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SAVANNAH RIVER SITE

HIGH LEVEL WASTE SALT DISPOSITION SYSTEMS ENGINEERING TEAM

POSITION PAPER

ON

SLUDGE BATCH 2 QUALIFICATION STRATEGY AND SIMULANT COMPOSITION

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Sludge Batch 2 Sample Testing and Qualification Strategy

Summary

In early calendar year 2001 DWPF will begin processing sludge batch 2. Prior to receiving this sludge, the batch will be qualified by testing with non-radioactive simulants and process simulation with the actual waste. This report targets the sludge compositions used for glass testing (the "Variability Study"), cold process simulation and makes recommendations as to sampling and qualification strategy.

The overall strategy is to base the variability study and non-radioactive processing compositions on the information in the HLW Database [1]. These sludge compositions for input into the variability study are in Tables G1 and G2, below.

The recipes for making Tank 40, Blend and Tank 8 sludge simulants are given below in tables S1, S2 and S3, respectively. These recipes do not add soluble sodium salts as stand-ins for insoluble sodium compounds in the sludge. Recipes with insoluble sodium stand-ins added are in tables SI1 (Tank 40), SI2 (Blend) and SI3 (Tank8).

Process Engineering recommends that an early, exploratory sample be taken in Tank 8, when it is slurried to make it representative of the tank contents, but prior to transfer.

Data Sources and Assumptions

The compositions shown below were taken from the High Level Waste Database [1]. This database has been critically reviewed against canyon production data and the relatively scarce sludge sample data. Its structure and assumptions are based on sound chemistry. It is the best single source of information available. Other input includes supernate chemistry samples and a single (non-representative) sample from tank 8. SRTC provided data useful for estimating noble metal concentrations [2, 3].

The compositions derived in this report were compared with samples taken from streams with similar histories. The waste source history was reviewed. Because of the good agreement with comparison data and the general soundness of the HLW Database and the fact that the waste sources for Batch 2 are uncomplicated; little technical risk is added by using this information.

However, the extent of sludge washing is somewhat uncertain. This impacts the sodium concentration and - to a lesser extent - the aluminum concentration in the glass testing and the ion balance in the supernate used for cold simulant testing. These uncertainties were accounted for in ranges of compositions provided for the glass. The supernate ion balance assumed less washing than is planned, and this assumption is conservative with respect to gas generation rates and ease of processing.

Tank 8 is to be blended into the Tank 40 sludge for Batch 2. It is possible that essentially all of the tank 8 may be transferred or none of it. These extremes were assumed. The only substantial impact of extent of transfer is the uranium concentration.

Tank 8 has received no material from inter-tank transfer. This simplifies estimation of the contents considerably. It received PUREX low heat waste from 6/56 through 7/59 and PUREX high heat waste from 4/60 until 6/74, then low heat waste from 10/77 until 12/80. The uranium, aluminum and iron concentrations were quite variable between the waste types and even between transfers. Therefore the single archived sample should not be expected to be representative of the entire sludge batch, so the HLW database was used to estimate concentrations.

Tank 40 has received no fresh waste from Separations. Sludges from tanks 22 and 18 were transferred into tank 40. Tank 22 was a low heat waste receiver for HM from 7/74 until 10/80; in addition one THOREX transfer thrown was received. Tank 18 was a PUREX low heat waste receiver 8/59 through 3/77. It received PUREX low heat waste from Tank 17 from 12/83 until 6/85. So, quite like Sludge Batch 1A, it is a combination of PUREX and HM waste. Batch 1A had PUREX low heat waste from Tank 18 and HM low heat waste from Tank 22, like Tank 40. It also received a large quantity of sludge from Tank 21, another HM low heat receiver. A negligible quantity of HM high heat waste was also transferred to Tank 21 from Tank 16. So composition data from Batch 1A (Tank 51) are good reference points for Tank 40 composition. This comparison is made in Table 1.

These compositions are quite similar, and the relatively small differences are because Batch 2 will have a considerably higher uranium concentration. Further, the comparison between the Batch 1A composition analyses (Tank 51 average and Batch 1A SRAT data) and Tank 40 is quite close and lends credibility to the estimates from the Database. Tank 40 projected values would be even closer, if the same level of sodium removal – that is level of washing – is assumed. If a sodium oxide concentration of 14 wt % is assumed then the other re-normalized oxides concentrations are 16.1 % Al, 50.4 % Fe and 4.2 % U. The blended Batch 2 values are shown for comparison and are notable only in the lower iron concentration and the high uranium. The total oxide values show that accounting for the four oxides shown account for most of the sludge oxides that will appear in the glass.

Table 1 – Comparison of Confirmed Sludge Metal Concentration to Estimates[1]

	Batch 1A Sludge		Batch 1A SRAT		Tank 40 Projected		Batch 2 Projected	
	Elemental	Oxide	Elemental	Oxide	Elemental	Oxide	Elemental	Oxide
Metal	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
Al	8.7	16.1	9.1	17.2	8.1	15.3	8.6	16.2
Fe	33.3	46.9	34.5	49.3	33.4	47.8	29.1	41.6
Na	11.8	15.7	10.5	14.2	13.1	17.7	13.4	18.0
U	4.6	5.4	3.9	4.6	3.4	4.0	8.6	10.2
Total		84.1		85.3		84.8		86.0

Variability Study Glass Composition

Glass composition estimates, varying the sludge washing and quantity of Tank 8 sludge blended (0% to entire contents of Tank 8), were made. Using these estimates of the washed sludge composition, estimates of the glass composition were made from low sludge loading (minimum homogeneity) to high loading (maximum allowable liquidus temperature). Two compositions, representing the extremes of uranium concentration, are shown in Table 2. The actual compositions used in testing will be varied to allow for uncertainties in the data and variation in the frit and sludge loading and frit composition. SRTC statisticians will use the sludge composition provided in Tables G1 and G2 and apply their usual methodology to develop glass compositions.

SRTC Hot Testing

Tank 40 will be sampled, after the material from Tank 8 has been blended. This sample will be used for analytical characterization and real waste testing. It will be washed in a manner that tracks the planned washing in the actual tank. It will be process through the SRAT and SME cycles. It will be melted in crucibles and the glass will be characterized (composition, PCT and so forth).

Use of the Tank 8 Sample

A sample will be pulled from Tank 8 as soon as it can be slurried and blended. The results from analyzing and testing this sample will NOT delay the transfer of this material to Tank 40. However, the results will be used to verify the compositions used for cold testing and give some earlier indication of potential issues with this material.

[1] Values in this table are normalized to wt. % on a calcine basis, using the same oxides that the Product Composition Control System uses. The starting values for Batch 1A Sludge are from [4], the starting values for Batch 1A SRAT are from DWPF Sample Data (archived on the Chem Group Server, Sample Data-Folder). Estimates for Tanks 40 and Blend are from the High Level Waste Database [1].

This sludge has been allowed to dry in the presence of supernate containing soluble $NaAlO_2$. This material may re-dissolve readily in the wash water, or may have been modified to other crystalline forms of Al, such as gibbsite ($Al_2O_3{\bullet}3H_2O$) or Boehmite ($Al_2O_3{\bullet}H_2O$). These are less soluble and require heat and high caustic concentration to dissolve. Understanding this is not particularly important for processing the Tank 40 / Tank 8 blend, because the overall aluminum concentration is not too great. However, understanding the phenomenon is important to subsequent waste processing.

After adding water to the sludge, the Tank 8 supernate will be analyzed and this result will give some indication as to how readily the $NaAlO_2$ re-dissolved. Xray diffraction analysis will indicate the ratio of gibbsite to boehmite. The sample could then be treated with warm caustic to simulate in-tank aluminum dissolution. Analysis of the residual sludge and the supernate will quantify the form and fate of the aluminum further.

The Tank 8 sample will also verify the compositions used in the non-radioactive process testing and the glass variability study.

A sample Tank 8 sludge which was taken before 1990 and was analyzed in 1998. The sample appears to represent only the part of the waste received in this tank and was not used to estimate the sludge composition.

Sludge Simulant for Non-Radioactive Testing

Sludge simulant is needed for cold demonstration of the feed preparation and to develop processing conditions for the radioactive testing. This simulant will be made to mimic the aqueous phase chemistry. There is no simple way to produce insoluble sodium compounds present in sludge, so the soluble stand-ins for these have been omitted. Depleted uranium creates a waste handling and processing problem, so the simulant was specified with the uranium omitted. Other compositions were normalized to compensate for the missing uranium. However, some limited test work may be done in radio-bench hoods with uranium added. Also, if some of the material is vitrified, the soluble sodium stand-ins for insoluble sodium can be added. Sludge simulant recipes without the insoluble sodium are shown it Tables S1 through S3. For comparison, recipes with the insoluble sodium included are shown in Tables SI1 through SI3.

Mercury and noble metals will be added to the purchased sludge simulant, after it is shipped to SRS and they are included in the attached recipe. The recipe is keyed to a specification for making sludge simulant [5], also attached. These are suggested concentrations, and the investigators can use the noble metal concentrations that match the particular experimental goals. However, noble metals should be present during cold testing at least to the levels suggested, when the SRAT and SME hydrogen and nitrous oxide evolution rates are to be measured.

References:

1. J. R. Hester, **High Level Waste Characterization System**, WSRC-TR-96-0264, December 1996.
2. M. J. Barnes et al, Examination of the Potential for Formation of Energetic Compounds in Dry Sludge, WSRC-TR-98-00407, November 2, 1998
3. N. E. Bibler, Personal Communication to H. H. Elder, January, 2000
4. M. S. Hay and N. E. Bibler, The Characterization and Centrifuge-Settled Washing of a Tank 51H Sludge Sample Obtained in October 1995, WSRC-RP-95-1003, November 25, 1995.
5. N. D. Hutson, Revision of Batch-1 Sludge Composition for Integrated Cold Runs in the DWPF, WSRC-TR-95-0079, February 16, 1995.

Table 2 – Batch 2 Glasses With the Maximum and Minimum Uranium Concentration

	Tank 8 / Tank 40 Blend Overwashed @ Liquidus Limit	Tank 40 Underwashed @ Homogeniety Limit
Element	Weight %, Calcine	Weight %, Calcine
Al	2.55	1.91
B	2.64	2.85
Ba	0.07	0.06
Ca	0.77	0.73
Ce	0.11	0.11
Cr	0.08	0.06
Cs	0.00	0.00
Cu	0.05	0.04
Fe	8.71	7.88
K	0.10	0.09
La	0.06	0.05
Li	1.64	1.77
Mg	0.90	0.96
Mn	0.63	0.33
Mo	0.00	0.00
Na	9.24	9.70
Nd	0.00	0.00
Ni	0.44	0.00
Pb	0.07	0.09
Si	23.44	25.25
Th	0.03	0.04
Ti	0.00	0.00
U	2.58	0.81
Y	0.00	0.00
Zn	0.09	0.08
Zr	0.17	0.16

Note: Sodium compositions varied from 9.03 to 10.17 wt. % calcine in the complete set of glasses. The full set of glass compositions has been sent to SRTC under separate cover.

Table G1 - Tank 40 Sludge Elemental Concentration
Weight % Elemental, Calcine Basis *

Element	Baseline	Less Washed	More Washed
Al	8.31	8.13	8.50
B	0.00	0.00	0.00
Ba	0.24	0.23	0.25
Ca	3.17	3.10	3.24
Ce	0.49	0.48	0.50
Cr	0.27	0.27	0.28
Cs	0.00	0.00	0.00
Cu	0.19	0.18	0.19
Fe	34.30	33.56	35.08
K	0.41	0.40	0.42
La	0.24	0.23	0.24
Li	0.00	0.00	0.00
Mg	0.16	0.16	0.16
Mn	1.42	1.39	1.46
Mo	0.00	0.00	0.00
Na	13.37	14.68	12.00
Nd	0.00	0.00	0.00
Ni	0.00	0.00	0.00
Pb	0.38	0.37	0.39
Si	1.08	1.06	1.10
Th	0.19	0.18	0.19
Ti	0.00	0.00	0.00
U	3.51	3.44	3.59
Y	0.00	0.00	0.00
Zn	0.36	0.35	0.37
Zr	0.68	0.66	0.69

* Values are elemental wt % normalized to 100 wt.% Calcine

Table G2 - Tank 8 Sludge Elemental Concentration
Weight % Elemental, Calcine Basis *

Element	Baseline	Less Washed	More Washed
Al	8.90	8.68	9.13
B	0.00	0.00	0.00
Ba	0.24	0.23	0.24
Ca	2.04	1.99	2.09
Ce	0.24	0.23	0.24
Cr	0.24	0.23	0.25
Cs	0.00	0.00	0.00
Cu	0.15	0.14	0.15
Fe	24.45	23.84	25.09
K	0.28	0.27	0.28
La	0.14	0.13	0.14
Li	0.00	0.00	0.00
Mg	0.12	0.11	0.12
Mn	2.74	2.67	2.81
Mo	0.00	0.00	0.00
Na	13.37	14.89	11.76
Nd	0.00	0.00	0.00
Ni	2.80	2.73	2.88
Pb	0.07	0.07	0.07
Si	0.76	0.74	0.78
Th	0.00	0.00	0.00
Ti	0.00	0.00	0.00
U	13.38	13.04	13.73
Y	0.00	0.00	0.00
Zn	0.27	0.26	0.28
Zr	0.47	0.46	0.49

* Values are elemental wt % normalized to 100 wt.% Calcine

Table S1 - Recipe for Tank 40 Sludge Simulant

For 1000 gallon batch sludge simulant
Insoluble Sodium NOT Included
This Recipe is keyed to Reference [5]

Phase 1			
[A]	66.8	lbs	50% Mn(NO3)2
[B]	59.7	gallons	Water
[C]	19.7	lbs	KMnO4
[D]	82.0	gallons	Water
[E]	40.0	gallons	Water
[F]	5878.8	lbs	7% Fe as Ferric Nitrate
[G]	0.0	lbs	Ni(NO3)2.6H2O
[H]	1788.4	lbs	50% NaOH
[I]	35.0	gallons	Water
[J]	87.2	lbs	CaCO3

This converts to these solids

	lbs
MnO2	27.1
Fe(OH)3	787.3
Ni(OH)2	0.0
CaCO3	87.2

The soluble portion is removed by washing.

Phase 4 Dry Chemical Additions

Chemicals	lbs	
Al (OH) 3	296.0	
BaSO4	4.9	
Ca3(PO4)2	2.7	
CaCO3	0.0	
CaSO4	9.2	
Cr2O3	4.8	
CsNO3	0.0	
CuO	2.6	
KNO3	4.4	
KOH	0.0	
MgO	3.2	
Na2CO3	2.6	
Na2SO4	2.3	
Na3PO4	2.0	
NaCl	32.7	
NaF	0.8	
NaI	0.5	
NaNO2	74.4	
NaNO3	55.2	
NaOH	73.5	
Nd2O3	0.0	
PbSO4	6.7	
SiO2	27.7	
SrCO3	1.7	
Zeolite	0.0	
ZnO	5.4	
ZrO2	11.0	
Dry Solids	1526.0	Includes Sludge + Supernate.
	1303.9	Sludge Solids
	16.4%	Total Solids
	2.4%	Soluble Solids

Noble Metals, Mercury and Silver
To Be Added On-Site

	lbs	ppm	Basis
HgO	6.64	5096	HLW DB Tank 40
AgO	4.30	3297	HLW DB Tank 40
Rh	0.35	270	Bibler's Tank 8 Measuement
Ru	6.20	4752	HLW DB Tank 40
Pd	2.95	2262	HLW DB Tank 40

		Table S2 - Recipe for Tank 40 + Tank 8 Blended Sludge Simulant								
For 1000 gallon batch sludge simulant						Phase 4 -Dry Chemical Additions				
Insoluble Sodium NOT Included						Chemicals	lbs			
This Recipe is keyed to Reference [5]						Al (OH) 3	331.3			
						BaSO4	5.3			
Phase 1						Ca3(PO4)2	2.9			
[A]	107.5	lbs	50% Mn(NO3)2			CaCO3	0.0			
[B]	96.0	gallons	Water			CaSO4	8.2			
[C]	31.6	lbs	KMnO4			Cr2O3	4.9			
[D]	131.8	gallons	Water			CsNO3	0.0			
[E]	40.0	gallons	Water			CuO	2.5			
[F]	5427.2	lbs	7% Fe as Ferric Nitrate			KNO3	2.4			
[G]	94.1	lbs	Ni(NO3)2.6H2O			KOH	0.0			
[H]	1716.5	lbs	50% NaOH			MgO	3.0			
[I]	35.0	gallons	Water			Na2CO3	28.6			
[J]	77.4	lbs	CaCO3			Na2SO4	4.0			
						Na3PO4	1.1			
This converts to these solids						NaCl	28.0			
	lbs					NaF	0.5			
MnO2	43.5					NaI	0.5			
Fe(OH)3	726.8					NaNO2	98.7			
Ni(OH)2	30.0					NaNO3	35.7			
CaCO3	77.4					NaOH	58.1			
						Nd2O3	0.0			
The soluble portion is removed by washing.						PbSO4	5.6			
						SiO2	25.5			
						SrCO3	1.9			
						Zeolite	0.0			
						ZnO	5.1			
						ZrO2	10.1			
						Dry Solids	1541.2	Includes Sludge + Supernate.		
							1303.9	Sludge Solids		
							16.5%	Total Solids		
							2.5%	Soluble Solids		
			Noble Metals, Mercury and Silver							
			To Be Added On-Site							
				lbs	ppm	Basis				
			HgO	3.87	2972	HLW DB Tank 40 & 40				
			AgO	3.74	2865	HLW DB Tank 40 & 8				
			Rh	0.35	270	Bibler's Tank 8 Measuement				
			Ru	6.20	4752	HLW DB Tank 40				
			Pd	2.95	2262	HLW DB Tank 40				

		Table S3 - Recipe for Tank 8 Sludge Simulant								
For 1000 gallon batch sludge simulatn						Phase 4				
Insoluble Sodium NOT Included						Chemicals	lbs			
This Recipe is keyed to Reference [5]						Al (OH) 3	368.3			
						BaSO4	5.7			
Phase 1						Ca3(PO4)2	3.1			
[A]	151.6	lbs	50% Mn(NO3)2			CaCO3	0.0			
[B]	135.3	gallons	Water			CaSO4	7.1			
[C]	44.6	lbs	KMnO4			Cr2O3	5.0			
[D]	185.9	gallons	Water			CsNO3	0.0			
[E]	40.0	gallons	Water			CuO	2.3			
[F]	4937.0	lbs	7% Fe as Ferric Nitrate			KNO3	1.2			
[G]	196.3	lbs	Ni(NO3)2.6H2O			KOH	0.0			
[H]	1638.4	lbs	50% NaOH			MgO	2.8			
[I]	35.0	gallons	Water			Na2CO3	40.4			
[J]	66.7	lbs	CaCO3			Na2SO4	4.7			
						Na3PO4	0.5			
This converts to these solids						NaCl	22.9			
	lbs					NaF	0.3			
MnO2	61.4					NaI	0.4			
Fe(OH)3	661.2					NaNO2	120.8			
Ni(OH)2	62.6					NaNO3	23.8			
CaCO3	66.7					NaOH	47.2			
						Nd2O3	0.0			
The soluble portion is removed by washing.						PbSO4	4.4			
						SiO2	23.1			
						SrCO3	2.0			
						Zeolite	0.0			
						ZnO	4.7			
						ZrO2	9.1			
						Dry Solids	1551.7	Includes Sludge + Supernate.		
							1303.9	Sludge Solids		
							16.7%	Total Solids		
							2.7%	Soluble Solids		
			Noble Metals, Mercury and Silver							
			To Be Added On-Site							
				lbs	ppm	Basis				
			HgO	1.16	887	HLW DB Tank 8				
			AgO	3.18	2440	HLW DB Tank 8				
			Rh	0.35	270	Bibler's Tank 8 Measuement				
			Ru	5.02	3850	HLW DB Tank 8				
			Pd	2.39	1833	HLW DB Tank 8				

		Table SI1 - Recipe for Tank 40 Sludge Simulant								
For 1000 gallon batch sludge simulant						Phase 4 Dry Chemical Additions				
Insoluble Sodium Included						Chemicals	lbs			
This Recipe is keyed to Reference [5]						Al (OH) 3	276.7			
						BaSO4	4.6			
Phase 1						Ca3(PO4)2	2.5			
[A]	62.2	lbs	50% Mn(NO3)2			CaCO3	0.0			
[B]	55.5	gallons	Water			CaSO4	8.6			
[C]	18.3	lbs	KMnO4			Cr2O3	4.4			
[D]	76.2	gallons	Water			CsNO3	0.0			
[E]	40.0	gallons	Water			CuO	2.5			
[F]	5469.0	lbs	7% Fe as Ferric Nitrate			KNO3	4.4			
[G]	0.0	lbs	Ni(NO3)2.6H2O			KOH	0.0			
[H]	1663.7	lbs	50% NaOH			MgO	3.0			
[I]	35.0	gallons	Water			Na2CO3	2.6			
[J]	81.1	lbs	CaCO3			Na2SO4	2.3			
						Na3PO4	2.0			
This converts to these solids						NaCl	30.5			
	lbs					NaF	0.8			
MnO2	25.2					NaI	0.5			
Fe(OH)3	732.4					NaNO2	74.4			
Ni(OH)2	0.0					NaNO3	77.4			
CaCO3	81.1					NaOH	142.2			
						Nd2O3	0.0			
The soluble portion is removed by washing.						PbSO4	6.3			
						SiO2	25.8			
						SrCO3	1.6			
						Zeolite	0.0			
						ZnO	5.0			
						ZrO2	10.2			
						Dry Solids	1527	Includes Sludge + Supernate.		
							1304	Sludge Solids		
							16.4%	Total Solids		
							2.4%	Soluble Solids		
			Noble Metals, Mercury and Silver							
			To Be Added On-Site							
				lbs	ppm	Basis				
			HgO	6.64	5096	HLW DB Tank 40				
			AgO	4.30	3297	HLW DB Tank 40				
			Rh	0.35	270	Bibler's Tank 8 Measuement				
			Ru	6.20	4752	HLW DB Tank 40				
			Pd	2.95	2262	HLW DB Tank 40				

		Table SI2 - Recipe for Tank 40 + Tank 8 Blended Sludge Simulant								
For 1000 gallon batch sludge simulant						Phase 4 -Dry Chemical Additions				
Insoluble Sodium Included						Chemicals	lbs			
This Recipe is keyed to Reference [5]						Al (OH) 3	310.7			
						BaSO4	4.9			
Phase 1						Ca3(PO4)2	2.7			
[A]	100.4	lbs	50% Mn(NO3)2			CaCO3	0.0			
[B]	89.6	gallons	Water			CaSO4	7.7			
[C]	29.5	lbs	KMnO4			Cr2O3	4.5			
[D]	123.1	gallons	Water			CsNO3	0.0			
[E]	40.0	gallons	Water			CuO	2.3			
[F]	5068.2	lbs	7% Fe as Ferric Nitrate			KNO3	2.4			
[G]	87.9	lbs	Ni(NO3)2.6H2O			KOH	0.0			
[H]	1602.9	lbs	50% NaOH			MgO	2.8			
[I]	35.0	gallons	Water			Na2CO3	28.6			
[J]	72.2	lbs	CaCO3			Na2SO4	4.0			
						Na3PO4	1.1			
This converts to these solids						NaCl	26.2			
	lbs					NaF	0.5			
MnO2	40.6					NaI	0.4			
Fe(OH)3	678.8					NaNO2	98.7			
Ni(OH)2	28.0					NaNO3	56.6			
CaCO3	72.2					NaOH	123.4			
						Nd2O3	0.0			
The soluble portion is removed by washing.						PbSO4	5.2			
						SiO2	23.8			
						SrCO3	1.7			
						Zeolite	0.0			
						ZnO	4.7			
						ZrO2	9.4			
						Dry Solids	1542	Includes Sludge + Supernate.		
							1304	Sludge Solids		
							16.6%	Total Solids		
							2.6%	Soluble Solids		
			Noble Metals, Mercury and Silver							
			To Be Added On-Site							
				lbs	ppm	Basis				
			HgO	3.87	2972	HLW DB Tank 40 & 40				
			AgO	3.74	2865	HLW DB Tank 40 & 8				
			Rh	0.35	270	Bibler's Tank 8 Measuement				
			Ru	6.20	4752	HLW DB Tank 40				
			Pd	2.95	2262	HLW DB Tank 40				

		Table SI3 - Recipe for Tank 8 Sludge Simulant								
For 1000 gallon batch sludge simulatn						Phase 4				
Insoluble Sodium Included						Chemicals	lbs			
This Recipe is keyed to Reference [5]						Al (OH) 3	346.6			
						BaSO4	5.4			
Phase 1						Ca3(PO4)2	2.9			
[A]	142.1	lbs	50% Mn(NO3)2			CaCO3	0.0			
[B]	126.9	gallons	Water			CaSO4	6.7			
[C]	41.8	lbs	KMnO4			Cr2O3	4.7			
[D]	174.4	gallons	Water			CsNO3	0.0			
[E]	40.0	gallons	Water			CuO	2.2			
[F]	4629.7	lbs	7% Fe as Ferric Nitrate			KNO3	1.2			
[G]	184.1	lbs	Ni(NO3)2.6H2O			KOH	0.0			
[H]	1536.4	lbs	50% NaOH			MgO	2.6			
[I]	35.0	gallons	Water			Na2CO3	40.4			
[J]	62.5	lbs	CaCO3			Na2SO4	4.7			
						Na3PO4	0.5			
This converts to these solids						NaCl	21.5			
	lbs					NaF	0.3			
MnO2	57.6					NaI	0.4			
Fe(OH)3	620.0					NaNO2	120.8			
Ni(OH)2	58.7					NaNO3	43.4			
CaCO3	62.5					NaOH	108.8			
						Nd2O3	0.0			
The soluble portion is removed by washing.						PbSO4	4.1			
						SiO2	21.6			
						SrCO3	1.9			
						Zeolite	0.0			
						ZnO	4.4			
						ZrO2	8.5			
						Dry Solids	1552	Includes Sludge + Supernate.		
							1304	Sludge Solids		
							16.7%	Total Solids		
							2.7%	Soluble Solids		
			Noble Metals, Mercury and Silver							
			To Be Added On-Site							
				lbs	ppm	Basis				
			HgO	1.16	887	HLW DB Tank 8				
			AgO	3.18	2440	HLW DB Tank 8				
			Rh	0.35	270	Bibler's Tank 8 Measuement				
			Ru	5.02	3850	HLW DB Tank 8				
			Pd	2.39	1833	HLW DB Tank 8				

Savannah River Technology Center

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Revision 1

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REVISION TO THE BATCH-1 SLUDGE COMPOSITION FOR INTEGRATED COLD RUNS IN THE DEFENSE WASTE PROCESSING FACILITY (U)

Background / Summary

This revision made two changes to the Batch-1 recipe developed earlier.[1] First, no radiolysis of Tank 51 sludge is assumed. This increases the sodium nitrate addition in the recipe and decreases the sodium nitrite addition. Second, the recipe is calculated for 2,220 and 5,000 gallons since DWPT will be ordering 2,200 gallons for IDMS and small scale batch 1 experiments.

The initial radioactive sludge to the Defense Waste Processing Facility (DWPF) was to be a blend of Tanks 42 and 51 and was referred to as "Batch-1". Inactive simulants were specified for the DWPF Integrated Cold Runs and included Batch-1 compositions at both low and nominal nitrite (NO_2^-) concentrations. However, HLW budgetary constraints forced a modification of the original anticipated Batch-1 composition to that of Tank 51 only (no blending with Tank 42 sludge). Therefore, the original inactive Batch-1 simulant for DWPF Cold Runs was modified to reflect this processing[1] This report details the revised recipe for this Batch-1 sludge simulant as well as the rationale and assumptions which were necessary for the recipe development.

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Technical Review

Bases

The basis for the sludge simulant is a Chemical Process Evaluation System (CPES) material balance which used actual analyses of Tank 51 sludge. The final CPES Batch-1 sludge to the DWPF was the Tank 51 material which was washed to 10 wt% Na (dry basis) and further diluted to 15 wt% total solids. In CPES, this sludge was blended with Precipitate Hydrolysis Aqueous (PHA) produced from the precipitate to be produced during the planned ITP Cycle 1. Sludge, PHA and Frit-Slurry blendings were taken from PCCS runs using predicted sludge and PHA compositions from the CPES material balance.[3] The PCCS recommended blending of

sludge	25.3 %
PHA	6.0 %
frit	68.7 %

made an acceptable glass product with respect to processability, predictability and durability. The results of this CPES evaluation are given in:

A. S. Choi, "HLW Flowsheet Material Balance for DWPF Startup with Tank 51 Sludge and ITP Cycle 1 Precipitate (U)," WSRC-TR-94-0019, Rev. 0.

Predicted Composition of Sludge

Appendix 1 shows the sludge components in the CPES material balance (lbs/hr) and the corresponding simulant sludge flows (lbs/hr).

There were several assumptions which were necessary during this simulant recipe development. These assumptions are summarized below:

1. As a general rule, components which were predicted to be <0.01 wt% (dry basis) were deleted. (Note: The exceptions to this rule were chloride (Cl^-), the noble metals (Ru, Rh, and Pd), and tellurium (Te).)
2. Plutonium, Pu, was deleted as it is predicted to be present at a very low concentration (≈ 0.013 wt% dry) and there is not a suitable inactive substitute.
3. Cerium Oxide, CeO_2, was originally considered as an inactive substitute for uranium oxide, U_3O_8. However, on the advice of M. J. Plodinec [4] uranium was deleted entirely from the formulation as there is no good substitute to adequately duplicate the chemistry of oxidized uranium which tends to be quite chemically benign in the glass.
4. Zirconium oxide, ZrO_2, was used as a substitute for thorium oxide, ThO_2, in the simulant (this substitution was done on a weight-for-weight basis).
5. The simulant was developed such that the elemental flows (lbs/hr) for simulant and the CPES material balance were nearly equal.

Note: M. J. Plodinec is with the Defense Waste Processing Technology Section of the Savannah River Technology Center. Concurrence of this assessment was obtained from H. H. Elder, DWPF Technical.

6. The elemental wt% (dry basis) for the simulant and the CPES material balance do not match very well because of two factors: (1) the deletion of U from the simulant, and (2) the amount of waters of hydration in the simulant. In CPES, hydrate water is used to balance the estimated total solids with the measured total solids (in CPES Al and Fe are assumed to be present as oxides rather than hydroxides), while the actual simulant must account for all hydroxide in the sludge. Therefore, the wt% solids for the simulant are higher (17.2% for the simulant versus 15.0% for the CPES material balance).

Revised Procedure for Vendor Makeup of the Batch-1 Simulant

Note: The production of the sludge simulants has been contracted and it is known that the vendor of choice uses a centrifugation system for solids separation in the washing step. Therefore, there is no procedure given for a settle/decant solids separation.

The amounts of chemicals, dilution water, *etc.* are given in Appendix 2. The amounts given are for production of a 2,200 and 5,000 gallon batch of sludge simulant. The amounts of materials may be adjusted linearly for increased or decreased batch volumes.

PHASE 1

Step 1 Combine **[A]** lbs of a 50 wt% manganese nitrate solution with **[B]** gallons of water. Adjust the temperature to 35°C to 40°C. Solution is to be stirred continuously.

Step 2. In a separate vessel, combine **[C]** lbs of potassium permanganate (with agitation) to **[D]** gallons of water. When the permanganate has dissolved, adjust the solution temperature to between 35°C to 40°C.

Step 3. Pump the permanganate solution prepared in Step 2 into the manganese nitrate solution prepared in Step 1 at a rate of 2.0 - 3.0 gallons per minute with constant agitation. Slurry temperature is to be maintained between 35°C and 40°C.

Stoichiometry

$$2KMnO_4 + 3Mn(NO_3)_2 + 2H_2O \dashrightarrow 5MnO_2\text{ (ins)} + 2KNO_3 + 4\,HNO_3$$

Step 4. With continued agitation, add **[E]** gallons of water, **[F]** lbs of a ferric nitrate solution at an Fe concentration of 7.0 (± 0.2) wt%, and **[G]** lbs of nickel nitrate hexahydrate to the slurry prepared in Step 3.

Step 5 In a separate vessel, add **[H]** lbs of 50 wt% sodium hydroxide solution to **[I]** gallons of water.

Step 6 Meter the caustic solution prepared in Step 5 into the slurry prepared in Step 4 with continuous agitation. The addition rate is dictated by the requirement that the slurry temperature be maintained between 35°C and 40°C.

Stoichiometry

$Fe(NO_3)_3 + 3NaOH \dashrightarrow Fe(OH)_3 \text{ (ins)} + 3NaNO_3$

$Ni(NO_3)_2 + 2NaOH \dashrightarrow Ni(OH)_2 \text{ (ins)} + 2NaNO_3$

$6Mn(NO_3)_2 + O_2 + 12NaOH \dashrightarrow 2Mn_3O_4 \text{ (ins)} + 6H_2O + 12NaNO_3$

Step 7 Measure the pH of the aqueous fraction of the slurry. If the pH is less than 10, add sufficient caustic to raise the pH to 10.5 (± 0.5 pH unit). Analytically confirm the pH if an adjustment was required.

Step 8 Add [J] lbs of calcium carbonate to the slurry prepared in Step 7. Continue agitating for 30 minutes.

PHASE 2

Step 1 Agitate the slurry prepared in Phase 1 and obtain a representative sample for analysis. Submit the sample to the WSRC Technical Representative for determination of the wt% total solids, Total Organic Carbon (TOC) and Na, Fe, Mn, Ni, and Ca concentrations.

Note: The WSRC Technical Representative will arrange for the sample to be washed with water which has been inhibited with NaOH to a pH of 10.5 ±0.25. Sufficient wash water will be used such that the soluble solids content of the aqueous fraction of the sample is reduced by at least 50-fold. The washed insoluble solids will then be taken to dryness at 115°C to 120°C. The insoluble solids will then be analyzed and the results evaluated. The desired composition is shown in Appendix 3.

Step 2 Proceed to Phase 3 only after the WSRC Technical Representative has approved of the slurry prepared in Step I.

PHASE 3

Continuous Washing

Step 1 With continuous agitation of the slurry, wash the slurry with inhibited wash water. (Note: Inhibited wash water is water which has been inhibited with NaOH to a pH of 10.5 ± 0.25.)

Step 2 Continue washing until the soluble solids concentration in the aqueous fraction of the slurry is between 0.15 and 0.20 wt%.

Step 3 Analytically confirm that the pH of the aqueous fraction of the slurry is between 10.0 and 11.0.

PHASE 4

Step 1 Add the remainder of required chemicals (shown in Appendix 4) to the washed slurry prepared in Phase 3 with constant agitation. Each chemical is to be added separately with at least 15 minutes between additions.

Step 2 Add sufficient water to adjust the total solids to the 17.2 wt%. Continue agitation for at least 30 minutes.

PHASE 5

Step 1 Agitate the final slurry and obtain a representative sample for analysis. Note: If the final batch of slurry is distributed between more than one vessel, samples from each vessel must be taken for final approval. Submit the sample(s), along with the "batch sheets", to the WSRC Technical Representative for determination of wt% total solids and total cationic and anionic analysis.

Step 2 An adjustment of the composition of the final slurry may be required to meet the acceptance criteria listed in Appendix 5. This adjustment may require additional chemical additions or washing steps to meet the sodium and nitrate concentration limits.

Step 3 Once analytical verification and concurrence has been received from the WSRC Technical Representative, the material may be shipped.

References

[1] N. D. Hutson, "BATCH-1 SLUDGE COMPOSITION FOR INTEGRATED COLD RUNS IN THE DEFENSE WASTE PROCESSING FACILITY (U)", USDOE Report WSRC-RP-95-0079, Rev 0, Savannah River Laboratory, Aiken, SC 29808 (Revised February 16, 1995).

[2] J. R. Fowler, J. T. Carter, L. F. Landon, J. C. Marek, C. L. Pearson, and S. M. Peters, "Development of Feed Simulant Specifications for Integrated Cold Runs in the Defense Waste Processing Facility (U)", USDOE Report WSRC-RP-89-0238, Rev 1, Savannah River Laboratory, Aiken, SC 29808 (Revised Nov. 1, 1990).

[3] A. S. Choi,, "HLW Flowsheet Material Balance for DWPF Startup with Tank 51 Sludge and ITP Cycle 1 Precipitate (U)," USDOE Report WSRC-TR-94-0019, Rev. 0, Savannah River Technology Center, Aiken, SC 29808.

[4] Plodinec, M. J., Personal Communication, February 10, 1995.

APPENDIX 1. Sludge Composition Basis (CPES Material Balance) and Simulant Comparison

Component	CPES, lb/hr	Simulant, lb/hr
$AgNO_3$	0.0102	0.0151
Al_2O_3	8.5880	8.7000
BaO	0.0000	0.1000
$BaSO_4$	0.0149	0.0000
$Ca_3(PO_4)_2$	2.0740	0.0000
$CaCO_3$	2.5560	0.0000
CaF_2	0.0151	0.0000
CaO	0.0034	2.5777
$CaSO_4$	0.0298	0.0000
Cr_2O_3	0.1636	0.1672
Cs_2O	0.0001	0.0000
CuO	0.0210	0.0211
Fe_2O_3	28.17	28.04
$Hg(NO_3)_2$	0.0000	0.1862
HgO	0.1390	0.0000
K_2O	0.0742	0.0000
KOH	0.0159	0.1037
MgO	1.5310	1.5248
MnO_2	3.2590	3.2463
NH_4OH	0.0006	0.0000
$Na_2C_2O_4$	0.2653	0.2651
Na_2CO_3	0.2469	2.9827
Na_2CrO_4	0.0093	0.0000
Na_2MoO_4	0.0015	0.0000
Na_2O	3.2440	0.0000
Na_2SO_4	0.1952	0.2948
Na_2SiO_3	0.0081	0.0000
Na_3PO_4	0.0011	2.1905
$NaAl(OH)_4$	0.3573	0.0000
NaCl	0.0068	0.0000
NaF	0.0342	0.0504
$NaNO_2$	5.2990	5.2990
$NaNO_3$	1.522	1.522
NaOH	3.0760	3.1829
NiO	0.2493	0.2500
PbO	0.0000	0.0939
$PbSO_4$	0.1280	0.0000
PdO	0.0005	0.0004
PuO_2	0.0099	0.0000
RhO_2	0.0010	0.0010
RuO_2	0.0062	0.0063
SiO_2	1.0660	1.0631
$SrCO_3$	0.0206	0.0000
SrO	0.0000	0.0144
TcO_2	0.0035	0.0000
TeO_2	0.0006	0.0006
ThO_2	0.0299	0.0000
TiO_2	0.0467	0.0466
U_3O_8	2.0920	0.0000
$Y_2(CO_3)_3$	0.0052	0.0000
ZnO	0.1184	0.1173
ZrO_2	0.0000	0.0352

APPENDIX 2. Recipe Amounts for Production of Batch 1 Sludge

Step	2,200 gallon batch	5,000 gallon batch	Description
[A]	398	904	lbs of 50% $Mn(NO_3)_2$ solution
[B]	355	807	gallons of dilution water
[C]	96.8	220	lbs of $KMnO_4$
[D]	405	920	gallons of dilution water
[E]	82.7	188	gallons of dilution water
[F]	12,926	29,377	lbs of Fe(NO3)3 solution (7% Fe)
[G]	44.4	101	lbs of $Ni(NO_3)_2 \cdot 6H_2O$
[H]	4,304	9782	lbs of 50% NaOH solution
[I]	86.2	196	gallons of dilution water
[J]	0	0	lbs of $CaCO_3$

APPENDIX 3. Nominal Cation Concentration in Phase 2 Insoluble Solids

Additive	wt%, dry
Fe (+3)	47.75%
Mn (+2,+4)	4.99%
Ca (+2)	0.00%
Ni (+2)	0.48%

Note: Acceptance criteria (i.e., ± x%) from the original purchase specification may be applied to the acceptance of this Batch-1 sludge simulant or DWPF-T&E may modify the acceptance criteria based on previous processing history.

APPENDIX 4. Phase 4 Trim Chemicals (Amounts, lbs for Batch)

Additive	2,200 gallons	5,000 gallons
$Al(OH)_3$	614.30	1396.13
BaO	0.46	1.05
CaO	118.92	270.28
Cr_2O_3	7.71	17.53
CuO	0.97	2.21
KOH	4.79	10.89
MgO	70.34	159.87
$NaNO_2$	240.92	547.54
$NaOH$	144.48	328.37
Na_2CO_3	137.61	312.75
Na_2SO_4	13.60	30.91
Na_3PO_4	101.06	229.68
$NaNO_3$	69.19	157.26
NaF	2.32	5.28
$Na_2C_2O_4$	12.23	27.8
PbO	4.33	9.84
SiO_2	49.05	111.47
SrO	0.66	1.51
TiO_2	2.15	4.88
ZnO	5.41	12.3
ZrO_2	1.62	3.69

APPENDIX 5. Expected Concentration of Final Vendor Product

Component	wt%, dry
Silver, Ag	0.000*
Aluminum, Al	6.001
Barium, Ba	0.012
Calcium, Ca	2.400
Chromium, Cr	0.149
Copper, Cu	0.022
Iron, Fe	25.553
Mercury, Hg	0.000*
Potassium, K	0.094
Magnesium, Mg	1.198
Manganese, Mn	2.673
Sodium, Na	8.741
Nickel, Ni	0.254
Lead, Pb	0.114
Palladium, Pd	0.000*
Rhodium, Rh	0.000*
Ruthenium, Ru	0.000*
Silicon, Si	0.648
Strontium, Sr	0.016
Tellurium, Te	0.000*
Titanium, Ti	0.036
Zinc, Zn	0.123
Zirconium, Zr	0.034
Oxalate, $C_2O_3^{2-}$	0.227
Carbonate, CO_3^{2-}	2.200
Chloride, Cl^-	0.000*
Fluoride, F^-	0.030
Nitrite, NO_2^-	4.53
Nitrate, NO_3^-	1.43
Free Hydroxide, OH^-	1.775
Phosphate, PO_4^{3-}	1.653
Sulfate, SO_4^{2-}	
Specific gravity	1.122
Total solids, wt%	17.200

* these components will be added at SRS prior to operation

Note: Acceptance criteria (i.e., ± x%) from the original purchase specification may be applied to the acceptance of this Batch-1 sludge simulant or DWPF-T&E may modify the acceptance criteria based on previous processing history.