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Low-Level Tank Waste Simulant Data Base

R. O. Lokken

April 1996

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352



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SUMMARY

The majority of defense wastes generated from reprocessing spent N-reactor fuel at Hanford are stored in underground Double-Shell Tanks (DST) and in older Single-Shell Tanks (SST). The Tank Waste Remediation System (TWRS) Program has the responsibility of safely managing and immobilizing these tank wastes for disposal. A reference process flowsheet is being developed that includes waste retrieval, pretreatment, and vitrification. Prior to the decision to vitrify the low-level wastes (LLW), the disposal choice for Hanford DST LLW was to solidify the liquid wastes using cementitious grouts. Several DSTs were sampled and characterized and waste simulants were prepared for testing the grouting process. Most of the testing was done with simulants because of the large quantities required and the hazards associated with using actual radioactive tank wastes. Although several simulants were prepared and tested for use in the grout disposal tests, their use in LLW vitrification testing is limited because characterization data was limited to chemical analyses and density measurements and because their compositions did not reflect any changes that would occur as result of ion exchange, blending, and evaporation. However, observations from some of the grout simulant studies indicated that precipitation of aluminum hydroxide could occur when the Al/OH ratio approached or exceeded one and that sodium phosphate may crystallize at ambient temperatures and/or when the phosphate levels were above about 0.2 molar.

For the first phase of LLW vitrification simulant development, two waste compositions were investigated. The simulated wastes were based on the analyses of six tanks of DSSF waste and on the projected composition of the wastes exiting the pretreatment operations. A simulant normalized to 6 M sodium was based on the anticipated concentration after ion exchange and initial separations. A 10 M sodium simulant would represent a waste that had been concentrated by evaporation to reduce the overall volume. A third LLW simulant, referred to as the remaining inventory, included wastes not included in the DSSF tanks and the projected LLW fraction of single-shell tank wastes. Additional simulant compositions will be developed and tested as retrieval sequences, blending strategies, and pretreatment flowsheets become finalized.

Laboratory prepared simulants were characterized for settled solids, density, viscosity, moisture content, and chemical analyses. Following laboratory development and characterization of the simulants, a procedure was recommended for use in preparing large quantities of LLW simulant for use in the melter vendor tests. About 42,000 liters of simulant were prepared for use in melter vendor testing and about 940 liters were prepared for use in small-scale testing at PNL. Chemical analyses of these simulants are reported and compared with the target composition.

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ACRONYMS

CC	Complexant Concentrate
CVS	Composition Variation Study
DSSF	Double-Shell Slurry Feed
DST	Double-Shell Tank
GDP	Grout Disposal Program
ICP	Inductively Coupled Plasma spectroscopy
LLW	Low-Level Waste
NCRW	Neutralized Cladding Removal Waste
PNL	Pacific Northwest Laboratory
PSW	Phosphate-Sulfate Waste
RI	Remaining Inventory
SST	Single-Shell Tank
TWRS	Tank-Waste Remediation System
WHC	Westinghouse Hanford Company

INTRODUCTION

The majority of defense wastes generated from reprocessing spent N-reactor fuel at Hanford are stored in underground Double-Shell Tanks (DST) and in older Single-Shell Tanks (SST) in the form of liquids, slurries, sludges, and salt cakes. The Tank Waste Remediation System (TWRS) Program has the responsibility of safely managing and immobilizing these tank wastes for disposal. A reference process flowsheet is being developed that includes waste retrieval, pretreatment, and vitrification.

Prior to the decision to vitrify the low-level wastes (LLW), the disposal choice for Hanford DST LLW was to solidify the liquid wastes using cementitious grouts. Westinghouse Hanford Company (WHC) managed the Grout Disposal Program (GDP) and Pacific Northwest Laboratory (PNL) provided support through tank waste characterization, simulants development, waste form development and testing, radioactive grout testing, pilot-scale tests, and performance assessments. Several types of liquid LLW were investigated for their potential disposal via grouting. These included Phosphate/Sulfate Waste (PSW), Neutralized Cladding Removal Waste (NCRW), Complexant Concentrate (CC), Double Shell Slurry Feed (DSSF), and Concentrated Phosphate Waste, i.e., from Tank 241-AN-106 (106-AN). Limited studies were performed with NCRW (Serne et al 1992) and with CC (Shade et al 1986). Extensive laboratory and pilot-scale studies have been conducted with PSW (Lokken et al 1987, Fow et al 1987, Serne et al 1992), DSSF (Claghorn 1987, Lokken 1992b,c Lokken and Martin 1992, Serne et al 1992, Whyatt 1994), and 106-AN (Bagaasen 1993, Hammitt and Welsh 1993, Lokken 1992a, Lokken et al 1993, Serne et al 1992, Serne et al 1989, Welsh 1994a). Several simulants of these waste types were prepared and the compositions and densities of selected DSSF and 241-AN-106 simulants and actual DST waste are reported.

Currently, PNL is assisting in the development of waste forms for vitrifying Hanford LLW and supporting the Westinghouse Hanford Company melter technology selection. An integral part of the process is to identify, prepare, and characterize representative LLW simulants for use in these studies. During FY-94, procedures were developed for preparing waste simulants for use in laboratory vitrification studies and for Phase I vendor

melter tests described in the PNL Project Work Plan and the WHC Vendor Test Statement of Work (Wilson 1994), respectively.

SCOPE

This report discusses three principal topics: the need for and the basis for selecting target or reference LLW simulants, tank waste analyses and simulants that have been defined, developed, and used for the GDP, and activities in support of preparing and characterizing simulants for the current LLW vitrification project. The procedures and the data that were generated to characterize the LLW vitrification simulants were reported by Lokken and Martin (1994) and for the most part, are presented in this report. Analyses of simulants prepared at Optima Chemicals for use by the melter vendors for Phase I testing, and for a simulant prepared at PNL for use in small-scale melter testing in direct support of the melter vendor tests are presented. The final section of this report addresses the applicability of the data to the current program and presents recommendations for additional data needs including characterization and simulant compositional variability studies.

LOW-LEVEL TANK WASTE SIMULANTS

One of the most important activities in waste form development and testing is the development of a suitable simulant that matches as closely as possible the characteristics of the actual waste stream that will be processed. Ideally, preparation of a waste simulant would follow the same chemical processes that were used to produce the waste. In practice, however, this is impractical because of the numerous processes and process conditions that have been employed at the site during the many years of operation and because of the lack of post-process characterization data. Other factors, such as time/temperature/radiation effects can be highly variable and nearly impossible to duplicate in the laboratory. As an alternative to process simulation, the actual waste would be "fully" characterized for important chemical and physical properties. A waste simulant could then be defined, prepared, and characterized to determine how well its properties match those of the actual waste. However, because of the varied nature of the actual

wastes and because of difficulties associated with representative sampling and precise characterization, simulants are often based on "best estimates" or "target" compositions of the actual wastes. Typical testing strategies also include simulant verification by conducting a limited number of tests with actual wastes.

Further difficulties encountered with producing representative simulants include cases where the waste streams cannot be defined because of unknown future process conditions, such as retrieval schemes and sequences, pretreatment operations, blending sequences, etc. In these cases, simulants are generally defined as an overall "volume-weighted" average composition based on a combination of waste tank analyses, waste volume projections, process knowledge, and/or other factors.

GROUT DISPOSAL PROGRAM SIMULANTS

Several DSTs have been sampled and characterized as part of an ongoing activity to determine the physical and chemical properties of the wastes stored at Hanford. Table 1 lists the concentration of some of the major species reported for eleven DSTs. The compositions of some of these tanks served as the basis for defining "reference" compositions for use in developing simulants and grout waste forms. For example, a Double-Shell Slurry Feed (DSSF) for use in grouting tests was based on analyses of tanks 241-AN-103 and 241-AW-101 (Claghorn 1987). Other simulants used in the GDP were based on the analyses of individual tanks, i.e., tank 241-AN-106 and 241-AP-102. Target compositions for the simulants representing these three wastes are shown in Table 2. The DSSF simulant composition was decreased by 50% from that reported in Claghorn (1987) because of the higher-than-allowable concentration of heat-producing radionuclides (Hendrickson 1991). The data in Table 1 also illustrate the variability in reported concentrations of species for individual tanks. For example, the analyzed Na concentration in tank 241-AW-101 ranges from 10 to 13.4 moles/L. These discrepancies, whether due to errors in sampling, inhomogenieties within the tank, sample preparation, analytical, or other factors, need to be addressed when preparing and testing simulants.

The effects of variability in the waste simulant compositions on grout properties have been reported (Hammit and Welsh 1993, Lokken et al 1993, Lokken et al 1987, Lokken and Martin 1992). The purpose of the waste compositional variability studies was to address the uncertainties associated with tank waste sampling and analyses and to define acceptable operating windows for which the grout process could produce acceptable waste forms. Another approach to waste variability was proposed in Anderson and Lokken (1993)^(a) by including waste ions as variables in a statistically designed study for formulation development of grouts. The results of this study would have allowed the grout formulation (i.e., dry blend component ratios) to be tailored to a specific waste composition once detailed chemical analyses of a candidate waste tank were available. A statistically designed Composition Variation Study (CVS) was conducted at PNL for defining high-level waste glass compositions (Hrma and Piepel et al 1994)^(b). This study, however, did not use waste simulants; rather, the waste constituents were added to the glass melts individually either as oxides or carbonates.

The simulants used for the GDP were generally solutions, because the GDP mission was to dispose of the liquid portion of the tank wastes. However, small quantities of solids were present in the tank waste samples and in the simulants, especially in the waste variability studies (Hammit and Welsh 1993, Lokken et al 1993, Lokken et al 1987, Lokken and Martin 1992). The phosphate concentration in the simulants representing both the 241-AN-106 and 241-AP-102 tanks exceeded the sodium phosphate solubility limits at room temperature, necessitating maintaining the simulants at temperatures above 40°C to prevent crystallization. Aluminum hydroxide precipitates can also be formed when the Al/OH ratio increases past one, either through intentional pH adjustments (Lokken 1992c) or by carbonation of the solutions.

(a) Anderson, C. M. and R. O. Lokken. 1993. Test Matrix for Grout Waste Envelope Study. HGTP-93-0307-01 (Draft), Pacific Northwest Laboratory, Richland, Washington.

(b) Hrma, P. R. and G. F. Piepel. 1994. Property/Composition Relationships for Hanford High-Level Waste Glasses Melting at 1150°C. PVTD-C95-02.01B, Pacific Northwest Laboratory, Richland, Washington.

TABLE 1. Reported Concentrations of Select Major Species in Double-Shell Tank Wastes

Tank	Reported (Analyzed) Concentration, M/L					References
	Al	Na	NO ₂	NO ₃	OH	
241-AN-103	2.5	13	2.2	3.5	5.7	Hendrickson (1990)
241-AN-103	1.5	12.9	3.29	2.94	5.6	Claghorn (1987)
241-AN-103	2.13	14.6	2.99	2.58	5.74	Shade (1994)
241-AN-104	1.6	11.2	2	3	4	Hendrickson (1990)
241-AN-104	1.39	12	1.92	3.1	4.09	Shade (1994)
241-AN-105	1.74	12	2.61	3.12	3.64	Shade (1994)
241-AN-106	0.39	5.3	0.73	1.3	0.71	Hendrickson (1990)
241-AN-106	0.4	4.1	0.83	1.43		Serne et al. (1989)
241-AN-106	0.46	5.3	0.8	1.45	1.35	Serne et al. (1989)
241-AN-106	0.344	3.93	0.644	1.1	0.474	Shade (1994)
241-AP-102	0.43	4.4	0.78	1.22	0.54	Welsh (1994a)
241-AP-105	0.43	7.3	1.05	2.69	3.17	Welsh (1994b)
241-AP-105	0.16	6.35	1.09	2.66	4.63	Shade (1994)
241-AP-106	0.008	0.24	0.03	0.07	0.08	Welsh (1994c)
241-AW-101	0.94	11	1.8	4.6	5.8	Hendrickson (1990)
241-AW-101	1.03	10	2.16	3.46	5.07	Hendrickson (1991)
241-AW-101	1.29	13.4	2.28	3.62	4.73	Hendrickson (1991)
241-AW-101	1.14	13	1.82	4.22	5.45	Claghorn (1987)
241-AW-101	1.03	10	2.19	3.46	5.07	Shade (1994)
241-AW-102	1.9	10.4	1.7	2.8	4.8	Hendrickson (1990)
241-AW-106	1.9	11.1	3.1	2.8	3.1	Hendrickson (1990)
241-SY-101	1.7	12.6	2.4	2.5	2	Hendrickson (1990)

TABLE 2. Target Compositions of Double-Shell Tank Simulants Used for the Grout Disposal Program

<u>Species</u>	<u>DSSF</u> ^(a)	<u>106-AN</u> ^(b)	<u>102-AP</u> ^(c)
Al	7.52E-01	4.21E-01	3.41E-01
B	9.71E-03	5.00E-04	2.60E-03
Ba	4.54E-03	8.00E-04	
Ca	4.99E-03		1.86E-03
Cr	2.21E-02	1.20E-02	
Fe	2.52E-02	2.00E-04	
K	2.49E-01		2.46E-02
Mg			1.07E-04
Mn	5.00E-02		
Mo	5.11E-04		
Na	5.30E+00	4.73E+00	3.95E+00
Si	1.99E-02	2.00E-04	1.58E-03
Zn	2.49E-02		
Cl	1.09E-01	1.50E-01	6.75E-02
CO ₃	1.50E-01	3.82E-01	3.41E-01
NO ₂	5.00E-01	7.58E-01	5.34E-01
NO ₃	2.49E+00	1.30E+00	1.13E+00
PO ₄	5.95E-02	1.55E-01	1.96E-01
SO ₄	5.26E-02	3.10E-02	2.73E-02
OH	2.05E+00	6.75E-01	4.97E-01
TOC	1.07E-01	4.14E-01	2.38E-01

(a) Reported in Lokken (1992b), Whyatt (1994)

(b) Reported in Lokken (1992a)

(c) Reported in Lokken et al (1993), Bagaasen (1993), Hendrickson and Welsh (1992)

Work with simulants is more convenient and often necessary because of costs or hazards associated with using actual radioactive wastes. This is especially true when large volumes of wastes are required. For the GDP, more than 75,000 L of simulated PSW waste (Fow et al. 1987), 10,000 L of simulated DSSF (Whyatt 1994), and 13,000 L of simulated 106-AN waste (Bagaasen 1993) have been prepared and used in pilot-scale and laboratory studies at PNL.

Simulants also allow for the determination of leach rates of low-activity radionuclides, when their presence would be masked by the higher-activity radionuclides (Serne 1992).

LLW VITRIFICATION SIMULANTS

For the first phase of LLW vitrification simulant development, two waste compositions were investigated. The simulated wastes were based on the analyses of six tanks of DSSF waste and on the projected composition of the wastes exiting the pretreatment operations (Shade 1994). A simulant normalized to 6 M sodium was based on the anticipated concentration after ion exchange and initial separations. A 10 M sodium simulant would represent a waste that has been concentrated by evaporation to reduce the overall volume. Development and characterization of this simulant is described in the following sections.

A third LLW simulant, referred to as the remaining inventory, included wastes not included in the DSSF tanks and the projected LLW fraction of single-shell tank wastes (Shade 1994). This waste was originally to be used in the second phase of melter system testing. Additional simulant compositions will be developed and tested as retrieval sequences, blending strategies, and pretreatment flowsheets become finalized.

LABORATORY DEVELOPMENT OF LLW VITRIFICATION SIMULANT

Laboratory tests were conducted to develop procedures that could be used for producing large quantities of LLW simulant for use in the melter vendor tests and in various laboratory studies. Simulants were prepared with reagent-grade chemicals to obtain the ionic concentrations listed in Table 3. The target values in Table 3 are estimated from the projected compositions of LLW discharged from the pretreatment and separation processes and from the initial characterization data for the starting waste compositions reported by Hendrickson and Conner (1994). The concentrations of several species (i.e. Mo, Sr, Cs, and IO_4) have been set higher than analyzed in order to monitor their behavior during vitrification. Molybdenum was used as a stand-in for technetium in these studies because of their similar chemical characteristics.

For each of the three simulants listed in Table 3, two solutions were prepared - one containing the acid-soluble compounds and the other containing the alkaline or neutral compounds. The final simulants were prepared by adding the acid solution to the alkaline solution. Separate acid and alkaline solutions were studied because it was not known whether significant quantities of precipitates would be present in the final simulant that would result in difficulties in providing a uniform feed to the melters.

The compounds and their concentrations used to prepared each of the three simulants are listed in Tables 4 through 6. The acid and alkaline compounds were added (in the order listed in the tables) to approximately 300 ml of water in a polypropylene jar. The solutions/slurries were constantly agitated during the chemical addition. The solutions/slurries were not heated during preparation; any temperature changes were from the heat of solution of the salts. After all the chemicals had been added, the solution/slurry was transferred to a graduated cylinder and the volume adjusted to 500 ml (for the acid and alkaline portions of each of the simulants). The densities of the solutions were then determined from the weight of 500 ml of solution. Final simulants were prepared by adding equal volumes of the acid components to the alkaline components. The simulant mixtures were constantly agitated until no more solids dissolved.

TABLE 3. Target Concentrations of Low-Level Waste Simulants for Vitrification Development, moles/L

<u>Component</u>	<u>DSSF 6 M Na</u>	<u>DSSF 10 M Na</u>	<u>Remaining Inventory</u>
Al	0.61	1.02	0.16
Ca	0.00063	0.00105	0.0004
Cr	0.0052	0.00867	0.0042
Fe	0.00046	0.000767	0.00024
K	0.30	0.50	0.0058
Mg	0.00062	0.00103	0.0000011
Mn	0.00025	0.000417	0.001
Mo	0.01	0.0167	0.01
Na	6.0	10.0	6.0
Sr	0.01	0.0167	0.01
Cs	0.01	0.0167	0.01
PO ₄	0.026	0.0433	0.11
IO ₃	0.01	0.0167	0.01
CO ₃	0.16	0.267	0.05
Cl	0.096	0.127	0.0092
F	0.15	0.25	0.13
SO ₄	0.026	0.0433	0.038
NO ₃	1.9	3.11	3.5
NO ₂	1.0	1.67	0.26
OH	2.3	3.8	1.5
TOC	0.81	1.35	0.11

TABLE 4. Recipe for DSSF Vitrification Simulant Normalized to 6 M Na

Compound	M/L	g/L
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.61	228.84
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.00063	0.15
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.0052	2.08
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.00046	0.19
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.00062	0.16
$\text{Mn}(\text{NO}_3)_2$ (50% sol'n)	0.00025	0.0447
$\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$	0.01	2.42
CsNO_3	0.01	1.95
Na_4EDTA	0.081	33.71
Total Acidic Compounds		269.54

NaNO_2	1	69.00
KOH	0.3	16.83
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	0.01	2.67
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.026	3.59
NaIO_3	0.01	1.98
Na_2CO_3	0.16	16.96
NaCl	0.076	4.44
NaF	0.15	6.30
Na_2SO_4	0.026	3.69
NaOH (pellets)	4	160.00
Total Alkaline Compounds		285.46

TABLE 5. Recipe for DSSF Vitrification Simulant Normalized to 10 M Na

Compound	M/L	g/L
$Al(NO_3)_3 \cdot 9H_2O$	1.02E+00	381.39
$Ca(NO_3)_2 \cdot 4H_2O$	1.05E-03	0.25
$Cr(NO_3)_3 \cdot 9H_2O$	8.67E-03	3.47
$Fe(NO_3)_3 \cdot 9H_2O$	7.67E-04	0.31
$Mg(NO_3)_2 \cdot 6H_2O$	1.03E-03	0.26
$Mn(NO_3)_2$ (50% sol'n)	4.17E-04	0.0746
$Na_2MoO_4 \cdot H_2O$	1.67E-02	4.03
$CsNO_3$	1.67E-02	3.25
Na_4EDTA	1.35E-01	56.19
Total Acidic Compounds		449.23

$NaNO_2$	1.67E+00	115.00
KOH	5.00E-01	28.05
$SrCl_2 \cdot 6H_2O$	1.67E-02	4.44
$NaH_2PO_4 \cdot H_2O$	4.33E-02	5.98
$NaIO_3$	1.67E-02	3.30
Na_2CO_3	2.67E-01	28.27
NaCl	1.27E-01	7.40
NaF	2.50E-01	10.50
Na_2SO_4	4.33E-02	6.16
NaOH (pellets)	6.67E+00	266.67
Total Alkaline Compounds		475.76

TABLE 6. Recipe for Remaining Inventory Vitrification Simulant
Normalized to 6 M Na

Compound	M/L	g/L
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.16	60.02
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	4.00E-04	0.09
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	4.20E-03	1.68
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	2.40E-04	0.10
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.10E-06	0.0003
$\text{Mn}(\text{NO}_3)_2$ (50% sol'n)	1.00E-03	0.1789
$\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$	0.01	2.42
CsNO_3	0.01	1.95
NaNO_3	3	255.00
$\text{Sr}(\text{NO}_3)_2$	0.01	2.12
Na_4EDTA	0.011	4.58
Total Acidic Compounds		328.14

NaNO_2	0.26	17.94
KOH	5.80E-03	0.33
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.11	15.18
NaIO_3	0.01	1.98
Na_2CO_3	0.05	5.30
NaCl	9.20E-03	0.54
NaF	0.13	5.46
Na_2SO_4	0.038	5.40
NaOH (50% Soln)	2.2	176.00
Total Alkaline Compounds		228.12

RECOMMENDED PROCEDURE FOR LLW SIMULANT PREPARATION

The following procedure was recommended for preparing 10 M simulated LLW for use in laboratory studies and for the Phase I melter vendor tests (Lokken and Martin 1994, Shade 1994). Preparation of a single solution was recommended because of the larger amount of solids present in the separate acid and alkaline solutions.

Start with water at approximately 60 vol% of the final solution volume required. Add the appropriate amounts of the following compounds in the order listed to the water while maintaining constant agitation (note: the solution may be heated to approximately 60°C to aid dissolution):

<u>Compound</u>	<u>g/L</u>
NaNO ₂	115
KOH	28.1
SrCl ₂ ·6H ₂ O	4.44
NaH ₂ PO ₄ ·H ₂ O	5.98
NaIO ₃	3.30
Na ₂ CO ₃	28.3
NaCl	7.40
NaF	10.5
Na ₂ SO ₄	6.16
NaOH	266
Al(NO ₃) ₃ ·9H ₂ O	381
Ca(NO ₃) ₂ ·4H ₂ O	0.25
Cr(NO ₃) ₃ ·9H ₂ O	3.47
Fe(NO ₃) ₃ ·9H ₂ O	0.31
Mg(NO ₃) ₂ ·6H ₂ O	0.26
Mn(NO ₃) ₂	0.075
Na ₂ MoO ₄ ·H ₂ O	4.03
CsNO ₃	3.25
Na ₄ EDTA	56.2

SIMULANT PREPARATION FOR MELTER VENDOR TESTS

Three batches of a nominal 10 M Na LLW simulant were prepared at Optima Chemical Company (Optima) for use in the Phase I melter vendor tests. A total of about 42,000 liters were prepared. A 945-liter batch of simulant was also prepared at PNL for use in pilot-scale tests in support of the melter vendor tests (See Appendix A). The quantities of chemicals used for the production of these simulants are shown in Table 7. Several of the compounds specified in the recommended procedure (Lokken and Martin 1994) were substituted with solutions because the solid compounds were not commercially available (See Table 7 footnotes).

The simulants prepared at Optima were prepared in three batches. The first two batches were supposed to be 13,230 liters each, and the third was 15,540 liters. The following discussion summarizes procedures used at Optima as discussed in the trip reports.

OPTIMA CHEMICAL - BATCH 1^(a)

Two solutions, a basic and an acidic solution, were prepared for the first batch of simulant. The basic solution maintained a chalky white appearance throughout the chemical additions. The acidic solution was clear after adding the $Al(NO_3)_3$ and then turned to a milky green after all the chemicals had been added. Prior to adding the acidic solution to the basic solution, the basic solution was recirculated through a heat exchanger that kept the solution around 52°C. As the acidic solution was added to the basic solution, a foam layer formed near the center of the solution surface and the layer eventually grew to cover about 75% of the surface. The color of the resulting solution turned from milky white to milky gray and finally to milky deep olive green.

After the two solutions had been prepared, it was recognized that the combined volumes of the two solutions would exceed the desired final volume of

(a) Optima Trip Report - Observe LLW (DSSF) Simulant Preparation, August 16, 1994, Internal Memo from Regan Seymour to Vitrification Development, Westinghouse Hanford Company, Richland, Washington.

simulant, i.e., ~13,200 liters. The overage was attributed to a miscalculation in the volume of the $\text{Al}(\text{NO}_3)_3$ and NaEDTA solutions added to the acidic solution. Several options to recover the simulant concentration were discussed and it was agreed that the current batch of simulant would be split in half. To one of the halves, the basic chemicals for the second simulant batch would be added but using solid NaOH flake instead of the 50% solution. The acidic solution for the second batch would be made in a separate tank and added to the basic solution. The remaining half of the first batch would then be recirculated with the other half of the first batch containing the second batch acidic and basic materials to form the final simulant.

OPTIMA CHEMICAL - BATCH 2^(a)

Approximately 8300 liters of the Batch 1 simulant was transferred to a 17,000-liter storage tank (ST1), leaving about 7500 liters in the original tank (Tank A). The acidic solution was prepared in a second 17,000-liter tank (Tank B). The resulting solution turned a dark violet color over time and the volume was ~6800 liters. The basic solution was prepared in the original tank which contained simulant from Batch 1. After addition of all the chemicals, the volume was ~10,600 liters and the solution was a milky olive green color. The acidic solution in Tank B was slowly added to the basic solution in Tank A. After all of the solution was added, Tank A contained ~17,400 liters of simulant, having a deep olive green color.

The simulants from Batches 1 and 2 were then mixed. One half of the contents of Tank A was transferred to Tank B and the solution in Tank ST1 was transferred into Tanks A and B in roughly equal proportions. Approximately 230 liters of wash water and 1625 liters of additional makeup water were added to Tank A to achieve the desired 26,460 liters of mixed simulant. The two tanks were valved to allow withdrawal from the bottom of each tank by a single pump. The solutions were mixed at the pump and transferred to the top of each tank in two relatively equal streams. After mixing for 3 hours, seven samples were taken for analyses.

(a) Optima Trip Report - Batch #2, August 24, 1994, Internal Memo from Eric Slaathaug to E. T. Weber, Westinghouse Hanford Company, Richland, Washington.

OPTIMA CHEMICAL - BATCH 3(a)

The acidic solution for Batch 3 was prepared by adding the chemicals (mostly in the form of solutions) to a 18,900-liter tank. The solution was a clear yellow color after addition of $\text{Al}(\text{NO}_3)_3$ and turned to a milky green at the end of the acid chemical additions. After sampling, the color of the solution appeared to be milky purple, rather than the green color seen in the tank.

The basic solution was also prepared in a 18,900-liter tank. The basic chemicals except for NaNO_2 and NaOH were added to ~1500 liters of water. After finding a ring of solids around the tank, an additional 750 liters of water were added before adding the NaNO_2 and NaOH . The NaNO_2 was added, and as the NaOH was added, the viscosity of the solution decreased until about 65% of the NaOH had been added. At this point, the solution quickly gelled, resulting in a sticky solid salt cake that froze the agitator. Addition of small quantities of the acid solution and manual mixing were required to dissolve the basic solution around the agitator. After about 1500 liters of acid solution were added incrementally to the basic solution, the acid solution was added slowly and continuously until about half (~3800 liters) had been added. Acid additions were then stopped because of high temperatures within the tank.

After the basic solution had cooled overnight, the remaining NaOH and acid solution were added. During the acid addition, a 15- to 20-cm thick foam formed on the surface of the solution which eventually increased in thickness up to ~46 cm. Spraying the remaining acid solution onto the foam broke up the layer, with a release of NO_x , and allowed a continuous addition until all the acid solution had been added.

(a) Optima Trip Report - Observe DSSF Simulant Preparation: 3rd Batch, August 16, 1994, DSI from R. G. Seymour to E. T. Weber, Westinghouse Hanford Company, Richland, Washington.

TABLE 7. Batch Sheet for Preparation of 10 M Na LLW Simulant at Optima Chemical for Melter Vendor Tests and at PNL for a Pilot-Scale Test. (See Appendices A, B, and C)

Compound	Moles/ Liter	Optima Chemical			PNL
		Batches 1&2		Batch 3	Pilot-Scale
		kg/ 13,230 L	kg/ 13,230 L	kg/ 15,540 L	kg/945 L
Al(NO ₃) ₃ ·9H ₂ O ^(a)	1.02	5084.09	5083.36	5950.80	383.5
Ca(NO ₃) ₂ ·4H ₂ O ^(b)	0.001	3.15	3.15	3.66	0.23
Cr(NO ₃) ₃ ·9H ₂ O ^(c)	0.0087	6.00	6.02	7.04	3.27
Fe(NO ₃) ₃ ·9H ₂ O ^(d)	0.00077	0.58	0.57	0.67	0.29
KOH	0.5	372.49	372.49	436.28	26.40
Mg(NO ₃) ₂ ·6H ₂ O ^(e)	0.001	3.42	3.39	3.99	0.25
Mn(NO ₃) ₂	0.00042	1.00	0.98	1.16	0.07
Na ₂ MoO ₄ ·H ₂ O	0.017	54.63	54.63	25.35	3.80
SrCl ₂	0.017	35.81	35.81	41.92	2.49
CsNO ₃	0.017	44.00	44.00	51.53	3.06
NaH ₂ PO ₄ ·H ₂ O	0.043	68.51	68.51	80.27	5.62
NaIO ₃	0.017	44.91	44.91	52.31	3.11
Na ₂ CO ₃	0.27	380.07	380.07	440.70	26.59
NaCl	0.13	97.83	97.83	114.57	6.97
NaF	0.25	139.44	139.44	163.34	9.89
Na ₂ SO ₄	0.043	81.14	81.14	95.02	5.80
NaNO ₂	1.7	1557.74	1557.74	1824.45	108.23
NaOH	6.7	3559.71 ^(f)	3559.09	4168.43	125.45 ^(g)
Na ₄ EDTA	1.4	707.01 ^(h)			52.88
Na ₄ EDTA·2H ₂ O	1.4		706.88	827.89	

(a) Added as a 60 wt% solution

(b) Added as a 66 wt% solution

(c) Added as a 9.7 wt% Cr solution

(d) Added as a 10.5 wt% Fe solution

(e) Added as a 66 wt% solution

(f) Added as a 50 wt% solution

(g) This quantity is half the amount required. Adjustments were made when glass formers were added (See Appendix A)

(h) Added as a 38 wt% solution

CHARACTERIZATION

This section describes the tests that were conducted on the LLW simulants and the data collected to determine the quantity of settled solids, density, viscosity, water content, and chemical composition. Where data were reported on other simulants or actual waste, these are also included in the tables.

SETTLED SOLIDS

The quantity of settled solids from the LLW vitrification simulant laboratory studies was estimated by allowing the freshly prepared solutions to remain undisturbed in a closed container until a clear supernate was observed and then estimating the total volume of solids by comparing the depth of solids to the total depth of sample. The two alkaline DSSF samples contained fairly large quantities of gelatinous solids (Lokken and Martin 1994). However, when mixed with their respective acid solutions, the total amount of solids was reduced to less than 5 vol%. The reduction in the solids content was likely because of the two-fold decrease in the overall concentration in the final solution.

The settling rates of the solids were very slow for the 6 M and 10 M Na DSSF, requiring several hours for a clear supernate to be seen. The remaining inventory (RI) simulant contained some light-colored undissolved solids that settled out rapidly (i.e., within minutes); and a finer, darker fraction that resembled the solids in the two DSSF simulants. Table 8 summarizes the estimated amount of settled solids for the laboratory-produced simulants, and from the PNL melter test and melter vendor test simulants.

An important property of slurries is the ability to resuspend the solids once they have settled to obtain a uniform feed to the vitrification facility. A qualitative evaluation of the "resuspendability" of the solids in the three laboratory-prepared simulants was done by allowing the solids to settle in a Teflon bottle overnight and then slowly turning the bottles end-over-end several times, each time inspecting the bottom for the presence of remaining solids. The solids in the 6 M and 10 M Na DSSF simulants and the finer, dark solids in the remaining inventory simulant were easily resuspended during the

first couple rotations of the bottles. The lighter-colored solids in the remaining inventory sample appeared gelatinous and "dripped" from the bottom when the bottle was inverted. After about five rotations of the bottle, all the solids were resuspended. Based on these observations, it appears that the solids in all the simulants could be easily resuspended by moderate agitation.

TABLE 8. Estimated Volume Percent Settled Solids After 24 Hours for LLW Vitrification Simulants

<u>Simulant</u>	<u>Mixture</u>
DSSF, 6 M Na ^(a)	<3
DSSF, 10 M Na ^(a)	<5
RI, 6 M Na ^(a)	10
DSSF, 10 M Na ^(b)	3.0
DSSF, 10 M Na ^(c)	2.7

(a) Simulants prepared in the laboratory

(b) Simulant from PNL small-scale test (See Appendix A)

(c) Batch 1 and 2 of Optima Chemical's simulant (See Appendix B).

DENSITY

Densities of the solutions/slurries were measured by weighing a known volume of the simulants. Table 9 summarizes the results of density determinations on the LLW vitrification simulants and reported values for tank waste samples and GDP simulants (note: the densities were either measured at ambient temperature, or the temperature was not reported).

TABLE 9. Densities of Simulated or Actual Wastes

<u>Simulant/Waste</u>	<u>Density, g/cm³</u>
DSSF, 6 M Na	1.31
DSSF, 10 M Na	1.42
RI, 6 M Na	1.28
DSSF, 10 M Na ^(a)	1.38
DSSF, 10 M Na ^(b)	1.45
DSSF, 10 M Na ^(c)	1.50
241-AN-106 ^(d)	1.23
241-AN-106 ^(e)	1.20
241-AW-101 ^(d)	1.56
241-AP-105 ^(d)	1.35
241-AP-105 ^(g)	1.336
241-AN-104 ^(d)	1.50
241-AN-105 ^(d,e)	1.50
241-AN-103 ^(d,e)	1.60
241-AN-102 ^(f)	1.2001
241-AP-106 ^(h)	0.9961
DSSF (GDP)	1.293

- (a) Simulant from PNL pilot-scale test (See Appendix A).
 (b) Batch 1 and 2 of Optima Chemical's Simulant (See Appendix B).
 (c) Batch 3 of Optima Chemical's Simulant (See Appendix C).
 (d) Reported in Shade (1994).
 (e) Reported in Hendrickson (1990).
 (f) Reported in Welsh (1994a).
 (g) Reported in Welsh (1994b).
 (h) Reported in Welsh (1994c).

VISCOSITY

Viscosity of the laboratory-produced LLW vitrification simulants was measured using a Haake Rotovisco RV20 using a CS20 measuring system and a DA45 sensor according to procedure WHC-053-01. The viscosities at room temperature (~23°C) are shown in Table 10.

TABLE 10. Viscosity of Laboratory-Prepared LLW Simulants

<u>Simulant</u>	<u>Viscosity, cP</u>
DSSF, 6 M Na	3.6 ± 0.2
DSSF, 10 M Na	11.1 ± 0.2
RI, 6 M Na	2.6 ± 0.2

MOISTURE CONTENT

Samples of the laboratory-produced and pilot-scale simulants were dried at 120°C in a vacuum oven for several days to determine evaporable water or moisture content. Table 11 shows the results calculated after allowing the samples to cool under desiccation. Exposure of the dried simulants to the atmosphere resulted in a rapid uptake of moisture because of the high salt content of the simulants. Moisture contents of samples from three waste tanks are also shown in Table 11.

TABLE 11. Moisture Content of Simulated or Actual Tank Waste Samples

<u>Simulant or Tank Waste</u>	<u>Moisture Content, wt%</u>
DSSF, 6 M Na	67
DSSF, 10 M Na	53
RI, 6 M Na	66
DSSF, 10 M Na ^(a)	57
241-AP-102 ^(b)	75
241-AP-105 ^(c)	60.3
241-AP-106 ^(d)	100.2

(a) From PNL pilot-scale test

(b) Reported in Welsh (1994a)

(c) Reported in Welsh (1994b)

(d) Reported in Welsh (1994c)

CHEMICAL ANALYSES

Chemical analyses were conducted on the LLW vitrification simulants to compare the analyzed concentrations with the target values. For the laboratory-produced samples, inductively coupled argon plasma emission spectrometry (ICP) was conducted with a Jarrell-Ash Model 975 ICP according to procedure PNL-AL0-211.2 Rev. 0. The solutions were acidified using 2 vol% nitric acid. Anion concentrations were measured using a Dionex Series 4000i Ion chromatograph according to procedure PNL-AL0-212 Rev. 1. Carbon analyses was conducted using a Xertex-Dohrmann Model DC-80 carbon analyzer according to procedure PNL-AL0-382.1 Rev. 0. The free hydroxide content was determined by titration. A summary of the analytical results are shown in Table 12. The analyzed composition of all of the major species in the laboratory-produced simulant, except for hydroxide and carbonate, were within 10% of the target composition. The hydroxide content for the DSSF simulants averaged about 23% lower than the target value and the average carbonate concentrations were ranged from 54 to 78% higher than the target values. These discrepancies are not unexpected because atmospheric CO₂ is readily absorbed by highly alkaline solutions consuming free hydroxide and producing additional carbonate ions.

Table 13 lists the chemical analyses results of the LLW vitrification simulants prepared by Optima Chemical. The analyses were conducted both at PNL and by Quanterra (See Appendices B and C). Discussions regarding the applicability of the analyses to the needs of the program are found in the narratives of Appendices B and C and will not be repeated here.

TABLE 12. Analyzed Chemical Composition of Laboratory-Produced Simulants, moles/L.

Component	DSSF 6 M Na		DSSF 10 M Na		Remaining Inventory	
	Target	Analyzed	Target	Analyzed	Target	Analyzed
Al	0.61	0.61	1.02	0.95	0.16	0.16
Ca	0.00063	0.00055	0.00105	0.00060	0.0004	0.00015
Cr	0.0052	0.0052	0.00867	0.0083	0.0042	0.0041
Fe	0.00046	0.00061	0.000767	0.00097	0.00024	<0.00018
K	0.30	0.27	0.50	0.44	0.0058	<0.010
Mg	0.00062	<0.00058	0.00103	<0.0016	0.0000011	<0.00082
Mn	0.00025	0.00015	0.000417	0.00022	0.001	0.00062
Mo	0.01	0.01	0.0167	0.015	0.01	0.01
Na	6.0	5.7	10.0	9.07	6.0	5.6
Sr	0.01	0.01	0.0167	0.016	0.01	0.01
Cs	0.01	NA ^(a)	0.0167	NA ^(a)	0.01	NA ^(a)
PO ₄	0.026	0.027	0.0433	0.047	0.11	0.012
IO ₃	0.01	NA ^(a)	0.0167	NA ^(a)	0.01	NA ^(a)
CO ₃	0.16	0.29	0.267	0.41	0.05	0.04
Cl	0.096	0.094	0.127	0.17	0.0092	0.0062
F	0.15	0.12	0.25	0.32	0.13	0.12
SO ₄	0.026	0.027	0.0433	0.042	0.038	0.037
NO ₃	1.9	1.8	3.11	2.90	3.5	3.5
NO ₂	1.0	1.0	1.67	1.65	0.26	0.24
OH	2.3	1.8	3.8	2.8	1.5	1.5
TOC	0.81	0.78	1.35	1.15	0.11	0.11

(a) Not analyzed

TABLE 13. Chemical Analysis of LLW Simulant Prepared By Optima Chemicals

<u>Component</u>	<u>PNL^(a) moles/L</u>		<u>Quanterra^(b) moles/L</u>		<u>Target Values</u>
	<u>Batch 1&2</u>	<u>Batch 3</u>	<u>Batch 1&2</u>	<u>Batch 3</u>	
Al	0.96	1.15	0.95	1.31	1.02
Ca	0.0025	0.009	0.0029	0.0037	0.001
Cr	0.0062	0.01	0.0074	0.0104	0.0087
Fe	0.00072	0.0013	0.00068	0.00115	0.00077
K	0.51	0.61	0.45	0.58	0.5
Mg	0.0025	0.0021	0.0031		0.001
Mn	0.00047	0.00064	0.00044	0.0006	0.00042
Mo	0.0177	0.02	0.016	0.022	0.017
Na	9.52	10.6	8.53	10.46	10
Sr	0.016	0.018	0.013	0.015	0.017
Cs	0.0154	0.017	0.0196	0.027	0.017
PO ₄	0.036	0.039	0.038	0.036	0.043
IO ₃	0.0197	0.025		0.017	0.017
CO ₃	0.29	0.38	0.25	0.3	0.27
Cl	0.127	0.14	0.16	0.18	0.13
F			0.04	0.02	0.25
SO ₄	0.037	0.045	0.04	0.039	0.043
NO ₃	3.03	3.05	2.95	2.34	3.1
NO ₂	1.65	1.9	1.63	2.03	1.7
OH	3.04	3.75			3.8
TOC	1.45	1.65	1.46	0.87	1.4

(a) Analyses conducted by PNL (See Appendices B and C)

(b) Analyses conducted by Quanterra (See Appendices B and C)

DATA NEEDS AND RECOMMENDATIONS

Tank waste simulants have been used for many years on the GDP for developing grout formulations and for testing process conditions. The DST simulants were based on tank waste analyses and were generally more dilute than the actual tank wastes because of the need for blending with dilute tanks to reduce the concentration of heat-producing radionuclides. The only properties that were routinely measured for both the tank wastes and the simulants were chemical composition and density. Moisture content was reported for some of the DST waste samples.

The simulants proposed for the first phase of LLW melter vendor tests are also based on the analyses of DSTs; however, these simulants reflect compositional changes that could occur as the wastes undergo ion exchange and evaporation. The main emphasis of the current LLW vitrification simulant development was to develop and recommend a procedure for preparing large quantities of simulants for use in melter vendor tests. Although a procedure to prepare the simulant for melter vendor tests was proposed (Lokken and Martin 1994 and Shade 1994), the actual procedures used by the vendor (Optima Chemical) deviated from the recommended procedure because of reasons discussed above. Although the deviations in the procedures and potential implications were discussed with knowledgeable personnel prior to implementation, no laboratory data were available to substantiate the anticipated results. In addition, the only acceptance criteria for the simulants were based on composition determined from chemical analyses.

The following describes recommendations for future simulant development and characterization:

- 1) Prepare the simulant(s) at an ionic concentration expected at the exit of the ion exchange process, i.e., relatively dilute.
- 2) Concentrate the simulant(s) by evaporation and determine chemical composition and moisture content; measure density, undissolved solids, and viscosity as a function of temperature.

- 3) Substitute other compounds in the simulant preparation procedure; prepare and characterize as in 1 and 2 above.
- 4) Conduct waste simulant compositional variability studies; prepare and characterize as in 1 and 2 above.
- 5) Determine the effects of "spikes", i.e., species added at concentrations greater than the nominal or average levels, on the properties of simulants; prepare and characterize as in 1 and 2 above.
- 6) Perform confirmation tests with actual wastes when they become available.

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APPENDIX A

Shafer, Phyllis. "LLW Simulant", DSI to Ryan Lokken, 9/7/94.

Interoffice Memo

Date: 09/07/94
 To: Ryan Lokken
 From: Phyllis Shafer 
 Subject: LLW Simulant

I have gone over all of my analysis results for the simulant, and discovered that the only complete test results I have are for the feed samples with glass formers added. I don't have a complete analysis for this simulant, therefore I would strongly recommend that you have it analyzed before working with it. Keep in mind that when we made up the feed, we initially only added 1/2 of the required NaOH. Later, we discovered the mistake and fixed it when we added the glass formers. This sample is still short on NaOH. Without a more accurate analysis, I can't tell you how much NaOH needs to be added because I don't know how dilute/concentrated this sample is. I can only tell you how much of each chemical was added to make up this sample, but there was an unknown amount of additional water added.

Here is the chemical list that made up this feed:

Compound	total lb
Al(NO ₃) ₃ *9H ₂ O (60 wt% solution)	1330
Ca(NO ₃) ₂ *4H ₂ O	0.50
Cr(NO ₃) ₃ *9H ₂ O	7.20
Fe(NO ₃) ₃ *9H ₂ O	0.64
KOH	58.08
Mg(NO ₃) ₂ *6H ₂ O	0.55
Mn(NO ₃) ₂	0.15
Na ₂ MoO ₄ *2H ₂ O	8.36
SrCl ₂	5.48
CsNO ₃	6.74
NaH ₂ PO ₄ *H ₂ O	12.36
NaIO ₃	6.84
Na ₂ CO ₃	58.5
NaCl	15.34
NaF	21.76
Na ₂ SO ₄	12.76
NaNO ₂	238.1
NaOH	276
Na ₄ EDTA	116.34

Note: the NaOH quantity should have been 552 lb.

APPENDIX B

Kelly, S. E. "Analysis of Optima Chemicals' 10 Na Molar DSSF Simulant", DSI to W. B. Haskins, 9/8/94.

Don't Say It --- Write It!!!

September 8, 1994

From: S. E. Kelly *SEK* SEK File/LB
G6-08/6-1566

To: W. B. Haskins G1-61

cc: K. C. Burgard R4-01
W. C. Eaton H5-27
D. W. Hendrickson L5-31
B. A. Higley H5-27
R. O. Lokken P8-37
K. N. Pool P8-44
R. G. Seymour H5-27
E. J. Slaathaug H5-49
J. S. Shade
G. E. Stegen H5-27
J. M. Perez P7-41
C. N. Wilson *CNW* H5-27
E. T. Weber H5-27

ANALYSIS OF OPTIMA CHEMICALS' 10 Na MOLAR DSSF SIMULANT

Attached are a summary of the chemical additions and analyses of samples from the 7000 gallons of 10 molar sodium (Na) DSSF simulant manufactured at Optima Chemicals. The analysis from PNL and Quanterra were reported in draft reports. Values are not expected to change in the final reports.

Quanterra reported low values for nitrate, nitrite, carbonate, and fluoride, and a high value for alkalinity (hydroxide). The analyses of these analities are suspect and were not used in the acceptance of the simulant. Quanterra also reported a sodium concentration of 15% below the simulant target value. This is hard to explain with the alkalinity number so high.

PNL reported low values for sodium (7% or 0.7 moles/liter below target concentration), alkalinity (27% or 0.8 moles/liter below target concentration), and fluoride. Karl Pool, from PNL, stated that sodium fluoride would precipitate out in a 10 molar sodium solution and that this has been observed in the past. Therefore PNL chose not to report a final fluoride value in the DSSF solution (this also explains the low value reported by Quanterra). Optima Chemicals chemical addition records show the correct amount of fluoride added. The sodium and hydroxide values indicate that the simulant could be approximately 0.7 moles per liter short in sodium hydroxide (NaOH). Optima Chemicals chemical addition records and WHC personnel overseeing the addition of simulant compounds verify the correct addition of sodium hydroxide. All other simulant components as analyzed by PNL were reported within limits acceptable to the Low Level Waste Program.

Based on discussions with WHC personnel who witnessed chemical additions, Karl Pool of PNL, and Optima Chemicals' chemical addition records, TWRS Vitrification Development Sections recommends the acceptance of the 10 M Na as manufactured on August 16, 1994.

To Make Life Last - Put Safety First.

Analysis of Optima Chemicals' 10 Molar DSSF Simulant

S. E. Kelly
00-Sept-94

- ** PNL data from Karl Pool "Draft Report" dated September 7, 1994.
- ** Quanterra data from Wade H. Price facsimile dated September 2, 1994.
- ** 222-S information was relayed on sample status report for R 6243. MISC-1 (Georgia) dated August 30, 1994. The chain of custody was broken on this sample, however there was no mention of indications of sample tampering.
- ** Development data is from WHC-SD - WM - 11-624 Rev. 0.

Component	Atomic WL	Compound	Formula	Moles/L Required	Batch		Total Added moles/liter	Target moles/liter	PNL moles/liter	Quanterra moles/liter
					Datch 1 lbs./3500 gal	Datch 2 lbs./3500 gal				
Al+++	26.981	Al(NO3)3*9H2O	375.14	1.02	1183.4	1.02	1.02	0.98	0.95	
Ca++	40.08	Ca(NO3)2*4H2O	236.16	0.001	6.93	0.0010	0.001	0.0025	0.0028	
Cr++	51.996	Cr(NO3)3*9H2O	400.17	0.0087	13.192	0.0087	0.0087	0.0062	0.0074	
Fe+++	55.847	Fe(NO3)3*9H2O	404.01	0.00077	1.2705	0.00077	0.00077	0.00072	0.00088	
K+	39.102	KOH	56.1	0.5	819.4775	0.5	0.5	0.51	0.4	
Mg++	24.312	Mg(NO3)2*6H2O	256.41	0.001	7.524	0.001	0.001	0.0025	0.0031	
Mn++	54.938	Mn(NO3)2	178.94	0.00042	2.2	0.00042	0.00042	0.00047	0.00044	
Mo+8	95.94	Na2MoO4*H2O	241.95	0.017	120.196	0.017	0.017	0.0177	0.0165	
Na+	22.99					10.0	10.0	9.26	8.5	
Sr++	87.62	SrCl2	150.52	0.017	78.771	0.017	0.017	0.0160	0.0130	
Cs+	132.9	CsNO3	194.91	0.017	96.806	0.017	0.017	0.0154	0.0106	
PO4---	94.98	NaH2PO4*H2O	130	0.043	150.7177	0.037	0.037	0.036	0.038	
IO3---	174.9	NaIO3	197.89	0.017	98.3066	0.017	0.017	0.0187	--	
CO3--	60	Na2CO3	106	0.27	836.163	0.27	0.27	0.29	0.05	
Cl-	35.453	NaCl	58.45	0.13	215.2185	0.13	0.13	0.127	0.16	
F-	19	NaF	42	0.25	306.778	0.25	0.25	(note 2)	0.04	
SO4--	98.064	Na2SO4	142.06	0.043	178.503	0.043	0.043	0.037	0.040	
NO3-	62					3.11	3.1	3.03	0.67	
NO2-	44	NaNO2	69	1.7	3427.0368	1.7	1.7	1.65	0.50	
OH-	17	NaOH	40	6.7	7031.3536	6.7	6.7	3.04	18.9	
TOC	12	Na4EDTA (C10)	416.2	0.14	1555.416	0.14	0.14	1.45	1.40	
pH									13.5	

Notes: 1) Cr and Fe were added based on element weight (52 and 55.8 respectively) as others were added based on component weight.
2) Karl Pool believes that accurate fluoride analysis is impossible due to the solubility of NaF in a 10 molar HCl solution.

Analysis	Development		Laboratory	
	Data	PNL	222-S	
Density (g/ml)	1.42	1.453	1.4274	
% Sulfid Solids (volume)	<5		2.7	
% Centrifuged Solid (volume)			1.5	

APPENDIX C

Kelly, S. E. "Analysis of Optima Chemicals' 10 Na Molar DSSF Simulant October 13th Batch", DSI to W. B. Haskins, 11/10/94.

Don't Say It — Write It!!!

November 10, 1994

From: S. E. Kelly
G6-08/6-1566

SEK File/LB



To: W. B. Haskins G1-61

cc: K. C. Burgard	R4-01
W. C. Eaton	H5-27
D. W. Hendrickson	
B. A. Higley	H5-27
R. O. Lokken	P8-37
K. N. Pool	P8-44
R. G. Seymour	H5-27
J. S. Shade	
G. E. Stegen	H5-27
J. M. Perez	P7-41
C. N. Wilson	H5-27
E. T. Weber	H5-27



ANALYSIS OF OPTIMA CHEMICALS' 10 Na MOLAR DSSF SIMULANT OCTOBER 13th BATCH
Attached are a summary of the chemical additions and analyses of samples from the 4100 gallons (batch 3) of 10 molar sodium (Na) DSSF simulant manufactured at Optima Chemicals.

Quanterra reported low values for nitrate (12%) and total organic carbon (35%), and a high values for aluminum (28%), potassium (16%), and nitrite (41%).

PNL reported high values for aluminum (13%), potassium (22%), sodium (6%), carbonate (42%), and total organic carbon (22%). As with the analysis of the first batch of simulant, PNL did not report a value for fluoride due to its solubility in the simulant and the laboratories in-ability to accurately recover it.

Optima Chemicals' chemical addition records show all chemicals added in correct amounts. Additions were witnessed by a WHC representative, R. G. Seymour.

Review of laboratory data shows that this simulant batch appears to be more concentrated than the simulant manufactured on August 16, 1994. The density analyses also support this conclusion. The most important components of the simulant, which are out of specification, are aluminum and sodium. Aluminum is also a component of each melter vendors glass formers and the amount of deviation in the simulant should not adversely affect melter operations (it is possible that the aluminum nitrate solution used for production was more concentrated than expected). The sodium values for the two analyses agree well and an average value indicates that the simulant is just above the 10.5 mole/liter sodium specification. The sodium concentration should not adversely affect melter testing.

TWRS Vitrification Development Sections recommends the acceptance of the 10 M Na as manufactured on October 13, 1994.

To Make Life Last - Put Safety First.

Analysis of Optima Chemicals' 10 Molar DSSF Simulant Batch #3, Manufactured on October 13, 1994 (4,100 gallons)

S. E. Kelly
09 - Nov - 94

** PNL data is from a facsimile of the summary and discussion section of the final report.

** Quantities data from Wade H. Price report dated November 1, 1994

** Development data is from WHC-SD-WM-11-624 Rev. 0.

** Optima additions are from Regan Seymour's trip report dated October 14, 1994.

** Results from the August 16th batch (1 & 2) of 7000 gallons of simulant are provided for comparison.

Component	Atomic WL	Compound	Formula	Moles/L. Required	Batch 2, Optima Additions		10 Molar Na DSSF Simulant Batch 3				Batch 1 & 2 Results	
					lbs./4100 gal	moles/liter	Target	PNL	Quantities	PNL	moles/liter	Quantities
Al+++	26.981	Al(NO3)3·9H2O	375.14	1.02	1309.176	1.02	1.02	1.02	1.31	0.96	0.95	
Ca++	40.08	Ca(NO3)2·4H2O	236.16	0.001	0.052	0.0010	0.0010	0.0037	0.0025	0.0025	0.0025	
Cr+++	51.996	Cr(NO3)3·9H2O	400.17	0.0007	15.4012	0.0007	0.0100	0.0015	0.0002	0.0002	0.0074	
Fe+++	55.847	Fe(NO3)3·9H2O	404.01	0.00077	1.4005	0.00077	0.00130	0.00072	0.00072	0.00072	0.00088	
K+	39.102	KOH	56.1	0.5	959.8164	0.50	0.61	0.58	0.51	0.51	0.45	
Mg++	24.312	Mg(NO3)2·6H2O	256.41	0.001	6.776	0.0010	0.0021	---	0.0025	0.0025	0.0031	
Mn++	54.938	Mn(NO3)2	178.94	0.00042	2.55	0.00042	0.00064	0.00060	0.00047	0.00047	0.00044	
Mo+6	95.94	Na2MoO4·H2O	241.95	0.017	95.7596	0.017	0.020	0.022	0.0177	0.0177	0.016	
Na+	22.99					10.05	10.60	10.46	9.52	9.52	8.53	
Sr+++	87.62	SrCl2	150.52	0.017	92.216	0.017	0.018	0.015	0.0160	0.0160	0.013	
Cs+	132.9	CsNO3	194.81	0.017	133.3728	0.017	0.017	0.027	0.0154	0.0154	0.0186	
PO4---	94.00	NaH2PO4·H2O	130	0.043	176.5995	0.043	0.039	0.036	0.039	0.039	0.038	
IO3---	174.9	NaIO3	197.89	0.017	115.0048	0.017	0.025	0.017	0.0197	0.0197	0.016	
CO3---	60	Na2CO3	106	0.27	869.5285	0.27	0.30	0.30	0.29	0.29	0.25	
Cl-	35.453	NaCl	50.45	0.13	262.0477	0.13	0.14	0.18	0.127	0.127	0.16	
F-	19	NaF	42	0.25	359.1406	0.25	---	0.02	---	---	0.04	
SO4---	96.064	Na2SO4	142.06	0.043	209.0485	0.043	0.045	0.039	0.037	0.037	0.040	
NO3-	62					3.11	3.05	2.34	3.03	3.03	2.95	
NO2-	44	NaNO2	69	1.7	4013.7804	1.70	1.90	2.03	1.65	1.65	1.63	
OH-	17	NaOH	40	6.7	9170.646	6.70	3.75	---	3.04	3.04	---	
TOC	12	Na4EDTA (C10)	380	0.14	1021.3545	1.40	1.40	0.87	1.45	1.45	1.46	
pH								13.76				

Notes: 1 O, Fe, and Mo were added based on element weight (82, 55.8, and 95.9 respectively) all others were added based on component weight.

2 KeflPool(PNL) believes that accurate fluoride analysis is impossible due to the solubility of NaF in a 10 molar Na solution.

3 Quantities results for NO3 and NO2 were based on nitrogen (or 14g/mole).

4 Quantities results for CO3 (16) is based on Carbon (or 12g/mole).

5 Quantities results for PO4 is based on Phosphorus (or 30.97g/mole). (ASSUMPTION)

6 Quantities results for IO3 is based on Iodine (or 126.9g/mole). (ASSUMPTION)

Analysis		Development Data		Laboratory Data	
Density	(g/ml)	1.42	1.499	PNL	1.522
% Solified Solids	(volume)	<5			
% Centrifuged Solids	(volume)				