedure). Analysis of the TCLP leachate by CV-AA for mercury showed a mercury content of <0.11 ppm. Therefore the samples are considered non-hazardous.

[1] "DOW Q2-3183A has demonstrated very good chemical and radiation stability while being most effective as an antifoam agent for both solids stabilized foaming and surfactant based foaming." WSRC-TR-2003-00216, REV. 0

Table 3-1. Formulation Producing Saltstone with Acceptable Processing Properties.

Saltstone Mix Data Sheet

MIX # 0016		**Date:** 11/22/2004	
Material	**%**	**WT%**	**Grams**
Waste Solution: H-Canyon blend/Tk50 **Wt% Solids #** 33.6 **Grams Water** 355.90		48.75	536.00
Admixture: Q2 (8 drops)		0.05	0.59
Admixture: Daratard 17 (24 drops)		0.08	0.90
Admixture:			
Premix		51.11	562.00
Cement (% of Premix)	10	5.11	56.20
Slag (% of Premix)	45	23.00	252.90
Fly Ash (% of Premix)	45	23.00	252.90
Total	100	100	1099.49
Water to Premix Ratio	0.63		

Table 3-2. Compressive Strength Results for H-Canyon Blend/Tank 50H Saltstone Mix.

SAMPLE	SAMPLE AREA (in^2)	LOAD AT FAILURE (lb)	COMPRESSIVE STRENGTH (psi)
HC/Tank 50H-1	3.14	2900	923
HC/Tank 50H-2	3.14	2000	637
HC/Tank 50H-3	3.14	2775	883
Average	3.14	2558	814

4.0 CONCLUSIONS

Salt solutions prepared with a 1:1 ratio of Tank 50H simulant and H-Canyon blended waste produced slurries that met the processing requirements in Table 2 of the TTQAP[1]. Additions of set retarder and antifoam were necessary to meet these processing requirements. The water to premix ratio used to achieve acceptable processing properties was 0.63. Slurries prepared solely with H-Canyon blended waste as the salt solution met the gel time and bleed water requirements, but did not set in the allotted time. Compressive strength samples prepared from the formulation with acceptable processing properties had an average compressive strength of 814 psi. TCLP analysis for mercury of the sample leachate indicated a concentration of mercury in the leachate <0.11 mg/L. The EPA-RCRA treatment limit for mercury is 0.2 mg/L[8]. SRNL recommends that without further testing; Tank 50H be limited to no more than 50 wt% H-Canyon material. It is also recommended that prior to the transfer of Tank 50H to the Saltstone Processing Facility; a sample of the Tank 50H waste be evaluated for processing properties.

5.0 REFERENCES

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5. Environmental Protection Agency Manual SW-846, Procedure 1311.
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7. Bronikowski, M.G. and Gray, J.H., "Decanting of Neutralized H-Canyon Unirradiated Nuclear Material High Activity Waste Streams," WSRC-TR-2004-00123, Rev. 0, (2004).
8. EPA Resource Conservation and Recovery Act, 40 CFR 261.24 Toxicity Characteristic.

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