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## **Analysis of the Salt Feed Tank Core Sample**

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## EXECUTIVE SUMMARY

The Saltstone Production Facility (SPF) immobilizes and disposes of low-level radioactive and hazardous liquid waste (salt solution) remaining from the processing of radioactive material at the Savannah River Site (SRS). Low-level waste (LLW) streams from processes at SRS are stored in Tank 50 until the LLW can be transferred to the SPF for treatment and disposal. The Salt Feed Tank (SFT) at the Saltstone Production Facility (SPF) holds approximately 6500 gallons of low level waste from Tank 50 as well as drain water returned from the Saltstone Disposal Facility (SDF) vaults. Over the past several years, Saltstone Engineering has noted the accumulation of solids in the SFT. The solids are causing issues with pump performance, agitator performance, density/level monitoring, as well as taking up volume in the tank. The tank has been sounded at the same location multiple times to determine the level of the solids. The readings have been 12, 25 and 15 inches. The SFT is 8.5 feet high and 12 feet in diameter, therefore the solids account for approximately 10 % of the tank volume.

Saltstone Engineering has unsuccessfully attempted to obtain scrape samples of the solids for analysis. As a result, Savannah River National Laboratory (SRNL) was tasked with developing a soft core sampler to obtain a sample of the solids and to analyze the core sample to aid in determining a path forward for removing the solids from the SFT.

The source of the material in the SFT is the drain water return system where excess liquid from the Saltstone disposal vaults is pumped back to the SFT for reprocessing. It has been shown that fresh grout from the vault enter the drain water system piping. Once these grout solids return to the SFT, they settle in the tank, set up, and can't be reprocessed, causing buildup in the tank over time. The composition of the material indicates that it is potentially toxic for chromium and mercury and the primary radionuclide is cesium-137. Qualitative measurements show that the material is not cohesive and will break apart with some force.

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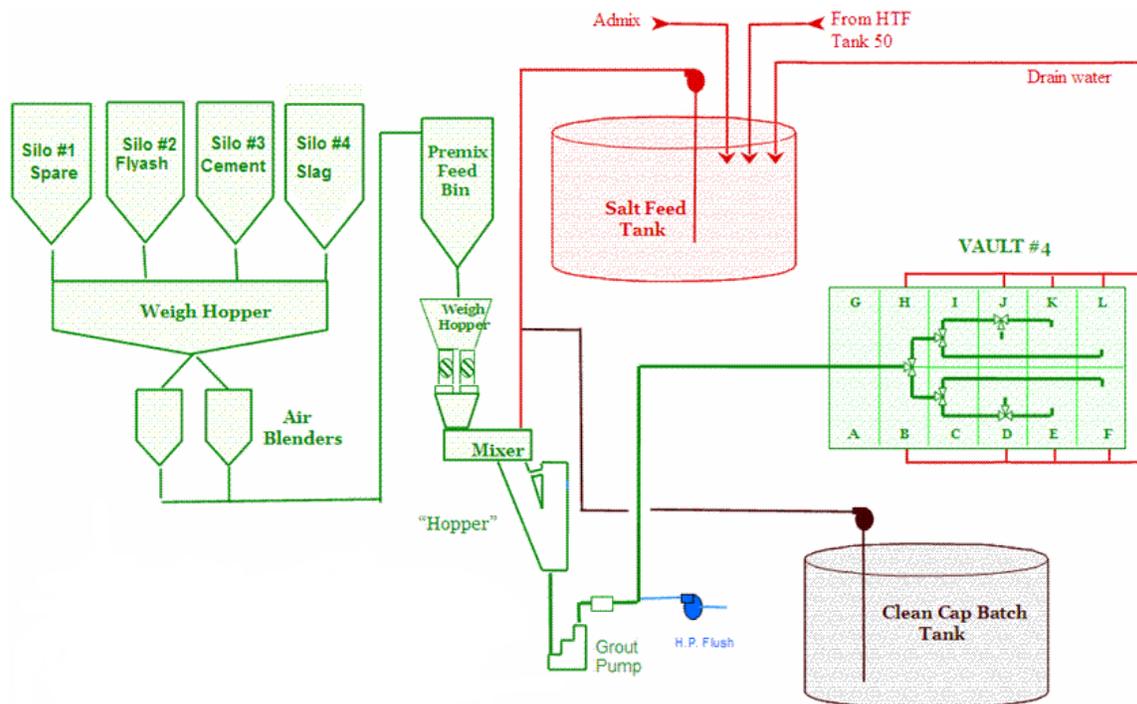
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## LIST OF ABBREVIATIONS

AA	Atomic Absorption
CVAA	Cold Vapor Atomic Absorption
ICP-ES	Inductively Coupled Plasma – (atomic)Emission Spectroscopy
MCL	Maximum Contaminant Level
RCRA	Resource Conservation and Recovery Act
SCS	Soft Core Sampler
SDF	Saltstone Disposal Facility
SFT	Salt Feed Tank
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCLP	Toxic Characteristic Leaching Procedure
UHC	Underlying Hazardous Constituent
UTS	Universal Treatment Standards
XRD	X-ray Diffraction

## 1.0 Introduction

The Saltstone Production Facility (SPF) immobilizes and disposes of low-level radioactive and hazardous liquid waste (salt solution) remaining from the processing of radioactive material at the Savannah River Site (SRS). Low-level waste (LLW) streams from processes at SRS are stored in Tank 50 until the LLW can be transferred to the SPF for treatment and disposal. The Salt Feed Tank (SFT) at the Saltstone Production Facility (SPF) holds approximately 6500 gallons of low level waste from Tank 50 as well as drain water returned from the Saltstone Disposal Facility (SDF) vaults. When the facility is not processing the liquid waste, the SFT serves as a hold tank for the returned drain water as well as any unprocessed material from Tank 50. Figure 1-1 is a simplified diagram of the Saltstone process flow diagram showing all inputs into the SFT.



**Figure 1-1. Simplified Saltstone process flow diagram showing inputs into the SFT.**

Over the past several years, Saltstone Engineering has noted the accumulation of solids in the SFT. The solids are causing issues with pump performance, agitator performance, density/level monitoring, as well as taking up volume in the tank. The tank has been sounded at the same location multiple times to determine the level of the solids. The readings have been 12, 25 and 15 inches.<sup>1</sup> The SFT is 8.5 feet high and 12 feet in diameter, therefore the solids account for approximately 10 % of the tank volume.

Saltstone Engineering has unsuccessfully attempted to obtain scrape samples of the solids for analysis. As a result, Savannah River National Laboratory (SRNL) was tasked with developing a soft core sampler to obtain a sample of the solids and to analyze the core sample to aid in determining a path forward for removing the solids from the SFT.<sup>1</sup>

## 2.0 Experimental Procedure

### 2.1 Soft Core Sampler

Two Soft Core Samplers (SCS) were developed utilizing commercially available soil samplers. A one inch and a two inch diameter SCS were chosen to address the unknown hardness of the heel accumulation in the SFT. The smaller one inch diameter sampler is more suitable for fairly hard material due to its smaller cross sectional area, while the larger two inch diameter sampler is more suitable for less compacted material. Both samplers were modified by: shortening the length of the sampler to obtain a 12 inch core, incorporating retaining baskets to assist in maintaining loose material from falling out of the sampler tip, replacing inner plastic core sleeve with stainless steel sleeve and added flats and holes to assist remote retrieval of sample core.

Due to the anticipated hard nature of the heel material, a weighted driver was developed as the impact mechanism to push the samplers into the heel. The sampler assembly consists of a driver at the top followed by a series of extensions of various available lengths to make up the sampling height and at the very end, the sampler end effector (Figure 2-1). The sampler is deployed by impacting the sampling end effector into the material and once the desired depth is reached, the sampler assembly is pulled out or reverse impacted out if necessary.



**Figure 2-1. Soft core sampler assembly.**

### 2.2 Extraction and Visual Examination

Due to the high dose rate, the sampler was unloaded and opened in the shielded cells. The ends of the sampler were unscrewed to expose the inner stainless steel tube. A plunger was utilized to push the sample out of the inner tube. The sample was visually analyzed to estimate the cohesiveness and consistency of the sample.

### 2.3 Sample Analysis

The elemental composition of the solids was determined by dissolving pieces of the core sample and analyzing the solutions by Inductively Coupled Plasma – (atomic) Emission Spectroscopy (ICP-ES). Triplicate samples of the material were digested by two separate methods: aqua regia digestion and sodium peroxide fusion digestion. A sample of the material digested by aqua regia

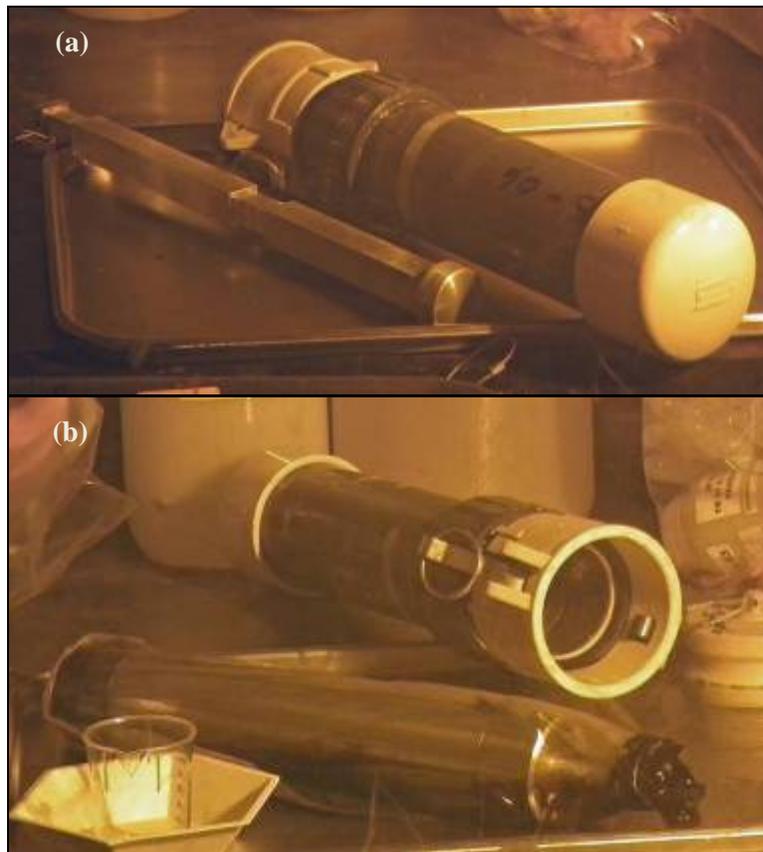
was used to analyze for mercury using cold vapor atomic absorption (CVAA). The requested detection limits and analytical methods support characteristic determination of hazardous waste per South Carolina Department of Health and Environmental Control (SCDHEC) regulations.

In addition, a sample of the material digested by alkali fusion was analyzed by gamma scan to determine the primary radionuclides present in the solids. Duplicate solid samples weighing approximately two grams each were submitted for x-ray diffraction (XRD) analysis to determine the crystalline phases present in the core sample.

### 3.0 Results and Discussion

#### 3.1 Extraction and Visual Examination

The sampler was packaged inside a plastic pipe for secondary containment and additional shielding (Figure 3-1). There was approximately 300 mL of liquid that had to be drained out of the sampler and secondary containment prior to opening the sampler.



**Figure 3-1. SFT core sampler (a) as received with plunger tool and (b) removed from secondary containment.**

The sample was extracted from the SCS by vertically orienting the inner tube of the sampler pushing down with the plunger. Minimal force was needed to remove the sample. The SFT core sample was approximately two and a half inches long and 2 inches in diameter (Figure 3-2). The

dark color is consistent with moist grout. The vertical lines approximately half way down the sample are due to the plastic retaining basket that became embedded in the sample during coring.



**Figure 3-2. Salt feed tank core sample.**

The sample was tapped with a hammer to get a qualitative measurement of the sample's consistency and in order to get samples for analysis. The sample deformed with one hit of the hammer, indicating the material is consolidated but not cemented and would require minimal force to break apart. Figure 3-3 shows the deformed sample. Note that the sample retained its shape because of the retaining basket embedded in the sample.



**Figure 3-3. Salt feed tank core sample after striking it with a hammer for cohesiveness testing.**

A waste is considered to be hazardous when it exhibits one or more of the following characteristics: ignitable, corrosive, reactive, and toxic.<sup>2</sup> The material from the SFT is not ignitable or corrosive since it is a solid material. It is not hazardous based on reactivity because the solids are not unstable or water reactive. However, based on the results discussed in Section 3.2, the sample is potentially characteristically hazardous for chromium and mercury.

### 3.2 Chemical and Radionuclide Analysis

The samples were analyzed by ICP-ES to determine the major elements that make up the solids in the SFT (Table 3-1). The aqua regia digestion did not completely dissolve all of the solids in the sample; therefore the results from this digestion were not used for some of the elements due to known bias of the results. The peroxide fusion method cannot be used to analyze calcium, zirconium, sodium or potassium since the reagents used in the dissolution contain these elements. Where noted, the measured values are the average of triplicates of two digestion methods.

**Table 3-1. Measured elemental concentrations in the SFT sample.**

Element	Result (mg/kg)	Digestion Method	Element	Result (mg/kg)	Digestion Method*
Ag	13.8	AR	Mn	1950.0	AF
Al	34666.7	AF	Mo	25.3	AR
B	41.9	AR	Na	62433.3	AR
Ba	209.8	AR/AF	Ni	189.0	AF
Be	4.2	AR/AF	P	879.7	AF
Ca	50733.3	AR	Pb	67.5	AR
Cd	6.0	AR	S	2193.3	AR
Ce	56.9	AR	Sb	120.0	AR
Co	10.1	AR	Si	54066.7	AF
Cr	353.7	AF	Sn	52.9	AR
Cu	27.5	AR/AF	Sr	219.2	AR/AF
Fe	9446.7	AF	Th	51.7	AR
Gd	53.2	AR	Ti	1141.7	AR/AF
Hg	162.0	AR	U	755.0	AR
K	1731.7	AR/AF	V	22.7	AR
La	15.5	AR	Zn	70.9	AR/AF
Li	35.5	AR	Zr	36.7	AR
Mg	11475.0	AR/AF			

\*AF – alkali fusion, AR- aqua regia

The Resource Conservation and Recovery Act (RCRA) metals and Underlying Hazardous Constituents (UHC's) are listed in Table 3-2 and Table 3-3, respectively. The results are compared to regulatory limits to aid in determining the hazardous nature of the solids in the SFT. A calculated toxic characteristic leaching procedure (TCLP) was performed on the SFT sample by dividing the result listed in Table 3-1 by 20. This in accordance with the Environmental Protection Agency (EPA) TCLP procedure which states: the solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase.<sup>2</sup> Assuming the total concentration of the element can be leached from the monolith; the material in the SFT is potentially characteristically hazardous waste for chromium and mercury (by calculation) and by definition would have to be treated to the Universal Treatment Standards (UTS) for all listed UHC's (Table 3-3). However, since Saltstone is formulated to treat for RCRA metals, an actual

TCLP should be performed on the solids accumulated in the SFT to determine the conservatism of the calculation and if the material is characteristic hazardous waste.

**Table 3-2. RCRA metals in TCLP leachate, calculated based on total concentration, compared to toxicity regulatory limits.**

<b>RCRA Metal</b>	<b>Concentration in Calculated TCLP Leachate (mg/L)</b>	<b>Toxicity<sup>a</sup> Regulatory Limit (mg/L)</b>
As	NM <sup>b</sup>	5.0
Ba	10.5	100.0
Cd	0.3	1.0
Cr	17.7	5.0
Pb	3.4	5.0
Hg	8.1	0.2
Se	NM <sup>b</sup>	51.0
Ag	0.7	5.0

<sup>a</sup> R.61-79.261.24(b) "Characteristic of Toxicity."

<sup>b</sup> Not Measured

**Table 3-3. UHC's in TCLP leachate, calculated based on total concentration, compared to the Universal Treatment Standards.**

<b>RCRA Metal</b>	<b>Concentration in Calculated TCLP Leachate (mg/L)</b>	<b>UTS Nonwastewater Standard (mg/L TCLP)</b>
Sb	6.0	0.07
As	NM	5.0
Ba	10.5	21
Be	0.2	0.02
Cd	0.3	0.2
Cr	17.7	0.85
Pb	3.4	0.75
Hg	8.1	0.20
Ni	9.5	13.6
Se	NM	5.7
Ag	0.7	0.11
Tl	NM	0.20
V	1.1	1.6
Zn	3.5	2.61

NM = Not Measured

A sample of the SFT material digested by the alkali fusion method was submitted for gamma spectroscopy analysis (Table 3-4). Several of the radionuclides were either not detected in the slurry samples or detected at values below the method reporting limit (MRL). For radionuclides not detected or detected below the MRL, the result is preceded by a “<” which indicates the result is an upper limit based on the sensitivity of the method. The results reported are either the average of triplicate samples or the lowest reported MRL of triplicate samples. As shown in Table 3-4, the primary radionuclide in the SFT material is cesium-137.

**Table 3-4. Radionuclide concentration in the SFT core sample.**

Radionuclide	Concentration (pCi/g)	Radionuclide	Concentration (pCi/g)
Cs-137	6.89E+06	Eu-155	< 3.12E+06
Na-22	< 8.60E+05	Ra-226	< 2.44E+07
Al-26	< 8.11E+05	Am-241	< 3.77E+06
Co-60	< 1.19E+06	K-40	< 2.26E+07
Nb-94	< 9.32E+05	Ag-108m	< 1.16E+06
Ru-106	< 7.57E+06	Ba-133	< 1.77E+06
Sb-125	< 3.92E+06	Bi-207	< 1.17E+06
Sb-126	< 1.22E+06	Ac-227	< 5.72E+06
Sn-126	< 2.79E+06	Ra-228	< 5.27E+06
Ce-144	< 6.98E+06	Th-228	< 2.97E+07
Eu-152	< 2.59E+06	Pa-231	< 4.26E+07
Eu-154	< 1.81E+06		

### 3.3 X-ray Diffraction

The crystalline phases identified in Figure 3-4 are typical of cured Saltstone grout. The quartz (SiO<sub>2</sub>) and gypsum (CaSiO<sub>4</sub>·H<sub>2</sub>O) are phases that are associated with hydrated fly ash and cement. The nitratine and oxalate are crystalline salt phases precipitated from the Tank 50 salt solution. Magnesium hydrotalcite, identified as magnesium aluminum hydroxide in Figure 3-4, is the second most common phase found in alkali-activated hydrated slag and cement mixtures.<sup>3</sup> Although the XRD pattern is better crystallized than other Saltstone grout patterns,<sup>4</sup> Figure 3-4 is indicative of Saltstone that has been aged and cured under excess liquid. The other phases identified in Figure 3-4 are typical phases associated with cement, slag and fly ash reacted with salt solution. The amorphous broad peak that ends at 10° two-theta is due to glassy phases of fly ash in the premix.

Based on the results of this analysis and previous studies, the source of the material in the SFT is the drain water return system where excess liquid from the Saltstone disposal vaults is pumped back to the SFT for reprocessing. It has been shown that fresh grout passes through the sheet drain material in the vault and enters the drain water system piping.<sup>4,5</sup> These solids are returned to the SFT, settle in the tank, set up, can't be reprocessed, and buildup in the tank over time.

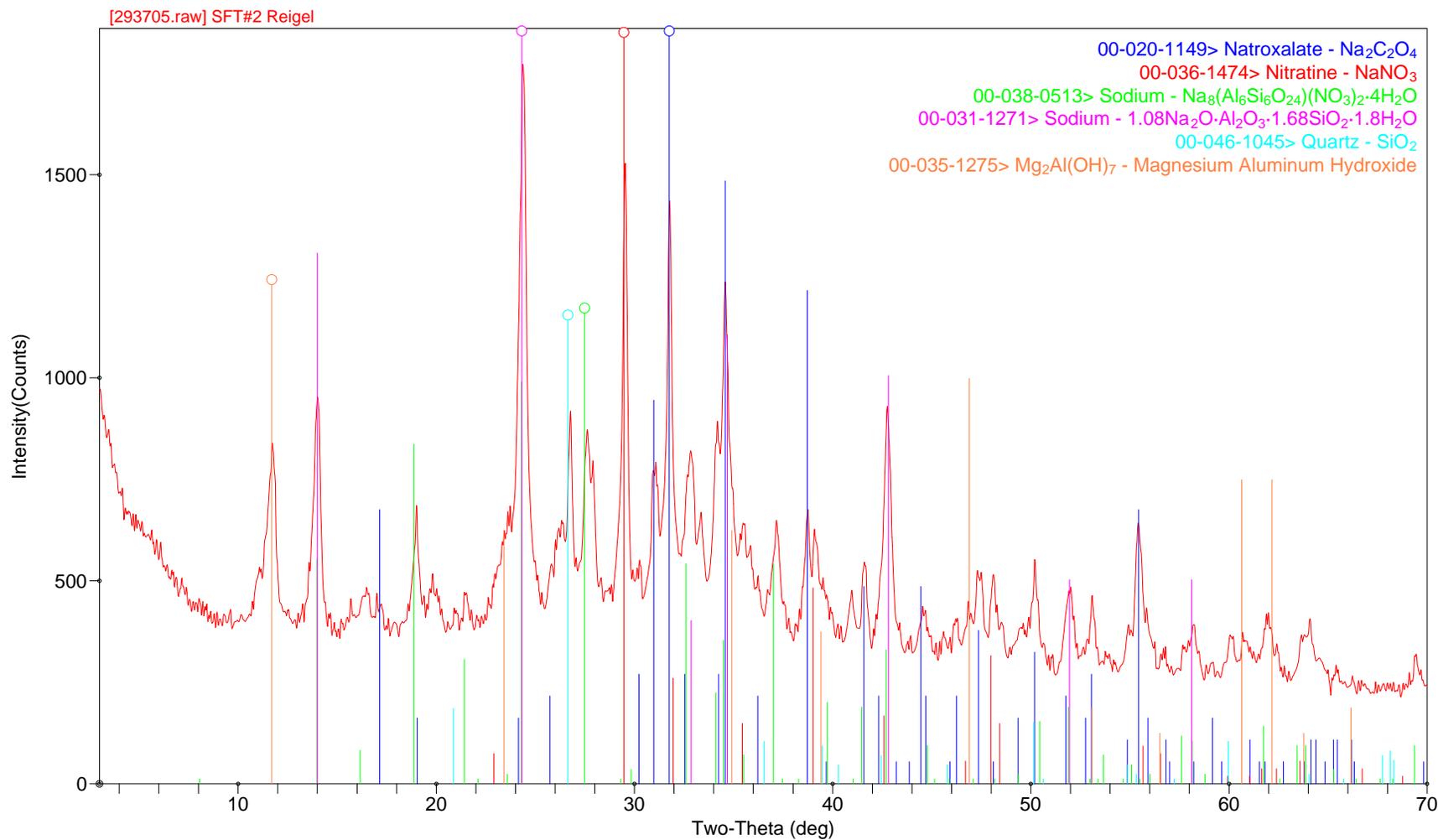


Figure 3-4. X-ray diffraction pattern for the SFT core sample.

#### **4.0 Conclusions**

The source of the material in the SFT is the drain water return system where excess liquid from the Saltstone disposal vaults is pumped back to the SFT for reprocessing. It has been shown that fresh grout from the vault enter the drain water system piping.<sup>4,5</sup> Once these grout solids return to the SFT, they settle in the tank, set up, and can't be reprocessed, causing buildup in the tank over time. The material in the SFT is potentially characteristically hazardous waste for chromium and mercury (by calculation) and by definition would have to be treated to the Universal Treatment Standards (UTS) for all listed UHC's applicable to Saltstone. However, since Saltstone is formulated to treat for RCRA metals, an actual TCLP should be performed on the solids accumulated in the SFT to determine the conservatism of the calculation. The primary radionuclide is cesium-137. Qualitative measurements show that the material is compacted but not cohesive or cemented and will break apart with some force.

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