PNNL-10988
UC-810
Project Technical Information

Feed Specification for the Double-Shell Tank/Single-Shell Tank Waste Blend for High-Level Waste Vitrification Process and Melter Testing

E. M. Tracey
M. D. Merz
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Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
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1.0 INTRODUCTION

The High-Level Waste (HLW) Vitrification Program is developing technology for the Department of Energy to immobilize high-level and transuranic waste as glass for permanent disposal. In support of the program, Pacific Northwest Laboratory (PNL) is conducting laboratory-scale melter feed preparation studies and HLW melter testing which require a simulated HLW feed. The simulant HLW feed represents a blend of the waste from 177 single shell and double shell tanks. The waste blend composition (Table 1) is based on normalized track radionuclide components (TRAC), historical tank data, and assumptions on the pretreatment of the waste.(a) The HLW simulant feed specification for the waste blend composition provides direction for the preparation of laboratory-scale and large-scale HLW blend simulant to be used in melter feed preparation studies and melter testing.

Previous HLW simulants have been prepared with a neutralized current acid waste (NCAW) composition excluding acutely toxic and radioactive elements. The feed specification for the waste blend simulant uses a procedure similar to the preparation procedure for NCAW simulant. The elements Bi, W, Co, Np, Re, Th, Tl, Hg, V, and Cm, and the anion, CN, which are present in the blend waste composition are not present in the NCAW simulant composition. Acutely toxic and radioactive species are either substituted or eliminated from the composition (Table 1). The waste blend preparation differs from the NCAW simulant preparation in the addition of mineral phases (boehmite, cancranite, sodium silicate, and silica) as the sources for Al and Si.(b) As a result, the preparation of $Al(OH)_3$ by addition of NaOH to $Al(NO_3)_3$ is eliminated. Cyanide (CN) will be added as $Na_2NiFe(CN)_6$ which has been reported to be the major source of CN in the tanks (Burger et al. 1991). The addition of $Na_2NiFe(CN)_6$ to the batch is necessary because of possible catalytic reactions and release of toxic gases involving CN. However, there is a possibility of an uncontrollable exothermic reaction with a critical temperature of 330°C and a -3012 kJ per mole energy release for reaction with $NaNO_3$, and a -3708 kJ per mole energy release for reaction with $NaNO_2$ (Burger et al. 1991). Therefore, the decision to add $Na_2NiFe(CN)_6$ in a particular application needs to be carefully considered. As with the NCAW, the organic component of the waste blend simulant will be added as oxalate. This decision was based on the prediction that organic complexants in the waste tanks break down into oxalate (Agnew 1994, p. 50).

The waste blend feed specification is written for the preparation of 1000 L of waste simulant and is summarized as follows. A stock simulant is prepared by first coprecipitating a hydroxide slurry containing major waste oxide elements (Fe, Ni, Nd, Zr, and Mn). The soluble/slightly soluble salts (halides, hydroxides, nitrates, nitrites, sulfates, borates, phosphates, oxides, and oxalate) are added dry to the major oxide slurry. Four other slurries are added to the major oxides and soluble/slightly soluble slurry: 1. minor components as an insoluble compound slurry (oxides, fluorides), 2.

(a) R.W. Powell. May 1995. "Double-Shell Tank/Single-Shell Tank Waste Blend Composition for High-Level Waste Vitrification Process Testing," Letter to J.M. Creer. #9452712.

(b) Bunker, B.C., and N.G. Colton, Personal Communication.

Table 1. HLW Blend Reference and Simulant Composition

	Reference Composition[a]			Simulant Composition		
Oxide	Wt% Oxide	Moles Element/ L Feed (125 WO/L)	Subst/ Del[b]	Moles Element/ L Feed (125 g WO/L)	Wt% Oxide	Source Chemical
Ag_2O	4.17E-03	4.50E-05		4.78E-05	4.43E-03	$AgNO_3$
Al_2O_3	1.30E+01	3.19E-01		3.39E-01	1.38E+01	$Na_8Al_6Si_6O_{24}$ $(NO_3)_2$ Al(OOH)
Am_2O_3	4.23E-04	1.98E-06	Del[c]	—	—	deleted
As_2O_3	8.18E-03	1.03E-04	Del[d]	—	—	deleted
B_2O_3	7.54E-02	2.70E-03		2.86E-03	8.01E-02	H_3BO_3
BaO	2.17E-02	1.77E-04		1.88E-04	2.30E-02	$Ba(OH)_2x8H_2O$
BeO	2.42E-04	1.21E-05	Sub Mg[d]	—	—	subst. MgO
Bi_2O_3	1.95E+00	1.05E-02		1.11E-02	2.07E+00	$Bi(NO_3)_3$ x $5H_2O$
CaO	2.06E+00	4.59E-02		4.88E-02	2.19E+00	$Ca(NO_3)_2x4H_2O$
CdO	9.07E-02	8.83E-04		9.38E-04	9.63E-02	$Cd(NO_3)_2x4H_2O$
CeO_2	2.73E+00	1.98E-02		2.11E-02	2.90E+00	$Ce(NO_3)_3x6H_2O$
Cl	3.26E-02	1.15E-03		1.22E-03	3.46E-02	NaCl
Cm_2O_3	2.43E-07	1.12E-09	Del[c]	—	—	delete
Co_2O_3	1.02E-02	1.54E-04		1.63E-04	1.08E-02	$Co(NO_3)_2x6H_2O$
Cr_2O_3	4.52E-01	7.43E-03		7.90E-03	4.80E-01	$Cr(NO_3)_3x9H_2O$
Cs_2O	1.21E-02	1.07E-04		1.14E-04	1.29E-02	$CsNO_3$
CuO	9.06E-03	1.42E-04		1.51E-04	9.62E-03	$CuSO_4x5H_2O$
Dy_2O_3	1.28E-05	8.58E-08	Sub Nd[e]	—	—	subst. Nd_2O_3
Er_2O_3	3.80E-07	2.48E-09	Sub Nd[e]	—	—	subst. Nd_2O_3
Eu_2O_3	2.49E-03	1.77E-05	Sub Nd[e]	—	—	subst. Nd_2O_3
F	5.55E-01	3.65E-02		3.88E-02	5.89E-01	NaF(see LaF_3&NdF_3)
Fe_2O_3	1.10E+01	1.72E-01		1.83E-01	1.17E+01	$Fe(NO_3)_3x9H_2O$
Gd_2O_3	4.56E-04	3.14E-06	Sub Nd[e]	—	—	subst. Nd_2O_3
GeO_2	1.94E-05	2.32E-07		2.46E-07	2.06E-05	GeO_2
HgO	8.28E-03	4.78E-05		5.08E-05	8.79E-03	HgO
Ho_2O_3	6.57E-07	4.35E-09	Sub Nd[e]	—	—	subst. Nd_2O_3
K_2O	2.22E-01	5.89E-03		6.26E-03	2.36E-01	KOH
La_2O_3	4.28E-01	3.28E-03		3.49E-03	4.55E-01	$La(OH)_3$ and LaF_3
Li_2O	6.90E-04	5.77E-05		6.13E-05	7.33E-04	Li_2O
MgO	7.65E-02	2.37E-03		2.53E-03	8.17E-02	$Mg(NO_3)_2x6H_2O$
MnO_2	1.82E+00	2.62E-02		2.78E-02	1.93E+00	$Mn(NO_3)_2$ and $KMnO_4$
MoO_3	7.35E-02	6.38E-04		6.78E-04	7.81E-02	MoO_3
Na_2O	2.53E+01	1.02E+00		1.08E+00	2.69E+01	NaOH
Nb_2O_5	8.13E-09	8.69E-11		9.23E-11	8.64E-09	Nb_2O_5
Nd_2O_3	7.13E-02	5.30E-04		6.83E-02	9.19E+00	$Nd(NO_3)_3x6H_2O$ and NdF_3
NiO	2.27E+00	3.80E-02		4.04E-02	2.41E+00	$Ni(NO_3)_2x6H_2O$

Table 1. HLW Blend Reference and Simulant Composition (cont.)

	Reference Composition[a]			Simulant Composition		
Oxide	Wt% Oxide	Moles Element/ L Feed (125 WO/L)	Subst/ Del	Moles Element/ L Feed (125 g WO/L)	Wt% Oxide	Source Chemical
NpO_2	8.56E-04	3.98E-06	Sub Zr[c]	—	—	subst. ZrO_2
P_2O_5	4.71E+00	8.30E-02		8.81E-02	5.00E+00	Na_3PO_4
PbO_2	3.21E-01	1.68E-03		1.78E-03	3.41E-01	$Pb(NO_3)_2$
PdO	1.48E-02	1.51E-04		1.61E-04	1.57E-02	$Pd(NO_3)_2$
Pm_2O_3	5.68E-03	4.20E-05	Sub Nd[c]	—	—	subst. Nd_2O_3
Pr_2O_3	1.89E-02	1.43E-04		1.52E-04	2.01E-02	$Pr(NO_3)_3x6H_2O$
PuO_2	5.57E-03	2.52E-05	Sub Ce[c]	—	—	subst CeO_2
Rb_2O_3	7.09E-03	8.10E-05		8.60E-05	7.53E-03	$RbNO_3$
Re_2O_3	4.12E-04	2.45E-06		2.60E-06	4.38E-04	Re_2O_7
Rh_2O_3	1.28E-02	1.26E-04		1.34E-04	1.36E-02	$Rh(NO_3)_2$
Ru_2O_3	4.69E-02	4.69E-04		4.98E-04	4.98E-02	$RuNO(NO_3)_3$
Sb_2O_3	2.06E-02	1.77E-04		1.88E-04	2.19E-02	Sb_2O_3
SeO_2	2.44E-02	2.75E-04		2.92E-04	2.59E-02	SeO_2
SiO_2	1.00E+01	2.08E-01		2.21E-01	1.06E+01	Na_2SiO_3 and SiO_2 (quartz)
Sm_2O_3	3.51E-04	2.52E-06		2.67E-06	3.73E-04	$Sm(NO_3)_3x6H_2O$
SnO	1.57E-04	1.46E-06		1.55E-06	1.67E-04	$SnCl_2x2H_2O$
SO_3	3.41E-01	5.32E-03		5.66E-03	3.62E-01	Na_2SO_4
SrO	4.14E-01	4.99E-03		5.30E-03	4.40E-01	$Sr(NO_3)_2$
Ta_2O_5	4.11E-04	2.33E-06		2.47E-06	4.37E-04	Ta_2O_5
Tb_2O_3	2.78E-05	1.90E-07	Sub Nd[e]	—	—	subst. Nd_2O_3
Tc_2O_7	2.10E-02	1.70E-04	Del[c]	—	—	delete
TeO_2	2.92E-03	2.29E-05		2.43E-05	3.10E-03	TeO_2
ThO_2	1.46E-01	6.91E-04	Sub Zr[c]	—	—	subst. ZrO_2
TiO_2	6.95E-03	1.09E-04		1.16E-04	7.38E-03	TiO_2
Tl_2O_3	5.52E-02	3.02E-04	Del[d]	—	—	deleted
Tm_2O_3	2.07E-11	1.34E-13	Sub Nd[e]	—	—	subst. Nd_2O_3
U_3O_8	1.43E+01	6.37E-02	Sub Nd[c]	—	—	subst. Nd_2O_3
V_2O_5	6.53E-04	8.98E-06	Del[d]	—	—	deleted
WO_3	1.74E-01	9.38E-04		9.96E-04	1.85E-01	$Na_2WO_4x2H_2O$
Y_2O_3	9.87E-03	1.09E-04		1.16E-04	1.05E-02	$Y(NO_3)_3x6H_2O$
ZnO	1.74E-02	2.67E-04		2.84E-04	1.85E-02	$Zn(NO_3)_2x6H_2O$
ZrO_2	7.08E+00	7.18E-02		7.70E-02	7.59E+00	$ZrO(NO_3)_2$

Table 1. HLW Blend Reference and Simulant Composition (cont.)

Volatiles Components of the HLW Blend

	Reference Composition		Simulant Composition		
Species	g/100g Total Oxide(f)	gmole Elmt/L	g/100 g Total Oxide(f)	g Anion/L (125 g oxide/L)	Source Chemical
NO_3^-	2.63E+01	5.30E-01	2.79E+01	3.29E+01	$NaNO_3$
NO_2^-	1.39E+00	3.78E-02	1.48E+00	1.74E+00	$NaNO_2$
OH^-	1.82E+01	1.34E+00	1.93E+01	2.28E+01	NaOH
CO_3^-	1.71E+00	3.56E-02	1.82E+00	2.14E+00	Na_2CO_3
I^-	3.16E-05	3.11E-07	3.36E-05	3.95E-05	$NaIO_3$
TOC	3.29E-01	3.42E-02	3.49E-01	4.11E-01	$Na_2C_2O_4$
^{14}C	1.23E-07	1.10E-08	1.31E-07	—	delete
CN^-	2.24E+00	1.08E-01	2.38E+00	2.80E+00	$Na_2NiFe(CN)_6$

(a) R.W. Powell. May 1994. "Double-Shell Tank/Single-Shell Tank Waste Blend Composition for High-Level Waste Vitrification Process Testing," Letter to J.M. Creer. #9452712.

(b) The additional amounts of Nd, Zr, Ce, and Mg due to substitutions are included in the simulant composition

(c) Radioactive

(d) Acutely toxic

(e) Expensive

(f) Target composition differs from reference composition because of substitution of lighter simulant oxides for reference oxides.

coprecipitated noble metals (Rh, Pd, Ru) slurry, 3. sodium nickel ferrocyanide slurry, and 4. a mineral slurry. Excess nitrate and sodium are removed by washing. The washed feed is analyzed for sodium, nitrite, and nitrate. These anions and cations have been added in various amounts with other elements and appropriate additions are made to bring these components to nominal levels. Figure 1 is a flowchart of the simulant preparation steps.

The waste blend feed specification represents a best effort to reproduce the speciation and particle size of the components in the waste tanks based on historical reports and process knowledge and within the programmatic funding and schedule constraints. An actual blend of the Hanford tanks combines wastes resulting from multiple process streams. The blend simulant preparation does not mimic each of these process streams, only the final composition of a blended waste. The feed specification includes many minor components except those which are acutely toxic. The deletion of these elements was carefully considered with regards to properties which may influence catalytic behavior or the glass properties. Additional deletions may be considered for melter evaluation testing depending on batch size, expense of minor components (i.e. noble metals), and safety issues, and should be carefully evaluated. Radioactive elements are deleted or substituted. Neodymium is the surrogate element for U. In the waste blend, component U is a major component (~14 wt %). When previously substituted for in the NCAW, U was a minor component (~5 wt%). This represents a limitation in the specification because Nd does not exactly mimic the properties of U, and its molecular weight is significantly less than the molecular weight of U. As a result, a HLW waste blend with a gram waste oxide loading of 125 g waste oxide/ liter (gWO/L) is equivalent to a waste blend simulant with a gram waste oxide loading of 117.8 gWO/L. These limitations need to be considered with respect to the application for which the feed specification is used.

A laboratory-scale preparation of the HLW blend simulant per the steps outlined in this specification is scheduled to be completed by February 1995. A revision to the specification will be issued to address any necessary changes.

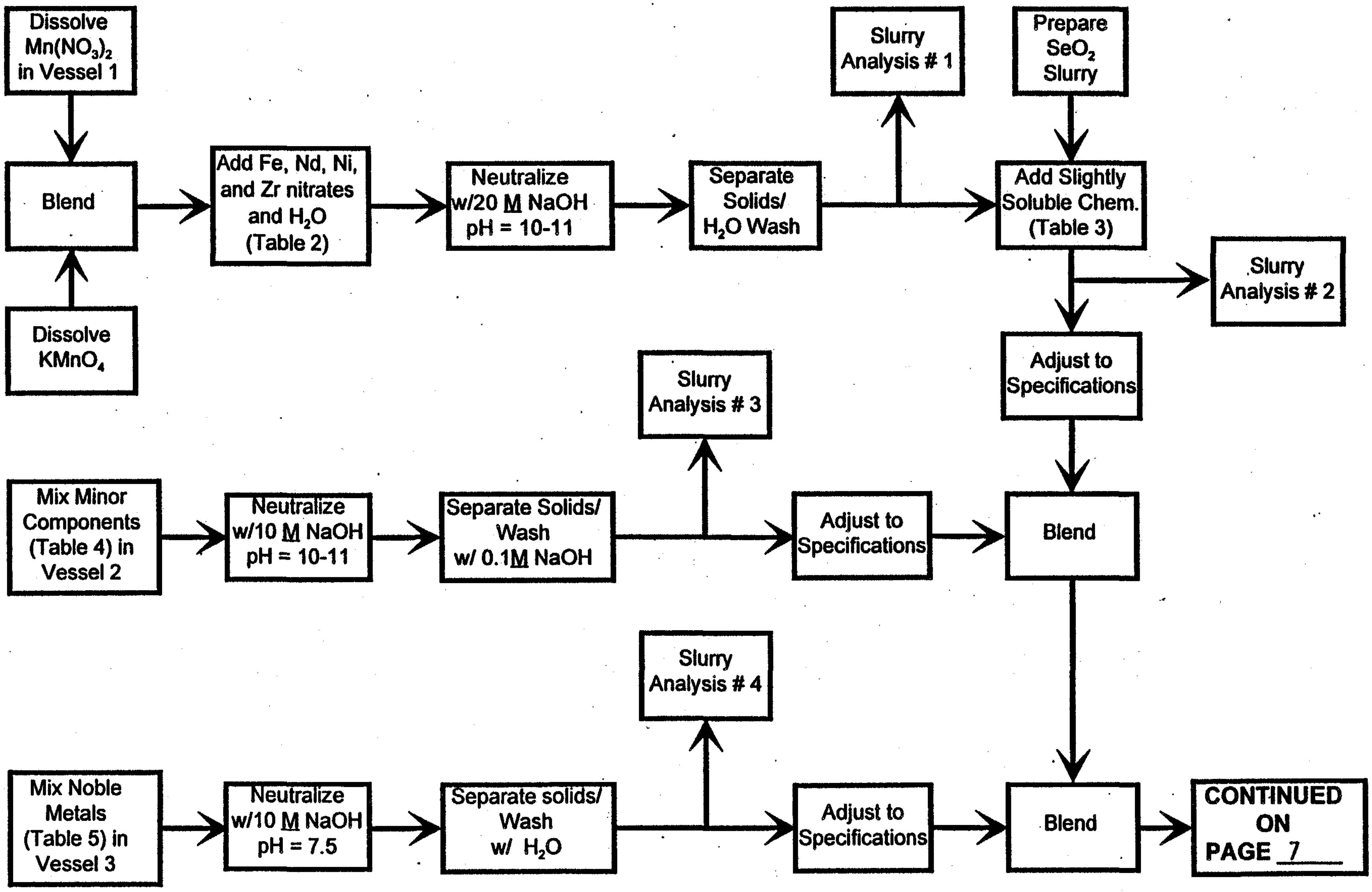
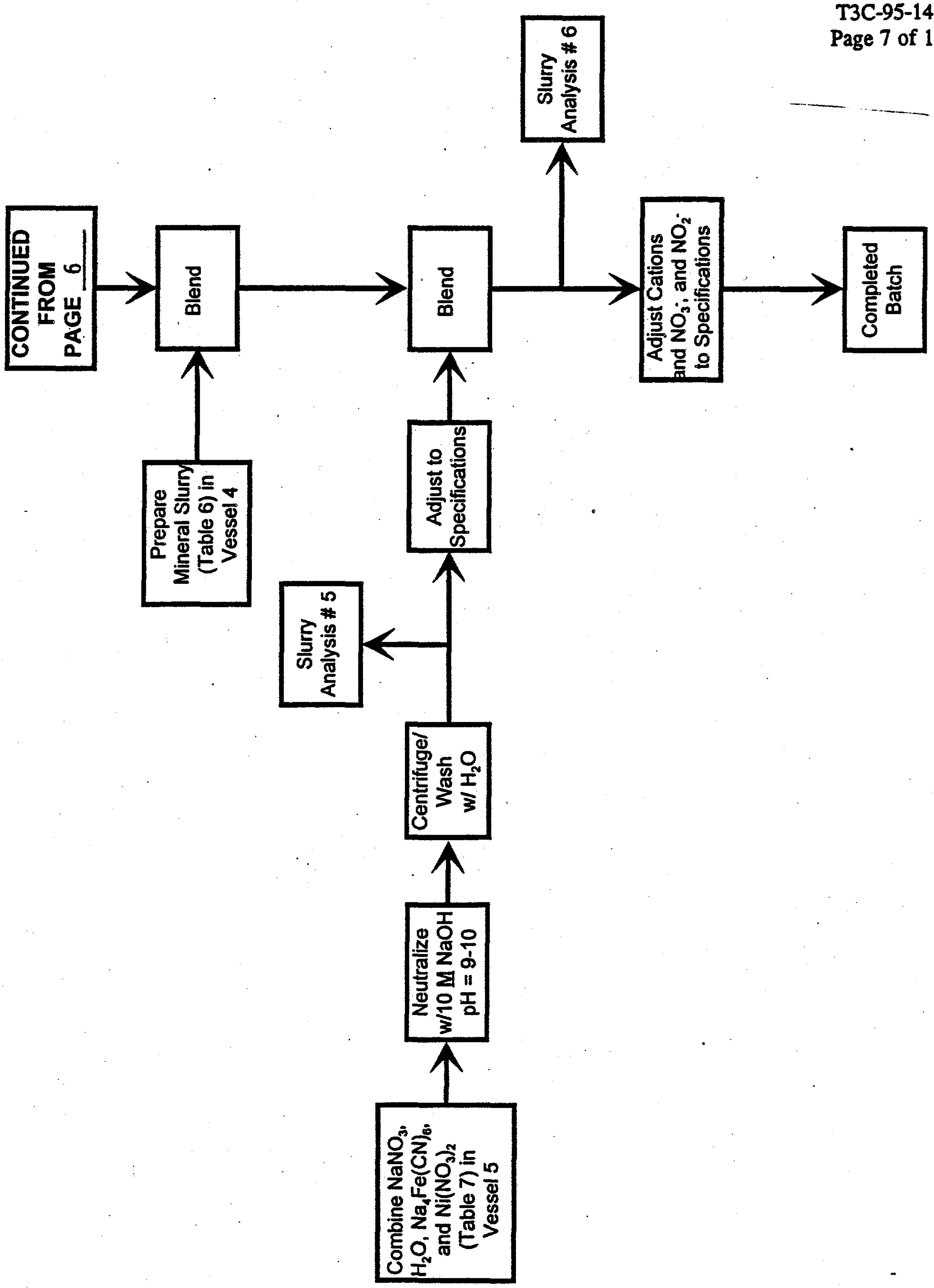


Figure 1. HLW Blend Simulant Preparation Flowsheet


CONTINUED FROM PAGE 6
Blend
Prepare Mineral Slurry (Table 6) in Vessel 4
Combine NaNO$_3$, H$_2$O, Na$_4$Fe(CN)$_6$, and Ni(NO$_3$)$_2$ (Table 7) in Vessel 5
Neutralize w/10 M NaOH pH = 9-10
Centrifuge/ Wash w/ H$_2$O
Slurry Analysis # 5
Adjust to Specifications
Blend
Slurry Analysis # 6
Adjust Cations and NO$_3^-$, and NO$_2^-$ to Specifications
Completed Batch

2.0 HLW BLEND SIMULANT PREPARATION PROCEDURE

Chemicals added as solids are to be in the form of fine powders to ensure that complete dispersion and homogeneity will occur. This may require some chemicals to be ground or crushed prior to addition. The use of a grinder pump or other shearing device to assure solids are broken down is acceptable. Highly toxic and carcinogenic materials are indicated in the tables by shading. These materials should be handled in ventilated areas with appropriate personnel protection.

The vessels used in this procedure should be equipped with a cooling capabilities, an agitating impeller, and tank ventilation. During the preparation, slurry temperatures should be maintained below 40°C to control exothermic reactions during the hydroxide precipitation steps. Agitation times should be sufficient to ensure complete dispersion and homogeneity of the slurries. Determination of the appropriate agitation times is left up to the user.

The capacity of the tanks used will determine the number of washing steps required to remove excess sodium nitrate. Analysis steps are to only be used as verification that all the chemicals were added and added in the correct amounts. Uncertainties in the analytical data should be considered before the use of these measurements for chemical adjustments.

A centrifuge should be used for all the solids separation steps. Primary constraints in the selection of solids separation methods include retention of solids to meet total quantity requirements and prevention of conditions that will alter physical properties and/or chemical species of components. Results of previous work at PNL have shown that the chemical species of iron and zirconium can be affected on exposure to air. For this reason, separation methods should be chosen to limit the solids concentration of the slurries to a maximum of 30 wt% during intermediate processing steps. Using a settle/decant separation method is not recommended due to the potential formation of a suspension that gels and requires large quantities of dilution water and extended settling times.

Quantities of the components used to prepare the simulant are identified in the following procedure by [X], where X is A, B, C, etc. Values of A, B, C, etc. can be found in the tables. Highly toxic or carcinogenic components are shaded and no radioactive constituents are added.

2.1 Preparation of Major Component Slurry

This part of the procedure provides instructions to precipitate MnO_2 and neutralize, precipitate, and wash a major component hydroxide slurry. Quantities of the components can be found in Table 2.

A. Charge vessel 1 with [A] L of water.

B. Add [B] g of manganese nitrate $\{Mn(NO_3)_2\}$ solution while continuously stirring. Maintaining the temperature between 35°C and 40°C will hasten $Mn(NO_3)_2$ dissolution.

Table 2: Major Components(a)

Item	Component	Unit	Quantity
[A]	Dilution Water	L	100
[B]	$Mn(NO_3)_2$	g	$3.62x10^3$
[C]	$KMnO_4$	g	$9.31x10^2$
[D]	Dilution Water	L	100
[E]	Dilution Water	L	300
[F]	$Fe(NO_3)_3\cdot 9H_2O$(b)	g	$6.23x10^4$
[G]	$ZrO(NO_3)_2$	g	$1.68x10^4$
[H]	$Ni(NO_3)_2\cdot 6H_2O$(c)	g	$5.83x10^3$
[I]	$Nd(NO_3)_3\cdot 6H_2O$	g	$2.79x10^4$
[J]	20 M NaOH	L	100
[K]	Wash Water	L	700

C. In a separate vessel, blend [C] g of potassium permanganate {$KMnO_4$} with [D] L of water under constant agitation. Adjust the temperature to 35°C to 40°C to assure the permanganate will fully dissolve.

D. Pump the permanganate solution (prepared in step C) into vessel 1 containing the $Mn(NO_3)_2$ (prepared in step B) at a rate such that the temperature of the slurry does not increase above 40°C. During this step, insoluble MnO_2 will form.

(a) Highly toxic or carcinogenic components are shaded.

(b) If sodium nickel ferrocyanide is omitted or if the amount is decreased from the value given in section 2.6, the amount of iron should be increased to account for the iron that would have been added with the sodium nickel ferrocyanide.

(c) If sodium nickel ferrocyanide is omitted or if the amount is decreased from the value given in section 2.6, the amount of nickel should be increased to account for the nickel that would have been added with the sodium nickel ferrocyanide.

E. With continued agitation, add [E] L of water, [F] g of ferric nitrate nonahydrate {$Fe(NO_3)_3 \cdot 9H_2O$}, [G] g of zirconium nitrate pentahydrate {$Zr(NO_3)_4 \cdot 5H_2O$}, [H] g of nickel nitrate hexahydrate {$Ni(NO_3)_2 \cdot 6H_2O$}, and [I] g of neodymium nitrate hexahydrate {$Nd(NO_3)_2 \cdot 6H_2O$} to vessel 1.

F. Agitate until the nitrates are completely dissolved. Please note that precipitated MnO_2 will not dissolve during this step.

G. In a separate vessel, prepare a 20 M NaOH solution of approximate volume [J] L.

H. Stirring constantly, add approximately [J] L of 20 M NaOH solution slowly to the solution in vessel 1 until the pH is in the range of 10 to 11 and stable (a variation of not more than ± 0.2 pH units over 10 minutes). Control NaOH addition rate and provide cooling if necessary during NaOH addition to maintain the temperature of the slurry below 40°C.

I. After a pH between 10 and 11 is reached, continue to agitate the slurry for 1 hour. If the pH has dropped below 10 after the 1 hr mixing period, add additional NaOH to return the pH to between 10 and 11.

J. Perform water wash/solids separation sequence (using a centrifuge and leaving a final volume such that the weight percent solids of the slurry is less than 20 wt%) to lower the total amount of soluble nitrate to less than 15 g for every liter of final total volume (i.e. 1000 L). It is estimated, based on past preparations, that 2 to 3 equivalent volumes, a total of [K] L of water, will be needed to reduce the amount of nitrate below the maximum allowable limit. SOLIDS CONCENTRATION MUST BE MAINTAINED BELOW 30 wt% DURING SEPARATION PROCESS so Zr and Fe species are not exposed to air.

K. Agitate the contents in vessel 1 and collect a representative sample for analysis. Analyze the sample (slurry analysis 1) and determine the amount of nitrate and cations retained in the slurry to confirm sufficient washing has occurred to decrease the nitrate and that major cationic species have not been lost (except for sodium). Major cations, excluding Na, should be within ±10% of target values listed in Table 2. The amount of nitrate retained should be less than 15 g for every liter of the final total volume (i.e. 1000 L).

2.2 Addition of Soluble and Slightly Soluble Components

This part of the procedure provides instructions to add the soluble and slightly soluble components to the major hydroxide slurry. Quantities of the components can be found in Table 3.

A. While continuously agitating vessel 1, add the soluble and slightly soluble components to the vessel in the order and amounts shown in Table 3. <u>The carcinogenic and highly toxic components should be pre-slurried in a ventilation hood using water with the appropriate respiratory precautions and poured into vessel 1.</u>

B. Agitate the vessel contents and collect a representative sample for analysis. Analyze the sample (slurry analysis 2) to confirm the amount of components in the slurry. Major cations should be within ±10% of target values listed in Table 2 and the soluble/slightly soluble components should be within ±15% of the values specified in Table 3.

Table 3: Soluble and Slightly Soluble Components(a)

Item	Component	Unit	Quantity
[A]	$NaCl$	g	$6.70x10^{1}$
[B]	$Na_2WO_4 \cdot 2H_2O$	g	$3.09x10^{2}$
[C]	$NaIO_3$	g	$6.20x10^{-2}$
[D]	$SnCl_2 \cdot 2H_2O$	g	$3.29x10^{-1}$
[E]	KOH	g	$3.31x10^{2}$
[F]	Na_2SO_4	g	$7.36x10^{2}$
[G]	$CuSO_4 \cdot 5H_2O$	g	$3.56x10^{1}$
[H]	H_3BO_3	g	$1.67x10^{2}$
[I]	Na_3PO_4	g	$1.36x10^{4}$
[J]	Na_2CO_3	g	$3.78x10^{3}$
[K]	$Na_2C_2O_4$	g	$4.59x10^{3}$
[L]	$Ba(OH)_2\ 8H_2O$	g	$5.58x10^{1}$
[M]	MoO_3	g	$9.19x10^{1}$
[N]	Sb_2O_3	g	$2.58x10^{1}$
[O]	Re_2O_7	g	$5.95x10^{-1}$
[P]	$CsNO_3$	g	$2.09x10^{1}$
[Q]	$Sr(NO_3)_2$	g	$1.06x10^{3}$
[R]	SeO_2	g	$3.05x10^{1}$

(a) Highly toxic or carcinogenic components are shaded.

2.3. Preparation and Addition of Minor and Insoluble Components Slurry

This part of the procedure provides instructions to neutralize, precipitate, and wash a mixture of minor components and insoluble chemicals. Quantities of the components can be found in Table 4.

A. To a second vessel (vessel 2) add approximately [A] L of water. Add components [B] through [Y] given in Table 4 in the order and amount shown. Any insoluble components should be ground to a maximum diameter of 0.1 mm prior to being introduced to the tanks.

B. In a separate vessel, prepare 10 M NaOH solution of approximate volume [Z] L.

C. Stirring constantly, add approximately [Z] L of 10 M NaOH solution slowly to the solution in vessel 2 until the pH is in the range of 10 to 11 and stable (a variation of not more than ± 0.2 pH units over 10 minutes). Control NaOH addition rate and provide cooling if necessary during NaOH addition to maintain the temperature of the slurry below 40°C.

D. After a pH between 10 and 11 is reached, continue to agitate the slurry for 1 hour. If the pH has dropped below 10 after the 1 hr mixing period, add additional NaOH to return the pH to between 10 and 11.

E. In a separate vessel, prepare a 0.1 M NaOH solution of approximate volume [AA] L.

F. Perform the wash/solids separation sequence (using a centrifuge and leaving a final volume such that the weight percent solids of the slurry is less than 20 wt%) to lower the amount of soluble nitrate less than 5 g for every liter of final total volume (i.e. 1000 L). The wash solution is to be a 0.1 M NaOH solution which will preserve the high pH of the solution. It is estimated based on past preparations, that 2 to 3 equivalent volumes, a total of [AA] L, of the NaOH solution will be needed to reduce the NO_3^- concentration below the maximum allowable limit.

G. Agitate the vessel contents and collect a representative sample for analysis. Analyze the sample (slurry analysis 3) and determine the amount of components retained in the slurry to confirm sufficient washing has occurred and that ionic species (except sodium) have not been lost. The amount of nitrate retained should be less than 5 g for every liter of the final total volume (i.e. 1000 L). The minor and insoluble components should be within ±15% of the values specified in Table 4.

H. Transfer the washed slurry to the blend in vessel 1 as shown in Figure 1.

Table 4: Minor Component Nitrates and Insolubles[a]

Minor Components				Insolubles			
Item	Compound	Unit	Quantity	Item	Compound	Unit	Quantity
[A]	Dilution Water	L	355	[P]	GeO_2	g	2.24×10^{-2}
[B]	$Cd(NO_3)_2 \cdot 4H_2O$	g	2.72×10^{2}	[Q]	HgO	g	1.04×10^{1}
[C]	$Cr(NO_3)_3 \cdot 9H_2O$	g	2.98×10^{3}	[R]	LaF_3	g	6.43×10^{2}
[D]	$Ce(NO_3)_3 \cdot 6H_2O$	g	8.62×10^{3}	[S]	Li_2O	g	8.63×10^{-1}
[E]	$Co(NO_3)_2 \cdot 6H_2O$	g	4.47×10^{1}	[T]	NaF	g	1.04×10^{3}
[F]	$Ca(NO_3)_2 \cdot 4H_2O$	g	1.08×10^{4}	[U]	Nb_2O_5	g	1.16×10^{-5}
[G]	$Mg(NO_3)_2 \cdot 6H_2O$	g	6.12×10^{2}	[V]	NdF_3	g	1.19×10^{2}
[H]	$Bi(NO_3)_3 \cdot 5H_2O$	g	5.07×10^{3}	[W]	Ta_2O_5	g	5.15×10^{-1}
[I]	$Pr(NO_3)_3 \cdot 6H_2O$	g	6.23×10^{1}	[X]	TeO_2	g	3.65×10^{0}
[J]	$Sm(NO_3)_3 \cdot 6H_2O$	g	1.12×10^{0}	[Y]	TiO_2	g	8.69×10^{0}
[K]	$Y(NO_3)_3 \cdot 6H_2O$	g	4.19×10^{1}	[Z]	10 M NaOH	L	50
[L]	$Zn(NO_3)_2 \cdot 6H_2O$	g	7.95×10^{1}	[AA]	0.1 M NaOH	L	200
[M]	$AgNO_3$	g	7.64×10^{0}				
[N]	$RbNO_3$	g	1.19×10^{1}				
[O]	$Pb(NO_3)_2$	g	5.56×10^{2}				

(a) Highly toxic or carcinogenic components are shaded.

2.4 Preparation and Addition of Noble Metals

This part of the procedure provides instructions to neutralize, precipitate, and wash a mixture of noble metals (Ru, Pd, and Rh). Quantities of the components can be found in Table 5.

A. Prepare the noble metal solution in vessel 3 by placing [A] g of $Rh(NO_3)_3$, [B] g of $RuNO(NO_3)_3$, and [C] g of $Pd(NO_3)_2$ in [D] L of 4 M HNO_3.
B. Add 10 M NaOH, approximately [E] L to the noble metal slurry until pH reaches 7.5 ± 0.5. A brown precipitate will form around a pH of 6.
C. Boil slurry for 10 minutes or until the supernate becomes clear.
D. Perform a wash/solids separation sequence (using a centrifuge and leaving a final volume such that the weight percent solids of the slurry is less than 20 wt%) to lower the amount of soluble nitrate to less than 5 g per final total volume (i.e. 1000 L). The wash solution is to be deionized water. It is estimated based on past preparations, that 2 to 3 equivalent volumes of water, a total of [F] L, will be needed to reduce the nitrate concentration below the maximum allowable limit.
E. Agitate the vessel contents and collect a representative sample for analysis. Analyze the sample (slurry analysis 4) and determine the amount of nitrate and cations retained in the slurry to confirm sufficient washing has occurred and that cationic species have not been lost. The amount of nitrate retained should be less than 5 g for every liter of the final total volume (i.e. 1000 L). The noble metal components should be within ±15% of the values specified in Table 5. Document the composition of the product slurry.
F. Transfer the washed slurry to the blend in vessel 1 as shown in Figure 1.

Table 5: Noble Metals Slurry Components[a]

Item	Component	Unit	Amount
[A]	$Rh(NO_3)_3$	g	$3.64x10^1$
[B]	$RuNO(NO_3)_3$	g	$1.49x10^2$
[C]	$Pd(NO_3)_2$	g	$3.48x10^1$
[D]	4 M HNO_3	L	25
[E]	10 M NaOH	L	5
[F]	Wash Water	L	25

(a) Highly toxic or carcinogenic components are shaded.

2.5 Preparation and Addition of Minerals

This part of the procedure provides instructions to prepare a mineral slurry. Quantities of the components can be found in Table 6.

A. Place [A] g of $Al_2Si_2O_5(OH)_4$ in a furnace and heat to 650°C. Hold at that temperature for 3 to 4 hours and cool.

B. To a fourth vessel (vessel 4) , add [B] L deionized water. Add [C] g of $NaNO_3$ and [D] g of NaOH will continuously stirring.

C. Add 1.03×10^4 g of the calcined $Al_2Si_2O_5(OH)_4$ while continuously stirring. Digest at 80°C for 5 hours with slow stirring.

D. Agitate the vessel contents and collect a representative sample for analysis. Analyze the sample (slurry analysis 5) and verify that cancrinite $\{Na_8Al_6O_{24}(NO_3)_2 \cdot 4H_2O\}$ was made. Document the composition of the product slurry.

E. Add approximately [E] L of water. Add components [F] through [H] given in Table 6 in the order and amount shown. This slurry should be prepared in a hood due to the carcinogenic nature of SiO_2 with respiratory protection provided for personnel protection. Any insoluble components should be ground to a maximum diameter of 0.1 mm prior to being introduced to the tanks.

F. Transfer the slurry to the blend in vessel 1 as shown in Figure 1.

Table 6: Mineral Phase Components[a]

Item	Compound	Unit	Amount
[A]	$Al_2Si_2O_5(OH)_4$	g	1.20×10^4
[B]	Dilution Water	L	4.00×10^4
[C]	$NaNO_3$	g	1.36×10^4
[D]	NaOH	g	6.40×10^3
[E]	Dilution Water	L	250
[F]	AlOOH	g	1.43×10^4
[G]	SiO_2	g	3.09×10^3
[H]	Na_2SiO_3	g	9.40×10^3

(a) Highly toxic or carcinogenic components are shaded.

2.6 Preparation and Addition of Sodium Nickel Ferrocyanide[a]

This part of the procedure provides instructions to prepare $Na_2NiFe(CN)_6$ (Scheele et al. 1992). Quantities of the components can be found in Table 7.

A. To a fifth vessel (vessel 5), add [A] L of 4 M $NaNO_3$ solution. Add [B] g of $Na_4Fe(CN)_6$ while stirring continuously.

B. In a separate vessel, dissolve [C] g of $Ni(NO_3)_2$ in deionized water. Stirring constantly, slowly add the dissolve $Ni(NO_3)_2$ to vessel 5.

C. Add approximately [D] L of 10 M NaOH solution slowly to the solution in vessel 5 until the pH is in the range of 9 to 10 and stable (a variation of not more than ± 0.2 pH units over 10 minutes).

D. After a pH between 9 and 10 is reached, continue to agitate the slurry for 1 hour at 70°C. If the pH has dropped below 9 after the 1 hr mixing period, add additional NaOH to return the pH to between 9 and 10. Turn heat off, and continue to stir for 12 hours or more.

E. Perform the wash/solids separation sequence (using a centrifuge and leaving a final volume such that the weight percent solids of the slurry is less than 20 wt%) to lower the amount of soluble nitrate to less than 5 g for every liter of the final total volume (i.e. 1000 L). The wash solution is to be deionized water. It is estimated based on past preparations, that 2 to 3 equivalent volumes of water, a total of [E] L, will be needed to reduce the nitrate concentration below the maximum allowable limit.

F. Agitate the vessel contents and collect a representative sample for analysis. Analyze the sample (slurry analysis 6) by drying in a vacuum oven at 60°C overnight and performing XRD analysis to verify that sodium nickel ferrocyanide was produced.

G. Transfer the washed slurry to the blend in vessel 1 as shown in Figure 1.

Table 7: Sodium Nickel Ferrocyanide Slurry Components[b]

Item	Compound	Unit	Amount
[A]	4 M $NaNO_3$	L	15
[B]	$Na_4Fe(CN)_6$	g	5.47×10^3
[C]	$Ni(NO_3)_2$	g	3.29×10^3
[D]	10 M NaOH	L	8
[E]	Wash Water	L	50

(a) This procedure produces a form of cyanide equivalent to the form of cyanide in the tanks (verified by XRD analysis). Currently, PNL is verifying that the CN source is sodium nickel ferrocyanide. If any changes to this procedure are needed, a revision will be issued.

(b) Highly toxic or carcinogenic components are shaded.

2.7 Final Blend Adjustment

This part of the procedure provides instructions to make the final concentration adjustments and lists the final requirements of the blend.

A. Agitate the vessel and collect a representative slurry sample of the final blend. Analyze the sample (slurry analysis 7) to determine the amount of the components. Major oxides, excluding sodium, should be within ±10% of the values listed in Table 2. All other components must be with ±15% of the values specified in Tables 3 through 8. The weight percent solids should be between 15% and 20%.

B. Adjust the nitrate, nitrite, and sodium concentrations using the values specified in Table 8. Nitrite should not be added until just before use because the nitrite degrades in the slurry. Sodium as NaOH should be added last since sodium will be also added in with the nitrate and nitrite.

C. The chemical composition and the physical properties of the slurry will constitute part of the acceptance documentation. The specifications required for acceptance are outlined in Section 3.0.

Table 8: Final Nitrate, Nitrite, and Sodium Ion Concentrations(a)

Item	Ion	Source	Target Concentration (g ion/L)
[A]	NO_3^-	$NaNO_3$	3.29×10^1
[B]	NO_2^-	$NaNO_2$	1.74×10^0
[C]	Na^+	NaOH	2.51×10^1

(a) Highly toxic or carcinogenic components are shaded.

3.0 REQUIREMENTS AND SPECIFICATIONS

1. The values of the following physical properties must be reported with the documentation:

- weight percent solids
- pH
- gWO/L
- density

2. Meeting the following specifications for the chemical composition is required. Certification must be included with the documentation:

Weight Percent Solids	15 to 20%
Major Oxides (excluding Na):	± 10% of values in Table 2
Other Oxides	± 15% of values in Tables 3, 4, 5, 6, and 7
Anions (excluding NO_2^-) and Total Organic Carbon	± 15% of values in Tables 3 and 4
Sodium (before final adjustment)	<0.4 g/L
Nitrite (before final adjustment)	<1.7 g/L
Nitrate (before final adjustment)	<32.9 g/L

3. Feed-stock chemicals are to be technical grade quality. Certification by the vendor of such (i.e. copies of supplier certification , etc) is required and copies must be included with the shipping documentation.

4. With the approval of a PNL technical representative, solutions of the nitrate chemicals or species having different waters of hydration can be used as starting material in place of the materials identified in the tables as long as the metal valence state remains the same.

4.0 REFERENCES

Agnew, S.F. 1994. *Hanford Defined Wastes: Chemical and Radionuclide Composition*. LAUR-94-2657, Los Alamos National Laboratory, Los Alamos, New Mexico.

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Scheele, R.D., L.L. Burger, J.M. Tingey, R.T. Hallen and M.A. Lilga. 1992. *Chemical Reactivity of Potential Ferrocyanide Precipitates in Hanford Tanks with Nitrates and Nitrites*. WM 1992 Conference Proceedings, Tuscon, Arizona.