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# CHARACTERIZATION OF HAZARDOUS CONSTITUENTS IN HLW SUPERNATE AND IMPLICATIONS FOR SOLID LLW GENERATION

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## Introduction

High level waste (HLW) generated during separations processing in the F- and H-Canyons is transferred to the F- and H-Area Tank Farms for storage in underground storage tanks. The waste is an aqueous solution containing dissolved sodium salts and insoluble metal oxides/hydroxides. The waste solution is evaporated to reduce the volume, and the resulting sludge, salt, and supernate are stored for eventual processing and final disposal. Currently, there are 46 HLW tanks in the F- and H-Area Tank Farms which are used for storage of free supernate liquid containing inventories of radionuclides and hazardous chemicals (Table 1). Of these tanks, Tanks 48 and 50 contain Sodium Tetraphenylborate (NaTPB) that resulted from the In-Tank Precipitation Process and, because benzene is the hazardous constituent that drives hazardous waste determinations for waste contaminated with NaTPB, these two tanks are managed differently from the other tanks containing supernate (Reference 1).

Over the approximate 50-year history of the F- and H-Area Tank Farms, routine supernate sampling has been conducted in support of the primary goal of safe storage of HLW. Special samples have also been collected to support the corrosion prevention program and the development of the Defense Waste Processing Facility and associated other facilities. Because of the costs (in dollars and personnel exposure) involved in the collection, preparation, and detailed analysis of samples, the extent of the sampling and analysis has been limited. Detailed component concentrations have been estimated using process knowledge complemented with the limited analytical data. The Waste Characterization System (WCS; Reference 2) has been developed to provide a database for this HLW information that is routinely updated based on current process knowledge and analytical data.

As a result of routine and non-routine activities that are part of managing HLW, secondary solid waste is generated. Job control waste items such as protective clothing, plastic for contamination prevention, contaminated tools, etc. are routinely collected as part of ongoing waste management activities and are containerized for disposal. Infrequent and non-routine activities also generate quantities of solid waste, e.g., contaminated equipment, contaminated soil, etc., that are containerized for disposal. Radioactive contamination of more than 90% of the solid waste generated is due to contamination from HLW supernate or salt. In order to comply with the waste acceptance criteria (WAC) for disposition of solid waste in Savannah River Site (SRS) treatment, storage, and disposal (TSD) facilities, the quantity of radionuclides and hazardous chemicals must be determined for each waste container and a declaration made as to the hazardous characteristics of the waste. However, routine smearing and analysis to characterize the radionuclide and chemical components is not practicable for solid waste due to ALARA (as low as reasonably achievable) concerns. Waste that has been contaminated with enough supernate for a smear to be definitive typically has too high a dose rate to allow collection of the smear, whereas waste that can be smeared without dose concerns is not contaminated with enough waste to allow detection of most

radiological components. Thus, this forces a reliance on analytical data from supernate samples to characterize the contamination.

To provide information needed to characterize and manifest supernate-contaminated solid waste for dispositioning to SRS TSD facilities, process knowledge in combination with the analytical data is used. The WCS houses the required information. This document revision provides an update to the previous characterization completed in 1994 (Reference 3) of hazardous components in the HLW supernate currently contained in the F- and H-Area Tank Farms. The update uses the data contained in the WCS 1.5 data base (Reference 4).

### **Supernate Hazardous Evaluation**

SRS high level waste tank supernate was evaluated for hazardous constituents in 1994 (Reference 3). Based on the supernate hazardous evaluation, mercury (Hg) was determined to be the hazardous constituent in supernate that drives whether resultant supernate-contaminated waste is hazardous or non-hazardous. A scaling factor of mercury concentration to cesium-137 (Cs-137) activity was determined from the analytical data evaluated in Reference 3, which has been used routinely for waste package characterization and hazardous determination (Reference 5).

This document's revision reevaluates the status of hazardous constituents in SRS high level waste tanks including verification of whether Hg remains the constituent that drives hazardous determinations and also determines scaling factors based on current tank contents data in WCS 1.5 (Reference 4).

Data on the chemical inventories (kg) of supernate hazardous constituents silver, arsenic, barium, cadmium, chromium, mercury, lead, and selenium, and radionuclide inventories (Ci) of Cs-137 were taken from WCS 1.5 (Reference 4). Actual analytical data for selenium are available for only nine of the 46 tanks (Tanks 25-30, 32, 38, and 43), with the selenium results limited to the "minimum detection limit" values (Reference 6). Concentrations of these hazardous and radionuclide constituents were calculated for each tank using total supernate volume data in WCS 1.5 (Reference 4). The tank supernate volumes, hazardous chemical concentrations, and Cs-137 activities for each tank are presented in Table 1.

Relative concentrations of the hazardous constituents compared to their respective Resource Conservation and Recovery Act (RCRA; 40 CFR 261) toxicity characteristic, hazardous waste concentration limits are in Table 1. Based on the average and maximum hazardous constituent concentrations in the supernate tanks, Hg is the driver for the hazardous waste determination for supernate-contaminated waste resulting from routine and non-routine HLW tank management activities.

Table 2 calculates for each supernate tank the maximum curies (Ci) of Cs-137 allowed to meet RCRA hazardous waste limits for mercury at various waste weights. The Cs-137 limits reflect Hg-to-Cs-137 ratios determined for each tank based on WCS 1.5 data contained in Table 1. The RCRA hazardous waste limit is based on the Toxicity Characteristic Leaching Procedure (TCLP; Reference 7) and is listed in Table 1. The maximum values for each tank are derived as follows:

$$\text{Cs-137 activity}_{\text{TCLP, Hg}} = 0.2 \text{ mg Hg/L} * (2,000 \text{ mL}/100 \text{ g}) (1\text{L}/1,000 \text{ mL}) * (W/R_{\text{Hg/Cs-137}}) * 454 \text{ g/lb}$$

where:

- Cs-137 activity<sub>TCLP, Hg</sub> = Cs-137 activity in Ci to reach the mercury hazardous threshold concentration of 0.2 mg/L in the TCLP
- 2,000 mL = volume of extraction fluid in a TCLP
- 100 g = waste sample weight for mercury in a TCLP
- W = weight in pounds of solid waste contaminated with tank supernate
- R<sub>Hg/Cs-137</sub> = mg Hg / Ci Cs-137 scaling factor ratio

which results in the following *working formula* using waste weight and the Hg/Cs-137 scaling factor for the tank to determine the Cs-137 activity in Ci to reach the hazardous threshold if mercury is the driver:

$$\text{Cs-137 activity}_{\text{TCLP, Hg}} = 0.2 \text{ mg Hg/L} * (2,000 \text{ mL}/100 \text{ g}) (1 \text{ L}/1,000 \text{ mL}) * (W/R_{\text{Hg/Cs-137}}) * 454 \text{ g/lb}$$

$$\text{Cs-137 activity}_{\text{TCLP, Hg}} = 1.82 * (W) / (R_{\text{Hg/Cs-137}})$$

where:

- W = weight in pounds of solid waste contaminated with tank supernate
- R<sub>Hg/Cs-137</sub> = mg Hg / Ci Cs-137 scaling factor ratio

## Conclusions

This document's revision concludes that (1) mercury continues to be the driver for the hazardous waste determination for supernate-contaminated waste resulting from routine and non-routine HLW tank management activities, (2) for all but 11 of the 46 HLW tanks in the F- and H-Area Tank Farms presently containing supernate, SW 21 Manual, Procedure HLW-006, Waste Package Curie Determination, Attachment 2, Hazardous Limit Table (Reference 5) remains conservative at 58 mCi Cs-137 per 100 lb of waste, and (3) for the 11 HLW supernate tanks for which Reference 5 is not conservative (i.e., Tanks 6, 7, 18, 19, 21-24, 40, 48 and 50), a data table and working formula to determine "Maximum Curies of Cs-137 Allowed to Meet Hazardous Waste Limits at Various Waste Weights" are provided (Table 2).

## Practical Considerations

In practice, determination of the maximum allowable Cs-137 activity level at a specific waste weight may be made using Table 2 as an "average" for the following reasons:

- Waste is not segregated by tank
- The 11 listed tanks have a smaller waste volume generated than the other 35 tanks and their Low Activity Waste (LAW) (<2.5 mrem/hr) is not hazardous
- Hg is limiting for Tank 50 when not slurried and LAW is not hazardous
- Tank 48 LAW is not hazardous for benzene
- Large equipment which has the potential to trip hazardous limits is evaluated on a case-by-case basis per characterization request from the Generator Certification Official (GCO)

When using either approach, some practical considerations apply; e.g.:

- When the waste contains contamination from more than one tank, the tank with the highest Hg/Cs-137 ratio may be conservatively used for all the contaminated waste weight or the contamination may be apportioned to fractions of the waste weight according to best professional judgment.
- When using Table 2 and the actual waste weight falls within the tabulated weight categories (e.g., waste weight = 867 lb and the tabulated weight categories are 750 lb and 1000 lb), it is recommended to conservatively use the next lowest tabulated value that does not exceed the actual waste weight. When using the Working Formula, the actual waste weight may be used in the calculation.

## Periodic Validation

Provisions of Procedure WAC 2.02, Revision 7 (Reference 7), require generators of routine wastes to review and confirm the certification of each waste stream periodically. The certification of the radionuclide status of supernate waste stream, FHW-00001 is on a five-year schedule. It is recommended that the revalidation of the hazardous status of the individual supernate tanks be accomplished as part of the revalidation efforts for waste stream FHW-00001 and become incorporated in that documentation.

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**Table 1**

**Comparison of Hazardous Constituent Concentrations in HLW Supernate  
Tanks vs. RCRA Toxicity Characteristic Regulatory Limits.**



Table 1. Comparison of Hazardous Constituent Concentrations in HLW Supernate Tanks vs. RCRA Toxicity Characteristic Regulatory Limits.

A	Tank/Data B	Ag (kg)	Ag (mg/l)	As (kg)	As (mg/l)	Ba (kg)	Ba (mg/l)	Cd (kg)	Cd (mg/l)	Cr (kg)	Cr (mg/l)	Hg (kg)	Hg (mg/l)	Pb (kg)	Pb (mg/l)	Sa (kg)	Se (mg/l)	Co-137 (Ci)	Co-137 (Ci)
		Suprinv	Supernate Conc.	Suprinv	Supernate Conc.	Suprinv	Supernate Conc.	Suprinv	Supernate Conc.	Suprinv	Supernate Conc.	Suprinv	Supernate Conc.	Suprinv	Supernate Conc.	Suprinv	Supernate Conc.	Suprinv	Supernate Conc.
		C	D=(C*1E6)/(B*3.785)	E	F=(E*1E6)/(B*3.785)	G	H=(G*1E6)/(B*3.785)	I	J=(I*1E6)/(B*3.785)	K	L=(K*1E6)/(B*3.785)	M	N=(M*1E6)/(B*3.785)	O	P=(O*1E6)/(B*3.785)	Q	R	S	T=S/
	Total Supernate Volume																R*only sample values available and are min. det. limit values		(B*3.785)
1	129,489	1.47E+00	3.00E+00	1.53E+02	3.13E+02			7.18E+00	1.46E+01	2.04E+02	4.16E+02	1.47E+01	3.00E+01					2.57E+06	5.24E+00
2	121,045	1.83E-02	4.00E-02	1.18E+02	2.54E+02			5.14E+00	1.12E+01	9.53E+01	2.08E+02	9.16E+00	2.00E+01					8.90E+05	1.94E+00
3	121,316	1.84E-02	4.00E-02	1.45E+02	3.16E+02			8.80E+00	1.48E+01	9.55E+01	2.08E+02	9.18E+00	2.00E+01					8.92E+05	1.94E+00
4	418,812	2.89E-01	1.82E-01	1.93E+02	1.22E+02			5.64E+00	3.56E+00	7.42E+02	4.68E+02	1.90E+01	1.20E+01					3.68E+06	2.32E+00
5	48,317	1.83E-02	1.00E-01	2.36E+01	1.29E+02			7.27E-01	3.98E+00	6.66E+01	3.64E+02	1.10E+01	6.00E+01					8.71E+04	4.76E-01
6	291,975	4.42E-02	4.00E-02	7.80E+01	6.87E+01			5.48E-01	4.96E-01	3.45E+02	3.12E+02	3.54E+02	3.20E+02					1.08E+04	9.82E-03
7	43,831	3.01E-02	1.82E-01	9.97E+00	6.04E+01			1.71E-03	1.03E-02	1.04E+02	6.30E+02	1.90E+01	1.15E+02					1.08E+05	9.48E-02
8	300,068	4.54E-02	4.00E-02	1.02E+02	8.97E+01			1.94E+00	1.71E+00	4.13E+02	3.64E+02	4.54E+01	4.00E+02					9.11E+05	1.90E+00
9	128,394	1.44E-01	3.00E-01	7.62E+01	1.59E+02			2.75E+00	5.74E+00	7.46E+01	1.56E+02	6.22E+01	1.30E+02					6.09E+04	3.32E-01
10	48,401	3.66E-02	2.00E-01	1.40E+01	7.83E+01			1.71E-01	9.33E-01	1.91E+01	1.04E+02	5.13E+01	2.80E+02					3.08E+05	3.45E-01
11	235,960	1.63E-01	1.82E-01	9.96E+01	1.11E+02			2.66E+00	2.97E+00	2.32E+02	2.80E+02	2.14E+02	2.40E+02					1.03E+07	3.48E+00
13	788,920	8.96E-01	3.00E-01	7.93E+02	2.66E+02			3.56E+01	1.19E+01	1.55E+02	5.20E+01	3.58E+02	1.20E+02					8.89E+05	4.41E+00
14	53,220	8.06E-01	4.00E+00	3.38E+01	1.68E+02			1.25E+00	6.23E+00	3.14E+01	1.56E+02	2.22E+01	1.10E+02					3.43E+03	5.05E-03
18	179,319	1.24E-01	1.82E-01	3.95E+01	5.81E+01			1.73E-02	9.82E-01	1.09E+01	6.20E+02	2.05E+00	1.16E+02					8.91E+01	5.05E-03
19	4,861	3.21E-03	1.82E-01	1.36E+00	7.71E+01			8.45E-01	2.53E-01	3.47E+02	1.04E+02	2.00E+02	6.00E+01					5.74E+03	1.72E-03
21	891,862	6.08E-01	1.82E-01	2.15E+02	6.46E+01			4.83E+00	1.13E+00	2.65E+03	8.19E+02	4.99E+02	1.18E+02					2.76E+03	6.43E-04
22	1,132,518	7.80E-01	1.82E-01	3.41E+02	7.96E+01			0.00E+00	0.00E+00	3.08E+03	8.32E+02	5.61E+02	1.18E+02					5.01E+02	1.03E-04
23	1,225,398	8.87E-01	1.82E-01	2.78E+02	5.67E+01			1.85E+00	3.99E-01	2.41E+02	5.20E+01	5.57E+02	1.20E+02					9.65E+03	2.08E-03
25	429,233	1.48E-01	9.00E-02	1.79E+01	1.10E+01	3.25E-02	2.00E-02	7.31E-01	4.50E-01	7.47E+01	4.60E+01	1.62E+01	1.00E+01	4.71E+01	2.90E+01		8.20E+01	1.52E+06	9.33E-01
26	1,105,590	4.77E+00	1.14E+00	6.98E+01	1.40E+01	1.63E+00	3.90E-01	1.63E+00	7.50E-01	9.63E+01	2.30E+01	5.10E+02	1.22E+02	1.46E+02	3.50E+01		8.60E+01	3.27E+06	7.82E-01
27	920,308	1.85E+00	5.30E-01	3.48E+01	1.00E+01	6.97E-01	2.00E-01	1.50E+00	4.30E-01	9.75E+01	2.80E+01	3.48E+01	1.00E+01	8.36E+01	2.40E+01		6.30E+01	3.75E+06	1.08E+00
28	418,811	6.18E-01	3.90E-01	2.06E+01	1.30E+01	2.38E-01	1.50E-01	9.04E-01	5.70E-01	1.47E+02	9.30E+01	1.59E+01	1.00E+01	5.23E+01	3.30E+01		1.09E+02	1.87E+06	1.18E+00
29	294,419	2.34E-01	2.10E-01	2.12E+01	1.90E+01	1.56E+00	1.40E+00	8.36E-01	7.50E-01	4.54E+02	4.07E+02	2.23E+01	2.00E+01	5.68E+01	5.10E+01		2.35E+02	5.25E+05	4.71E-01
30	981,522	7.43E-01	2.00E-01	4.48E+01	1.20E+01	1.49E-01	4.00E-02	3.72E-01	1.00E-01	6.58E-02	1.77E+02	7.43E+01	2.00E+01	7.43E+01	2.00E+01		1.16E+02	1.69E+07	4.54E+00
31	499,977	3.24E-01	1.82E-01	4.00E+02	2.25E+02			1.70E+01	9.53E+00	9.56E-02	5.37E+02	2.21E+02	1.24E+02					5.34E+06	3.00E+00
32	910,389	6.89E-01	2.00E-01	3.45E+01	1.00E+01	1.38E-01	4.00E-02	3.45E-01	1.00E-01	4.03E-02	1.17E+02	3.45E+01	1.00E+01	6.55E+01	1.90E+01		8.70E+01	1.50E+06	4.36E-01
33	543,573	3.74E-01	1.82E-01	1.90E+02	9.23E+01			3.83E+00	1.86E+00	1.28E+03	6.12E+02	2.41E+02	1.17E+02					1.53E+05	7.54E-02
34	1,084,527	7.47E-01	1.82E-01	1.03E+03	2.51E+02			4.54E+01	1.11E+01	2.14E+03	5.23E+02	5.16E+02	1.29E+02					4.30E+06	1.05E+00
35	1,080,838	7.52E-01	1.82E-01	8.22E+02	1.99E+02			3.32E+01	8.04E+00	2.28E+03	5.52E+02	5.08E+02	1.23E+02					8.44E+06	2.04E+00
36	451,456	3.11E-01	1.82E-01	5.46E+02	3.20E+02			2.57E-01	1.50E+01	8.27E+02	4.84E+02	2.21E+02	1.30E+02					9.44E+06	5.52E+00
37	500,799	3.45E-01	1.82E-01	1.56E+02	8.21E+01			2.40E+00	1.27E+00	1.17E+03	6.18E+02	2.21E+02	1.16E+02					5.19E+05	2.74E-01
38	439,241	3.82E-01	2.30E-01	2.18E+01	1.30E+01	8.31E-02	5.00E-02	6.85E-01	4.00E-01	8.46E+02	5.09E+02	1.66E+01	1.00E+01	4.99E+01	3.00E+01		2.25E+02	5.00E+05	3.00E-01
39	855,212	5.89E-01	1.82E-01	4.02E+02	1.24E+02			1.20E+01	3.70E+00	1.92E+03	5.94E+02	3.85E+02	1.19E+02					3.07E+06	9.48E-01
40	353,106	2.43E-01	1.82E-01	7.51E+01	5.62E+01			4.68E+00	4.59E+00	5.99E+02	5.85E+02	1.22E+02	1.20E+02					1.44E+04	1.08E-02
41	268,957	1.65E-01	1.82E-01	1.42E+02	1.39E+02			2.99E+01	6.20E+00	2.72E+03	5.70E+02	5.79E+02	1.21E+02					4.20E+05	4.12E-01
42	1,262,640	8.70E-01	1.82E-01	7.99E+02	1.67E+02			2.99E+01	6.20E+00	2.72E+03	5.70E+02	5.79E+02	1.21E+02					1.21E+06	2.54E-01
43	1,176,447	8.91E-01	2.00E-01	4.45E+01	1.00E+01	1.78E-01	4.00E-02	1.07E+00	2.40E-01	1.92E+03	4.31E+02	2.44E+02	5.49E+01	1.16E+02	2.80E+01		2.00E+02	6.59E+05	1.48E-01
44	489,200	3.43E-01	1.82E-01	7.45E+02	3.95E+02			3.88E+01	1.84E+01	8.32E+02	4.41E+02	2.52E+02	1.34E+02					2.64E+06	1.40E+00
45	416,873	2.87E-01	1.82E-01	6.70E+02	4.24E+02			3.33E+01	2.11E+01	6.70E+02	4.25E+02	2.14E+02	1.35E+02					2.09E+06	1.32E+00
46	520,628	3.59E-01	1.82E-01	5.31E+02	2.89E+02			2.39E+01	1.21E+01	1.01E+03	5.12E+02	2.50E+02	1.27E+02					3.49E+06	1.77E+00
47	367,653	2.53E-01	1.82E-01	1.78E+02	1.28E+02			5.47E+00	3.93E+00	8.24E+02	5.82E+02	1.68E+02	1.19E+02					5.97E+05	4.29E-01
48	231,309	1.59E-01	1.82E-01	7.36E+01	8.41E+01			1.21E+00	1.39E+00	5.40E+02	6.17E+02	1.02E+02	1.17E+02					1.59E+04	1.81E-02
49	850,473	5.86E-01	1.82E-01	8.24E+02	2.56E+02			3.65E+01	1.13E+01	1.67E+03	5.20E+02	4.06E+02	1.26E+02					8.93E+06	2.74E+00
50	87,399	6.02E-02	1.82E-01	2.57E+01	7.77E+01			3.38E-01	1.01E+00	2.05E+02	6.20E+02	3.85E+01	1.16E+02					4.49E+00	1.36E-05
51	922,498	6.36E-01	1.82E-01	2.32E+02	6.65E+01			1.29E+00	3.68E-01	2.19E+03	6.26E+02	4.04E+02	1.16E+02					2.44E+05	6.98E-02
	Mean (mg/l)		0.4		131			0.3		5.0	390		98		30		133		1.17E+00
	Max (mg/l)		4.0		424			1.4		21	632		320		51		235		5.52E+00
	Min (Ci/l)																		1.38E-05
	RCRA Limit (mg/l)		5.0		5.0		100.0		1.0		5.0		0.2		5.0		1.0		
	Ratio of Mean Tank Value / Reg. Limit		0.07		26.1		0.003		5.0		77.9		490.5		5.9		133.3		
	Ratio of Max Tank Value / Reg. Limit		0.8		85		0.01		21		126		1600		10		235		

Source of Data: WCS 1.5, Reference 3.

**Table 2**

**Maximum Curies of Cesium-137 Allowed to Meet  
Hazardous Waste Limits at Various Waste Weights.**

