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# Simulation and Characterization of a Hanford High-Level Waste Slurry

R. L. Russell  
H. D. Smith

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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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Pacific Northwest National Laboratory  
Richland, Washington 99352

## QA Level

This work was performed to satisfy IHLW Glass Characterization Data Support milestone number H22A511E and was conducted in accordance with Impact Level II quality assurance requirements as defined by the PNNL *Quality Assurance Manual* PNNL-MA-70.

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## Summary

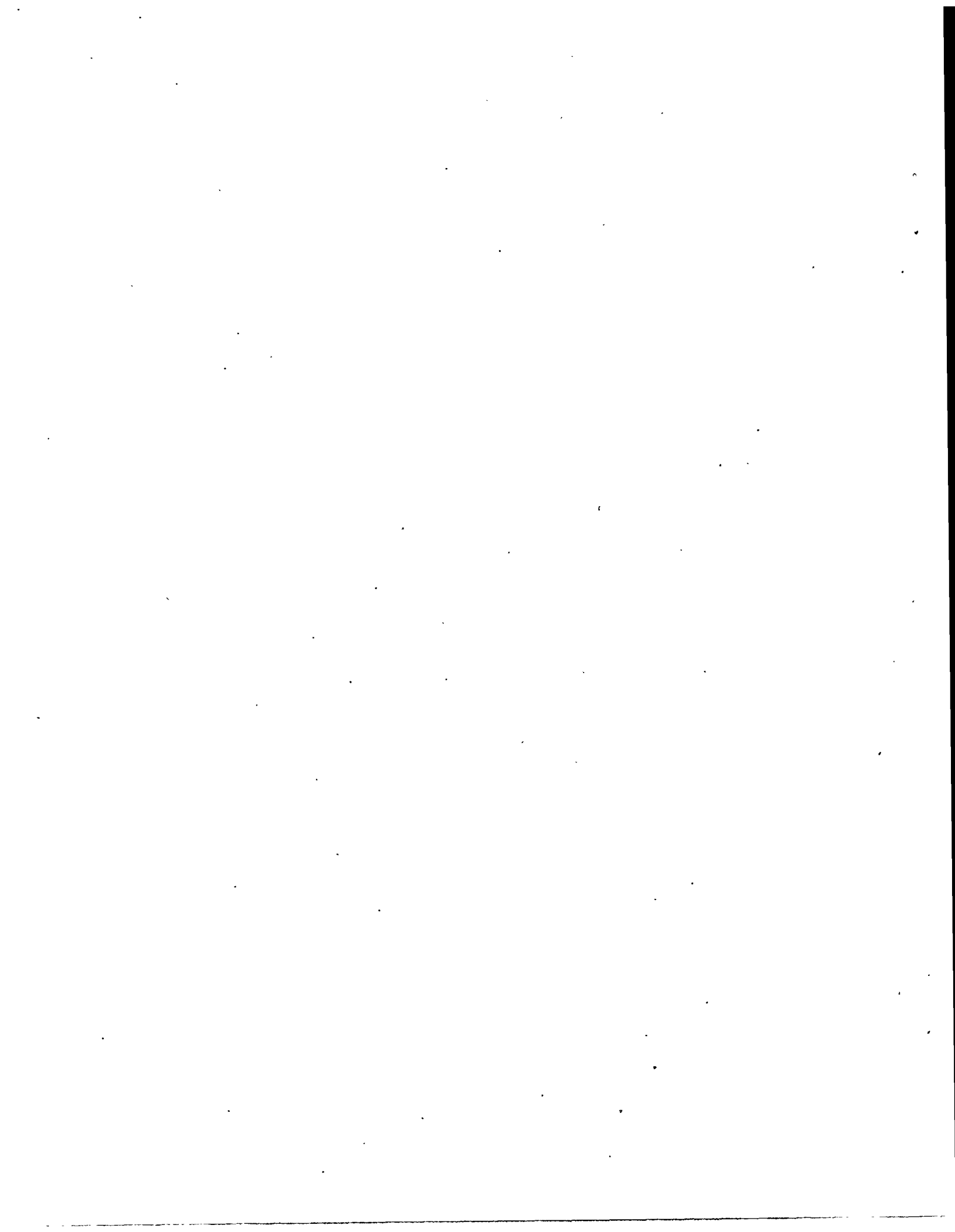
The baseline waste used for this simulant is a blend of wastes from tanks 101-AZ, 102-AZ, 106-C, and 102-AY that have been through water washing. However, the simulant used in this study represents a combination of tank waste slurries and should be viewed as an example of the slurries that might be produced by blending waste from various tanks. It does not imply that this is representative of the actual waste that will be delivered to the privatization contractor(s).

This blended waste sludge simulant was analyzed for grain size distribution, rheological properties both as a function of concentration and aging, and calcining characteristics. The grain size distribution allows a comparison with actual waste with respect to rheological properties. Slurries with similar grain size distributions of the same phases are expected to exhibit similar rheological properties. Rheological properties may also change because of changes in the slurry's particulate supernate chemistry due to aging. Low temperature calcination allows the potential for hazardous gas generation to be investigated.

The sludge simulant had a mean particle size (volume density) of 12.4 microns with the majority of the particles in the 7-22 micron range. This compares favorably with the actual waste which has particles sizes of 5.4 to 9.0 microns and is smaller than the NCAW simulant of 25.6 microns.

The simulant showed pseudoplastic behavior with increasing viscosity and yield stress with increasing weight percent solids. The viscosity and shear stress for the simulant were slightly higher than the actual waste but lower than the NCAW simulant. Neither the viscosity nor shear stress could be correlated as a function of solids loading or slurry age for either the 205 gWO/L or the 263 gWO/L slurries. However, the 125 gWO/L slurry did follow a trend of increasing viscosity and yield stress with age.

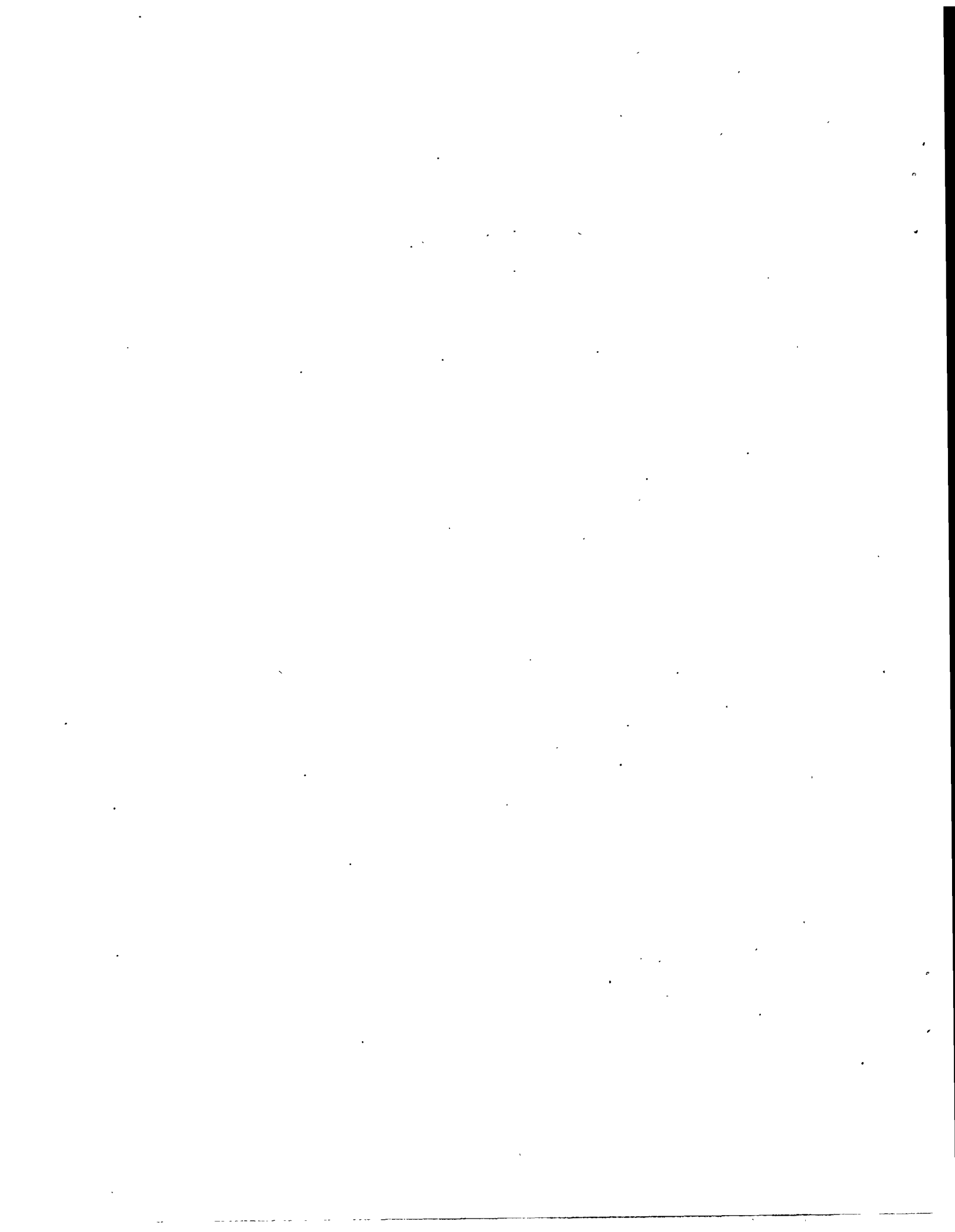
In the low temperature calcination test, essentially all of the water was driven off of the slurry before the temperature of the slurry rose significantly above 100°C. Both CO<sub>2</sub> and NO were detected. Other gases such as N<sub>2</sub>O and NO<sub>2</sub> were observed at trace levels (100 ppm) only. Ammonia was not observed at any time during the test.



## Abbreviations and Acronyms

g	gram
HLW	high-level waste
ICP	inductively coupled plasma
k	consistency factor
L	liter
mPa	millipascal
n	degree of non-Newtonian behavior
NCAW	neutralized current acid waste
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
R <sup>2</sup>	correlation coefficient
RFP	request for proposal
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company
WO	waste oxide
Wt%	weight percent
$\tau$	shear stress
$\tau_0$	yield stress
$\gamma$	shear strain rate





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## 1.0 Introduction

This report details work done for Westinghouse Hanford Company (WHC) by the Pacific Northwest National Laboratory (PNNL) in support of the Tank Waste Remediation System (TWRS) privatization activities by the Department of Energy at the Hanford site. The objective of this activity is to develop and verify a procedure for preparing simulated high-level waste (HLW) slurry similar in composition to that presented in the draft request for proposals (RFP). The base case waste used in these experiments is a blend of wastes from tanks 101-AZ, 102-AZ, 106-C, and 102-AY that have been through water washing.<sup>1</sup> The baseline feed composition was provided by WHC.<sup>2</sup> This simulant represents a combination of tank waste slurries and should be viewed as an example of the slurries that might be produced by blending waste from various tanks. It does not imply that this is representative of the actual waste that will be delivered to the privatization contractor(s).

The purpose of a simulant is to simulate chemical and physical properties of the waste that are important in the actual waste processing. A simulant is an engineered material that has the important physical properties of the actual waste slurry but does not have its radiological or toxicity hazards. To prepare an appropriate simulant, it is necessary to establish what the simulant must simulate; for example, a waste slurry will be characterized by rheological properties, solid phases present and their grain size distribution, and the tendency for a supernate to form. The waste slurry simulant in combination with other glass components should reproduce the melting characteristics of the actual waste glass batch.

The waste simulant should accurately simulate the actual waste in the following areas: rheology, calcining (alone and in combination with glass components), and glass batch melting. Rheological properties of a slurry typically depend on solids loading, the phases present and their grain size distribution, and the pH of the supernate. The calcining characteristics of the waste feed simulant are a function of the phases present and their grain size distribution. Melting of the feed is also most strongly influenced by the phases present and their grain size distribution. Hence, a good simulant will simulate the phase composition, grain size distribution and supernate pH of the actual waste slurry. In previous comparisons of HLW simulants and actual waste, the simulant's apparent viscosity was twice that of the actual waste. The simulant also was more chemically active during processing with formic acid than the actual waste (Morrey 1995). Hence, for these properties, the simulants provided conservatively high numbers, and any engineering design produced to handle the simulants would be more than adequate to handle the actual waste. Therefore, this blended waste sludge simulant was analyzed for grain size distribution, rheological properties both as a function of concentration and of aging, and calcining characteristics.

Previous HLW simulants were prepared with a neutralized current acid waste (NCAW) composition or an "all-blend" composition of the Hanford tanks, both of which exclude highly toxic and radioactive

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1. Lambert, Steve, Westinghouse Hanford Company, Personal Communication.
  2. Wasenfelder, DS. 1996. "Revised Estimates of Pretreated HLW Sludge Composition for Incorporation in Pacific Northwest National Laboratory's Feed Process Studies (Scheduled Activity Number H29A4)," (letter to ML Elliott, dated January 29, 1996), Westinghouse Hanford Company, Richland, WA.

elements (PNNL 1995). The specification for the preparation of RFP blended waste simulant uses a procedure similar to that of NCAW simulant. Highly toxic and radioactive species are either substituted or eliminated from the composition of the RFP simulant. The blended waste simulant preparation differs from the NCAW simulant in the source of aluminum.<sup>3</sup> The aluminum source in the NCAW simulant is precipitation of  $\text{Al}(\text{OH})_3$  by addition of  $\text{NaOH}$  to  $\text{Al}(\text{NO}_3)_3$ . In the blended waste simulant, aluminum is added as the mineral boehmite ( $\text{AlOOH}$ ). As with the NCAW simulant, the organic component of the waste blend simulant is added as oxalate because organic complexants in the waste tanks are expected to break down into oxalate (Agnew 1994, p. 50). The carbon in the washed and blended waste is expected to be mainly in the form of carbonate<sup>4</sup>, which is the form added to the simulant.

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3. Bunker, BC and NG Colton, Pacific Northwest National Laboratory, Personal Communication.

4. MaClean, Graham, Westinghouse Hanford Company, Personal Communication.

## 2.0 Slurry Preparation

A 16-liter batch of blended waste sludge simulant at 107.8 g waste oxide/L was prepared according to the following procedure (see Appendix A for complete procedure). The sludge simulant was prepared by first coprecipitating a hydroxide slurry from a nitrate solution containing the major waste elements (Fe, Ni, Nd, Zr, and Mn). The soluble and slightly soluble salts (halides, hydroxides, nitrates, nitrites, sulfates, borates, phosphates, oxides, and oxalates) were added dry to the major element slurry. Two other slurries were added to the major element, soluble and slightly soluble slurry: 1.) minor components as an insoluble-compound slurry (oxides, fluorides), and 2.) a mineral slurry. Excess sodium and nitrate were removed by washing both the major and minor component slurries separately with a solution of 0.4 g/L NaOH and 0.69 g/L NaNO<sub>2</sub>. The final weight percent solids of the sludge simulant was 13.5. The final composition of the sludge simulant is listed in Table 2.1. The table shows the results of inductively coupled plasma spectroscopy (ICP) analyses using both acid digestion and fusion preparation procedures. The two ICP analyses are compared to the actual batched concentration that represents estimates of the final slurry concentration based on mass balances around the feed preparation procedure. The difference between the ICP by acid digestion concentration and the actual added concentration can be attributed to incomplete digestion of the sample. The sample was digested in a solution of HNO<sub>3</sub> and HCl. However, the presence of the insoluble white precipitate reported to remain after the digestion would explain why the silicon is an order of magnitude less than the amount added to the batch and the calcium and lanthanum values were also low. Consequently, concentrations of the remaining elements were higher than what was actually added to the slurry. Therefore, the slurry was also analyzed with ICP after the sample was fused. As can be seen in Table 2.1, most of these numbers are much closer to the actual batched concentration. Calcium was low in both ICP analyses, however, and there is no apparent reason why. Because of the problems with the acid digestion, the analyses using the fusion were used for comparison with the target composition.

Programmatic changes in the target concentration were made after the sludge simulant preparation had been started. Therefore, several of the components were added to the original target concentration rather than the new target concentration, and consequently the final simulant concentrations differ from the final target concentrations. However, this simulant is still representative of possible privatization feeds. Table 2.2 compares the original and new target concentrations with the actual batched concentration.

Table 2.1. Final Slurry Composition

Element	ICP by acid digestion (g/L)	ICP by fusion (g/L)	Actual Batched (g/L)	Element	ICP by acid digestion (g/L)	ICP by fusion (g/L)	Actual Batched (g/L)
Ag	0.125	0.122	0.151	Mn	0.787	0.513	0.578
Al	7.5	7.31	9.46	Mo	---- <sup>(b)</sup>	0.038	0.007
B	0.14	0.043	0.044	Na	10.55	8.46	---- <sup>(a)</sup>
Ba	---- <sup>(b)</sup>	0.379	0.547	Nd	1.085	0.828	0.850
Ca	0.383	0.451	1.639	Ni	1.32	1.16	0.966
Cd	1.97	1.205	1.385	P	---- <sup>(b)</sup>	0.229	0.454
Ce	0.269	0.104	0.133	Pb	0.32	0.224	0.360
Cl	---- <sup>(b)</sup>	---- <sup>(b)</sup>	0.093	Re	---- <sup>(b)</sup>	---- <sup>(b)</sup>	0.100
Co	0.25	0.167	0.175	Sb	---- <sup>(b)</sup>	---- <sup>(b)</sup>	0.125
Cr	0.39	0.241	0.259	Se	---- <sup>(b)</sup>	---- <sup>(b)</sup>	0.143
Cu	---- <sup>(b)</sup>	0.038	0.056	Si	0.81	6.82	7.534
F	---- <sup>(b)</sup>	---- <sup>(b)</sup>	0.102	Sr	---- <sup>(b)</sup>	0.067	0.068
Fe	29.0	17.61	20.16	S	---- <sup>(b)</sup>	0.212	0.126
K	0.48	0.95	---- <sup>(a)</sup>	Te	0.17	0.095	0.120
La	0.124	0.479	0.520	Ti	---- <sup>(b)</sup>	0.049	0.039
Li	---- <sup>(b)</sup>	0.003	0.005	Zn	0.057	0.036	0.036
Mg	1.28	0.778	1.224	Zr	3.4	2.304	2.816

(a) Actual added cannot be compared because a significant portion of the added Na and K was washed out of the simulant during the wash procedure.

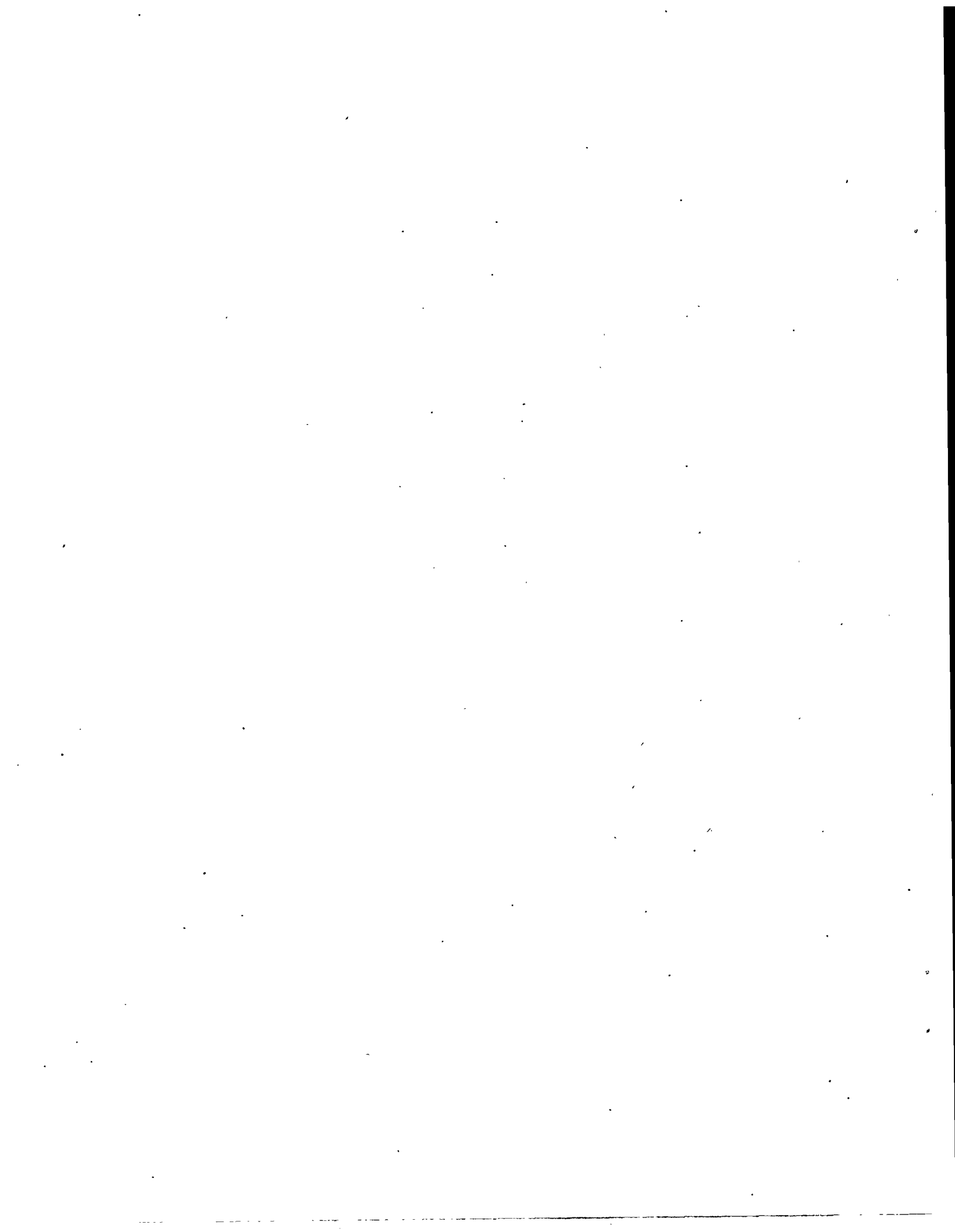
(b) Not analyzed for in this procedure.

Table 2.2. Comparison of Original and New Target Concentrations

Element	Original Target (g/L)	New Target (g/L)	Actual Batched (g/L)	Element	Original Target (g/L)	New Target (g/L)	Actual Batched (g/L)
Ag	0.150	0.056	0.151	Mn	0.578	0.486	0.578
Al	4.994	9.46	9.46	Mo	0.009	0.007	0.007
B	0.061	0.043	0.044	Na	18.818	17.665	----- <sup>(a)</sup>
Ba	0.600	0.546	0.547	Nd	0.850	0.874	0.850
Ca	1.639	1.43	1.639	Ni	0.965	0.809	0.966
Cd	1.386	1.13	1.385	P	0.168	0.454	0.454
Ce	0.133	0.101	0.133	Pb	0.360	0.315	0.360
Cl	0.027	0.093	0.093	Re	0.0035	0.486	0.100
Co	0.175	0	0.175	Sb	0.132	0.125	0.125
Cr	0.259	0.224	0.259	Se	0.148	0.142	0.143
Cu	0.060	0.056	0.056	Si	8.083	7.534	7.534
F	0.106	0.090	0.102	Sr	0.076	0.067	0.068
Fe	20.17	17.19	20.16	S	0.171	0.126	0.126
K	0.587	0.357	----- <sup>(a)</sup>	Te	0.120	0.112	0.120
La	0.520	0.432	0.520	Ti	0.039	0.036	0.039
Li	0.006	0	0.005	Zn	0.036	0.032	0.036
Mg	0.966	0.721	0.965	Zr	2.816	2.504	2.816

(a) Actual added cannot be compared because a significant portion of the added Na and K was washed out of the simulant during the wash procedure.





## 3.0 Slurry Characterization Procedures

This waste simulant was characterized by the following laboratory tests :

- grain size analysis
- rheology measurements as a function of time (7 and 28 days) and concentration (125, 205, 263 gWO/L)
- dry-out, low temperature (to 400°C) calcination test.

The grain size distribution provides a comparison of rheological properties with actual wastes. Slurries with similar grain size distributions of the same phases are expected to exhibit similar rheological properties (Morrey 1995). Rheological properties may also change because of changes in the slurry's particulate supernate chemistry due to aging. Low temperature calcination allows the potential for hazardous gas generation to be investigated, so the user of the simulant will be forewarned when the simulant is used in calcining or melter tests.

### 3.1 Slurry Grain Size Analysis

Grain size analysis on the blended waste sludge simulant was performed with a Microtrac FRA particle size analyzer following standard operating procedures. The slurry was homogenized and a representative sample was diluted (~ 10 times) with deionized water. The dilute solution was then injected into the sample chamber of the analyzer. The number and diameter of the particles were then measured by laser diffraction.

### 3.2 Slurry Rheology Measurements

After the slurry was concentrated to the target concentration, it was transferred to the mixing vessel so that the slurry could be aged. The mixing vessel was a closed system with constant agitation, and was monitored for water losses by measuring changes in slurry weight as a function of time. Deionized water was added to the slurry whenever water losses were measured. Samples were aged at room temperature (~ 22°C) under constant agitation. During the aging process, samples were taken at 0, 7, and 28 days. These samples were subjected to the following tests:

- rheological characterization (at ~ 22°C)
- pH measurement (at ~ 22°C).

The initial concentrated slurry was also measured for density, weight percent solids, and waste oxide concentration (gWO/L) using the technical procedure WTC-006-4 to determine the exact starting point of each slurry. Density was measured by weighing a known volume of slurry and dividing the weight by the volume. Weight percent solids was measured by drying the slurry at 105°C for 24 hours and comparing the wet and dry weights. The waste oxide concentration was determined by heating the slurry to 1050°C and holding for 30 minutes and then dividing the weight of the remaining residue by the original volume.

Every sample was rheologically characterized (at  $\sim 22^{\circ}\text{C}$ ) in a Haake CV20 measuring system with the ME45 sensor. Rheograms were generated by increasing the applied shear rate linearly from 0 to  $300\text{ s}^{-1}$  in a 5 minute interval.

The Herschel-Bulkley model describes a typical pseudoplastic behavior. It is a modification of a power law fluid curve fit, which takes into account a yield stress. The exponential component of the equation quantifies the non-Newtonian behavior. The closer the exponent is to 1.0, the more Newtonian the behavior. When  $n = 1$ , the equation becomes a Bingham fit. The increasing shear rheology data were fit with the pseudoplastic equation:

$$\tau = \tau_0 + k\dot{\gamma}^n$$

where  $\tau$  = shear stress,

$\tau_0$  = yield stress,

$\dot{\gamma}$  = shear strain rate,

$k$  = consistency factor, and

$n$  = measure of deviation from Newtonian flow.

In pseudoplastic liquids viscosity appears to decrease as the shear rate is increased. This is known as “shear thinning” and is common fluid behavior for emulsions, suspensions, and dispersions. Under shear conditions, particles and molecules acquire an orientation more conducive to flow, which lowers viscosity. For a classic pseudoplastic liquid, shear thinning is reversible. As the shear rate drops, the apparent viscosity climbs with little or no lag time because the orientation of particles and molecules is lost as quickly as it is achieved.

### 3.3 Slurry Dry-Out, Low Temperature Calcine Test

The slurry dry-out, low temperature calcine test was performed using approximately 500 mL of blended waste sludge simulant in a 2 L Pyrex<sup>®</sup> reaction vessel placed in a temperature controlling mantle (Wiemers 1988). The offgas was monitored with a Nicolet 550 Fourier Transform Infrared Spectrometer (FTIR) gas analyzer and a chemiluminescent NO/NO<sub>x</sub> analyzer. Total exit gas flow rate was monitored by reference to calibrated inlet flow of helium with the argon purge gas. The nominal argon flow was 1.95 L/min. The slurry was first dried by setting the temperature at  $100^{\circ}\text{C}$  until the temperature of the slurry reached or passed the set point. The temperature was then increased  $5^{\circ}\text{C}$  above the current temperature and allowed to equilibrate for 5 minutes and then repeated until the slurry appeared to be completely dry. Then the set point was increased  $20^{\circ}\text{C}$  above the current temperature until its temperature reached or passed the set point. Then the temperature was raised again with this process continuing until the temperature reached  $400^{\circ}\text{C}$ . After reaching  $400^{\circ}\text{C}$ , the system was allowed to cool while still measuring offgas.

## 4.0 Slurry Test Results and Discussion

### 4.1 Slurry Grain Size Distribution

The sludge simulant contains a range of particle sizes with equivalent spherical diameters from ~ 1 to ~ 400 microns. The mean particle size (volume density) is 12.4 microns. Most of particles are in the 7 - 22 micron range, as shown in Figure 4.1. The mean particle sizes of previous waste simulants and core samples from tanks 101-AZ and 102-AZ are compared in Table 4.1 (Morrey 1995). This simulant compares favorably with the particle sizes of the actual tank waste and previous waste simulants. Although it is slightly larger than the actual waste, it is considerably smaller than the NCAW simulant; therefore, its rheological properties should be more similar to those of the actual waste.

Table 4.1 Particle Size Comparison of Tank Waste and Simulants

	101-AZ Core 1	101-AZ Core 2	102-AZ Core 1	NCAW Simulant	RFP Simulant
Mean Particle Size (microns)	9.0	5.4	47.4 <sup>(a)</sup>	25.6	12.4

(a) Slurry was inadvertently dried before processing and data is suspect.

### 4.2 Slurry Rheology as a Function of Time

Table 4.2 includes the physical property and rheology data for the initial concentrated slurries. Physical properties include gWO/L, pH, weight percent solids, and density. Rheology data includes yield stress, viscosity, consistency factor, the degree of non-Newtonian behavior, and the least squares correlation coefficient for the data fitted to the Herschel-Bulkley pseudoplastic model. As can be seen in this table, the 263 gWO/L slurry did not fit the model very well with a correlation coefficient of only 0.66. Therefore, the values given for the viscosity and yield stress may not be accurate. However, the general trend of increasing viscosity and yield stress with increasing weight percent solids can still be seen.

Table 4.3 documents the rheological properties as a function of sample age for each of the concentrated slurries. Rheological properties include pH, Herschel-Bulkley pseudoplastic yield stress, viscosity, consistency factor, non-Newtonian factor, and least squares correlation for the data fitted to the Herschel-Bulkley model. Neither the viscosity nor shear stress could be correlated as a function of solids loading or slurry age for either the 205 gWO/L or the 263 gWO/L slurries. However, the 125

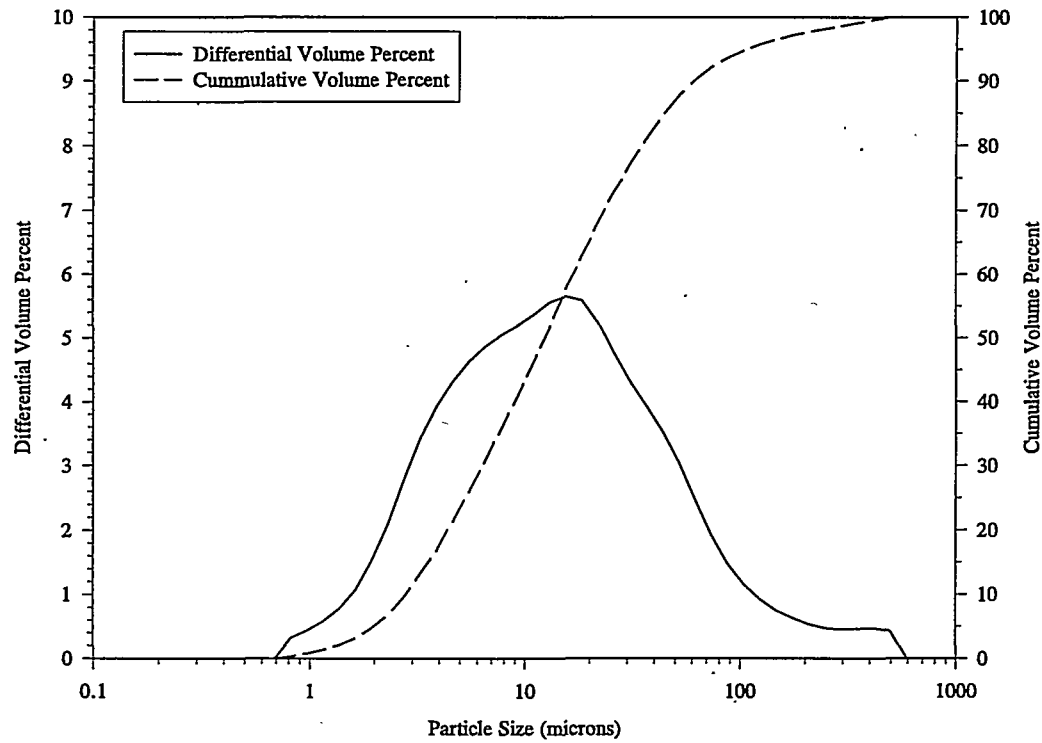


Figure 4.1 Grain Size Distribution of the RFP Blend Slurry Simulant

Table 4.2 Physical Property and Rheology Data

Actual gWO/L	125.3	205.4	263.7
Wt % Solids	14.9	21.1	27.5
Density (g/mL)	1.02	1.17	1.15
pH (@ 22°C)	11.42	11.65	11.49
Pseudoplastic Yield Stress (Pa)	0.54	12.1	52.0
Pseudoplastic Viscosity @ 300 1/s (mPa •s)	7.6	71.2	191
Consistency Factor (mPa •s)	2.75	6.92	1.15
Degree of non-Newtonian Behavior, n	1.13	1.26	1.48
Correlation Coeff. (R <sup>2</sup> )	0.95	0.90	0.66

gWO/L slurry did follow a trend of increasing viscosity and yield stress with age. Viscosity could not be correlated as a function of solids loading and yield stress was determined not to be a function of solids loading for the actual waste (Tracey 1996).

The flow behavior of the slurry was best represented as a Hershel-Bulkley pseudoplastic, agreeing with the actual waste as well as previous simulants. These non-Newtonian behaviors are indicative of an aggregated dispersion and indicate that the suspensions are coagulated. This is expected because both the simulant and the actual waste contain a high electrolyte concentration, which causes formation of a particle network resulting in coagulation of the slurry.

Figures 4.2 and 4.3 compare the shear stress and the viscosity, respectively, of the tank core samples with various simulants. The simulants have higher shear stresses and viscosities than the tank core samples, which may be a result of the larger particle sizes of the simulants. The RFP simulant approaches the characteristics of the actual waste more closely than previous simulants. The smaller particle size of this simulant would also explain why its shear stress and viscosity are lower than those of previous simulants. However, the higher viscosities of the simulants mean that any plant designed to work with the simulant should be capable of working with the actual waste.

Table 4.3 Rheological Properties as a Function of Time

gWO/L	Age (days)	pH (@ 22°C)	Yield Stress (Pa)	Viscosity (mPa •s)	Consistency Factor (mPa •s)	Non-Newtonian Factor, n	Correlation Coeff. (R <sup>2</sup> )
125	0	11.42	0.54	7.6	2.75	1.13	0.95
125	7	11.40	0.46	8.4	2.61	1.17	0.91
125	28	11.85	1.92	13.1	11.3	0.91	0.98
205	0	11.65	12.12	71.2	6.92	1.26	0.90
205	7	11.74	7.77	41.8	201	0.56	0.95
205	28	12.32	8.95	43.1	27.7	0.87	0.88
263	0	11.49	52.05	191	1.15	1.48	0.66
263	7	11.60	3.77	22.4	2.73	1.23	0.90
263	28	12.26	14.90	63.2	10.6	1.04	0.90

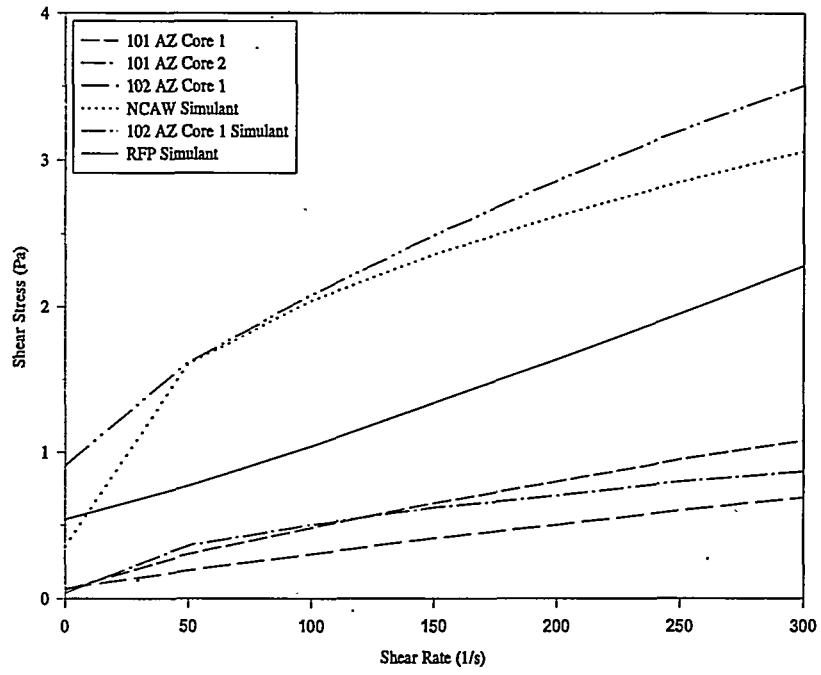


Figure 4.2 Shear Stress of Tank Core Samples and Simulants Compared

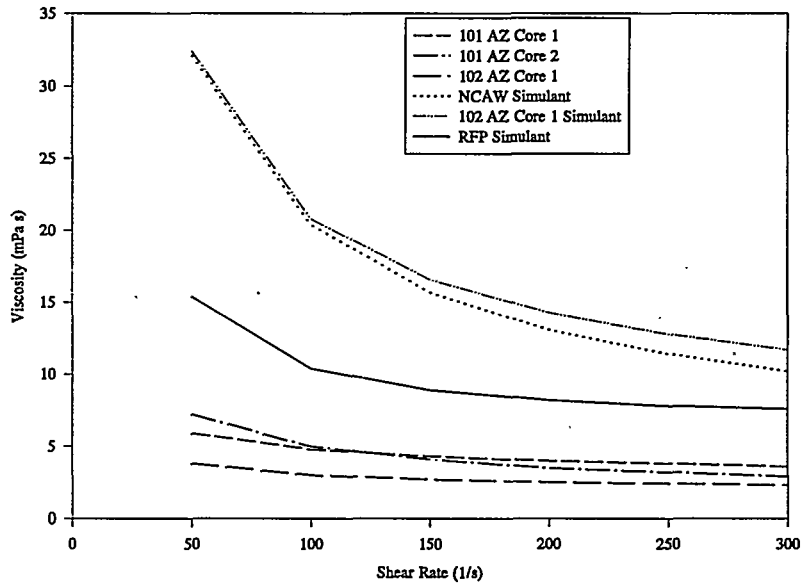


Figure 4.3 Viscosity of Tank Core Samples and Simulants Compared

### 4.3 Slurry Dry-Out, Low Temperature Calcine Behavior

As shown in Figure 4.4, essentially all of the water was driven off the slurry before its temperature rose significantly above 100°C. The slurry had begun to solidify after about 60 to 70% of the water had been driven off. The slurry dried from the outside in, with the center being the last part of the slurry to dry. As the slurry dried, cracks began to form throughout it. The drier the slurry became, the more cracks there were in the slurry. These observations are consistent with similar measurements on other slurry simulants (Smith 1996).

The offgas results are shown in Figure 4.5. The CO<sub>2</sub> profile is based on FTIR spectra taken at approximately 15 minute intervals. The NO profile was plotted from the NO<sub>x</sub> analyzer output recorded manually. The correlation between the CO<sub>2</sub> and the NO suggests that these gases were generated by a common reaction such as between oxalate and nitrate-nitrite. A mass balance was not performed, but the amount of gases generated appears to be of the correct order of magnitude. This is also suggested by the fact that both the CO<sub>2</sub> and NO fell off considerably while the temperature was still around 400°C. Other gases such as N<sub>2</sub>O and NO<sub>2</sub> were observed at trace levels (100 ppm) only. Ammonia was not observed at any time during the test.

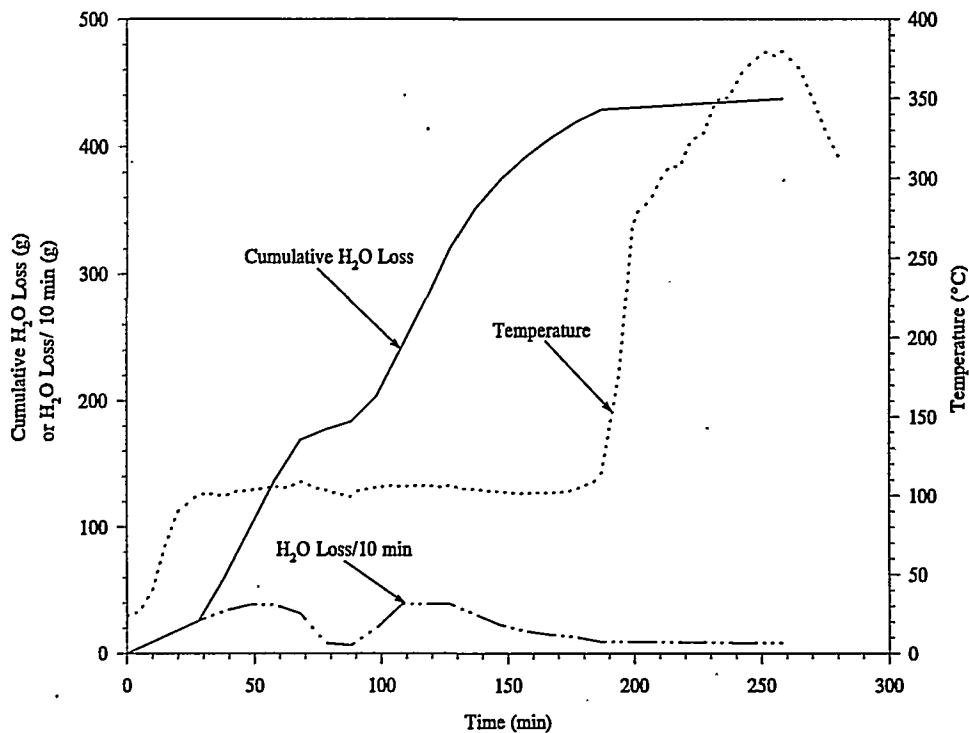


Figure 4.4 RFP Blend Slurry Simulant Water Loss During Calcination



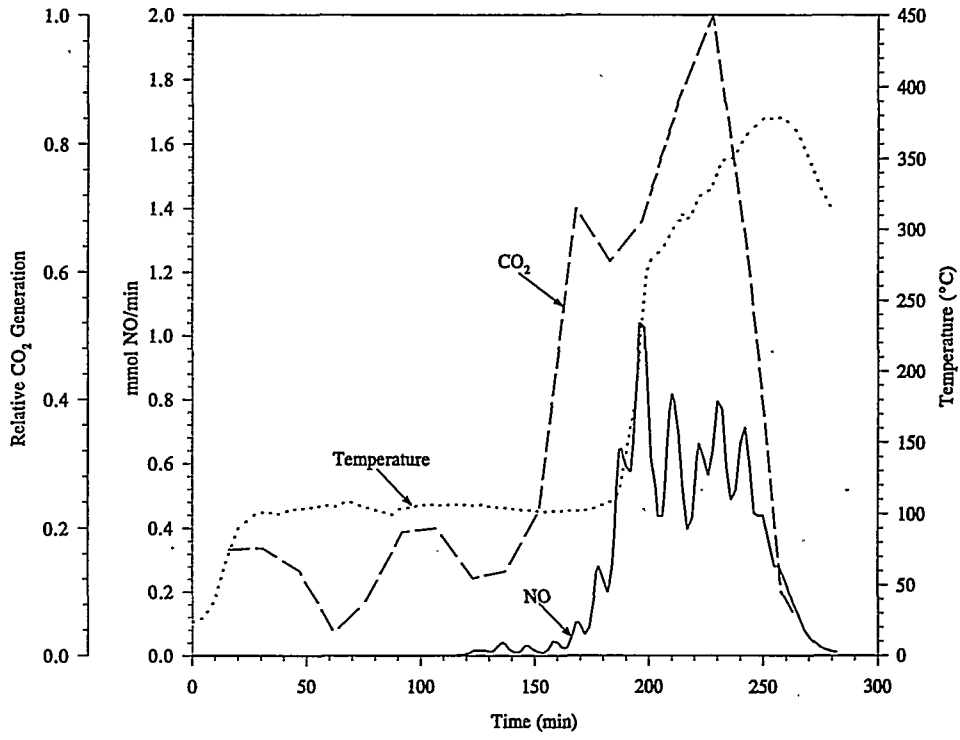


Figure 4.5 RFP Blend Slurry Simulant Offgas Profile During Calcination

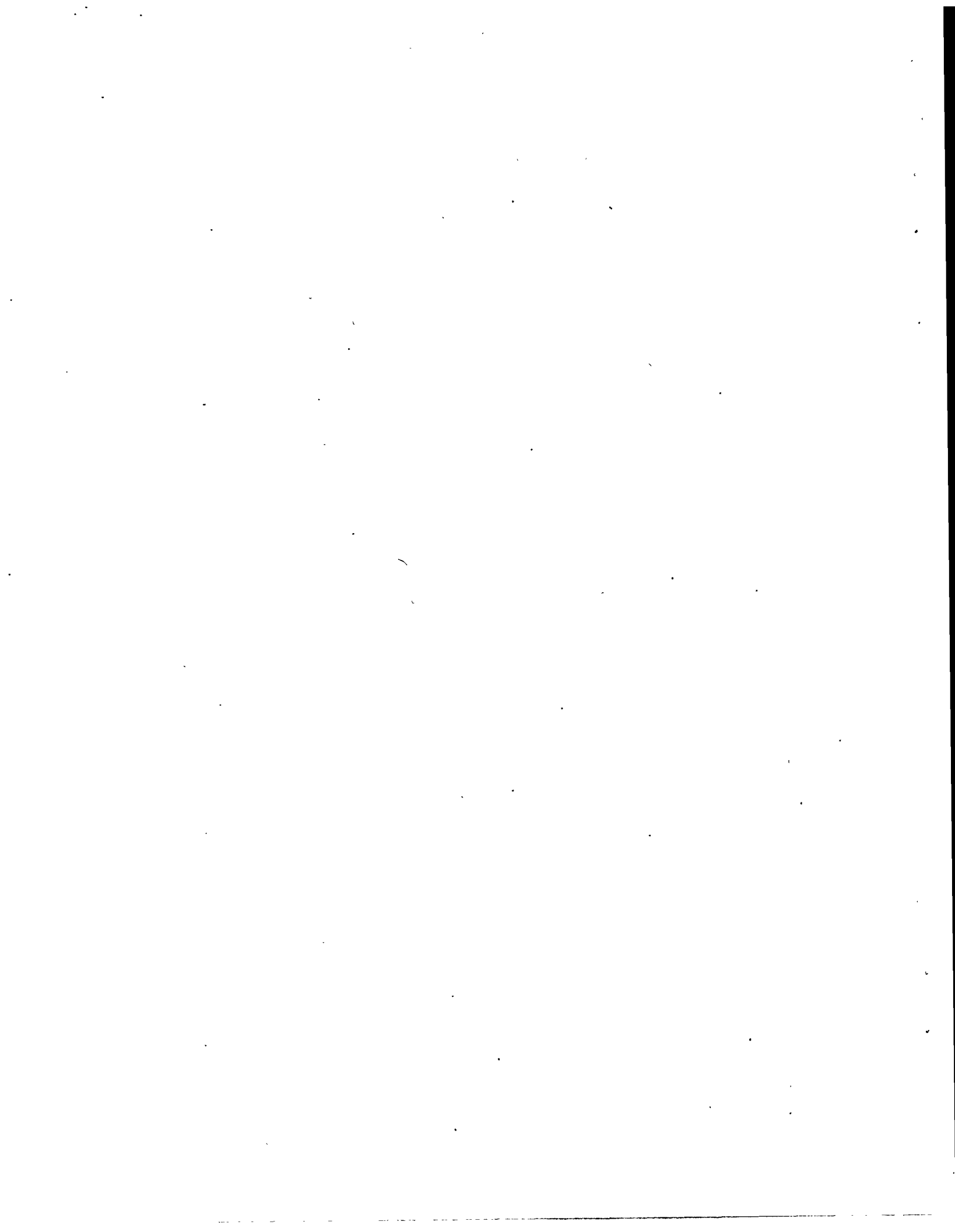
## 5.0 Conclusions

The average particle equivalent spherical diameter of the slurry simulant was 12.36 microns, which was slightly larger than the actual waste and half the size of the NCAW simulant. Most of the particles were in the range of 7-22 microns. Therefore, this simulant more closely resembles the actual waste in particle size (which is reflected in rheological properties) than does the NCAW simulant.

The flow behavior of the slurry was best represented as a pseudoplastic, consistent with the actual waste as well as previous simulants. The viscosity and shear stress could not be correlated as a function of solids loading or slurry age for the more concentrated slurries. However, the 125 gWO/L slurry did follow a trend of increasing viscosity and shear stress with age. The viscosity and yield stress of this simulant, while higher than the actual waste, were lower than those of previous simulants. Therefore, a plant built to process the simulant should be capable of processing the actual waste.

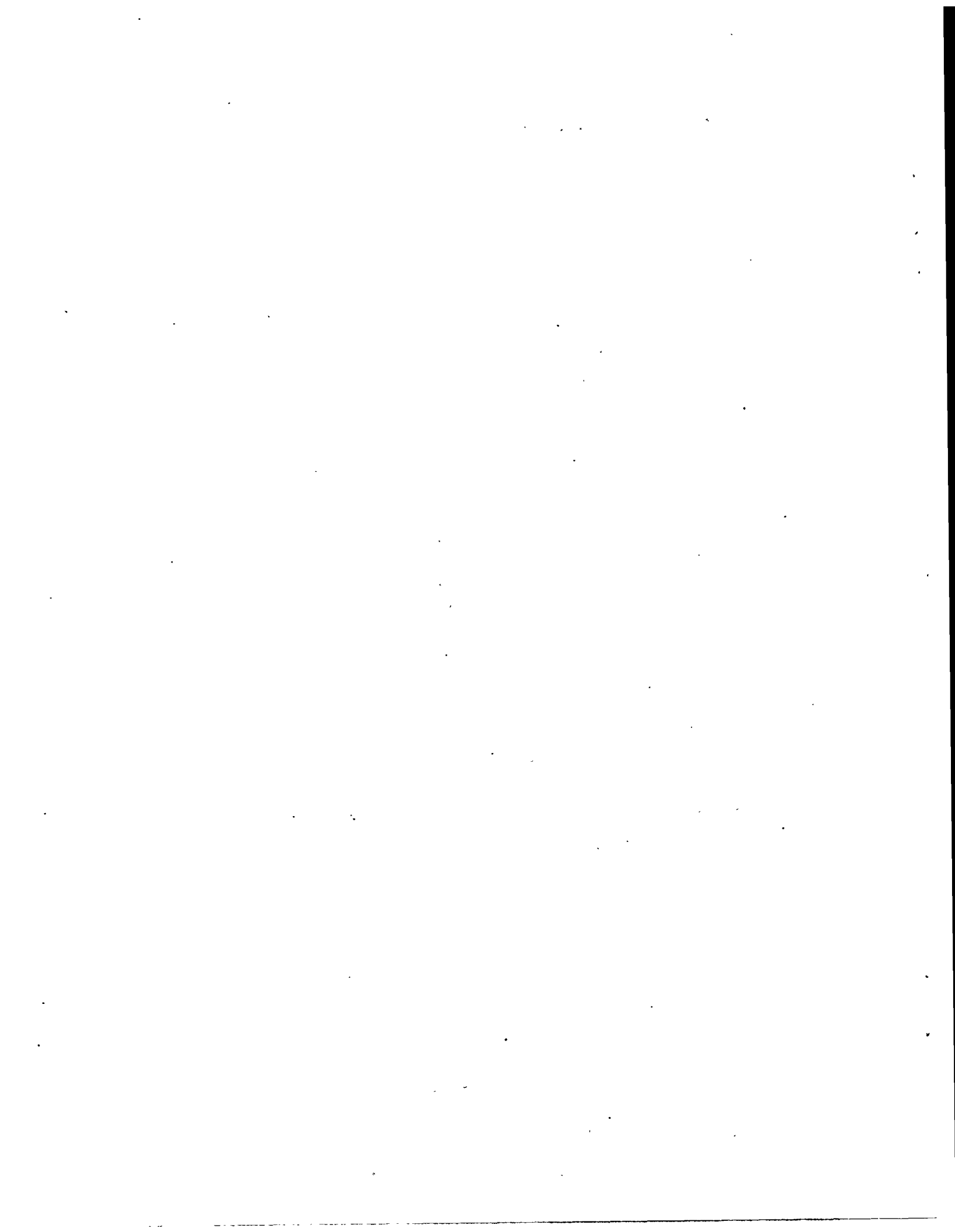
The slurry seemed to show characteristics similar to those of other slurries when calcined to 400°C, and no unexpected reactions occurred. Both CO<sub>2</sub> and NO were observed as well as a trace of N<sub>2</sub>O and NO<sub>2</sub>, and amounts of all four gases increased as the temperature rose above 100°C. The correlation between the CO<sub>2</sub> and NO suggests that these gases were generated by a common reaction, such as between oxalate and nitrate-nitrite. Ammonia was not observed in this test.

The slurries conservatively simulated actual HLW such that the feed preparation procedure can be used for nonradioactive process testing.



## 6.0 References

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- Wiemers, KD. "Evaluation of Process Off Gases Released During the Formating of Simulated HWVP Feed." A paper presented at the American Institute of Chemical Engineers National Meeting, Denver, Colorado (August 21-24, 1988).



## **Appendix A**

### **Simulant Specification for the Blended Privatization Tank Waste for the High-Level Waste Vitrification Process Specified in the RFP**

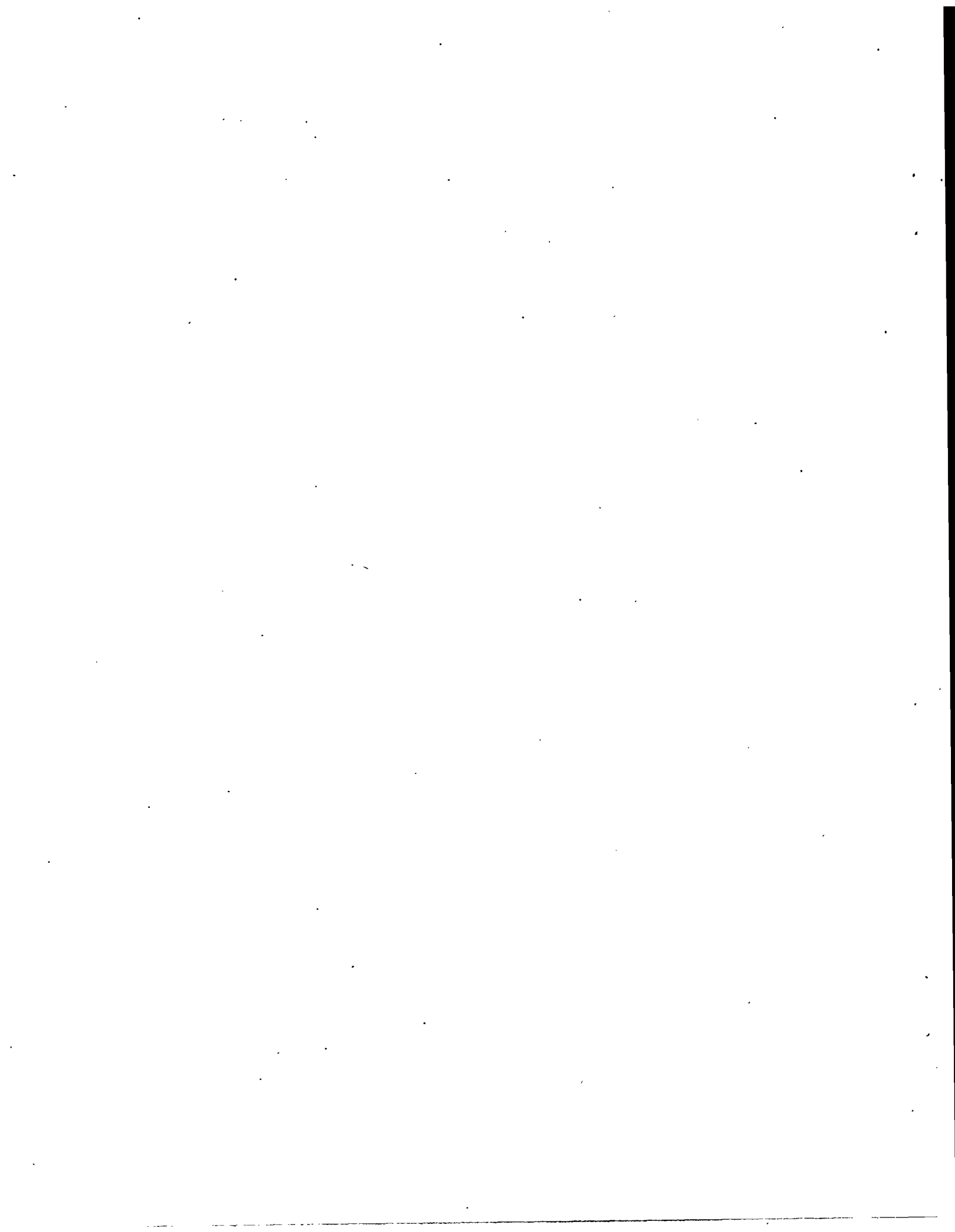
**Simulant Specification for the Blended Privatization  
Tank Waste for the High-Level Waste Vitrification  
Process Specified in the RFP**

R. L. Russell  
H. D. Smith

September 1996

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Pacific Northwest National Laboratory  
Richland, Washington 99352





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## 1.0 Introduction

This feed specification describes a method for preparing a waste simulant which corresponds to the high-level waste (HLW) slurry composition provided in the privatization draft request for proposal (RFP).

A simulant duplicates chemical and physical properties of the waste that are important in processing the actual waste. A simulant is an engineered material that has the important physical properties of the actual waste slurry but does not have the radiological or the toxicity hazards of the actual waste slurry. For example, a waste slurry will be characterized by rheological properties, solid phases and their grain size distribution, and the tendency to form a supernate. The waste slurry simulant in combination with other glass components should reproduce the melting characteristics of the actual waste glass batch.

The waste simulant should be as accurate as possible in rheology, calcining alone and in combination with glass components, and glass batch melting. Rheological properties of a slurry typically depend on solids loading, the solid phases and their grain size distribution, and the pH of the supernate. The calcining and melting characteristics of the waste feed simulant will be a function of the phases present and their grain size distribution. Hence, the goal is to simulate the phase composition, grain size distribution, and supernate pH of the actual waste slurry. In previous comparisons, the HLW simulants had an apparent viscosity twice that of the actual waste and was more chemically active during processing with formic acid (Morrey 1995). Hence, for these properties, the simulants provided conservatively high numbers and any engineering design produced to handle them would be more than capable of handling the actual waste.

The HLW slurry composition presented in the draft RFP is a blend of wastes from tanks 101-AZ, 102-AZ, 106-C, and 102-AY that have been through water washing.<sup>(a)</sup> Table 1 shows the simulant composition at 100 g oxide/L in terms of metal oxides. The baseline feed composition was provided by WHC.<sup>(b)</sup> Appendix A.1 describes the HLW simulant composition at 31 g oxide/L in terms of elements. It differs slightly from the nominal composition given in the draft RFP (the final RFP did not give a nominal composition) because certain oxides were deleted or substituted (amounts shown as zero). The amount of substituted oxide (molar basis) is included with the rest of that oxide in the table. Additional rhenium was included in this blended waste simulant as a surrogate for technetium. Rhenium and cesium are volatile under many melter conditions. Table 2 lists the nitrogen and carbon components of the simulant. This simulant represents a combination of tank waste slurries and should be viewed as an example of slurries that might be produced by blending waste from various tanks.

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(a) Lambert, Steve, Westinghouse Hanford Company, Personal Communication.

(b) Washenfelder, DS. 1996. "Revised Estimates of Pretreated HLW Sludge Composition for Incorporation in Pacific Northwest National Laboratory's Feed Process Studies (Scheduled Activity Number H29A4)," (letter to ML Elliott, dated January 29), Westinghouse Hanford Company, Richland, Washington.

Table 1. RFP Simulant Composition at 100 g oxide/L

Element	Batched Oxide Wt%	Source Chemical	Formula Wt. (incl. water)	Oxide Factor (or elem equiv.)	Chemicals g/L (100 g oxide)
Ag	0.060	AgNO <sub>3</sub>	169.87	0.682	0.088
Al	17.870	Al(OOH)	59.98	0.850	21.024
As	0	deleted	0	0	0
B	0.139	H <sub>3</sub> BO <sub>3</sub>	61.83	0.563	0.247
Ba	0.610	Ba(OH) <sub>2</sub> · 8H <sub>2</sub> O	315.48	0.486	1.255
Bi	0.060	Bi(NO <sub>3</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	485.07	0.480	0.125
Ca	2.000	Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	236.16	0.237	8.439
Cd	1.290	Cd(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	308.47	0.416	3.101
Ce	0.119	Ce(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	434.23	0.378	0.315
Cl	0.090	NaCl	58.44	0.590	0.153
Cr	0.328	Cr(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	400.15	0.190	1.726
Cs	0.617	CsNO <sub>3</sub>	194.91	0.723	0.853
Cu	0.070	CuSO <sub>4</sub> · 5H <sub>2</sub> O	249.68	0.319	0.219
F	0.090	NdF <sub>3</sub>	201.24	0.283	0.318
Fe	24.626	Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	404.00	0.198	124.374
K	0.430	KOH	56.11	0.839	0.513
La	0.507	La(NO <sub>3</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	414.91	0.393	1.290
Mg	1.194	Mg(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	256.41	0.157	7.605
Mn	0.770	Mn(NO <sub>3</sub> ) <sub>2</sub>	178.95		0.950
		KMnO <sub>4</sub>	158.04		0.560
Mo	0.010	MoO <sub>3</sub>	143.95	1.00	0.010
Na	23.820	NaOH	40.00	0.775	30.735
Nd	1.020	Nd(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	438.35	0.384	2.656
Ni	1.030	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	290.81	0.257	4.008
P	1.040	Na <sub>3</sub> PO <sub>4</sub>	163.94	0.433	2.402
Pb	0.340	Pb(NO <sub>3</sub> ) <sub>2</sub>	331.20	0.674	0.504
Pd	0.020	Pd(NO <sub>3</sub> ) <sub>2</sub>	230.41	0.531	0.038
Pu	0	deleted	0	0	0
Re	0.570	ReO <sub>2</sub>	218.21	1.00	0.570
Rh	0.050	Rh(NO <sub>3</sub> ) <sub>3</sub>	288.92	0.439	0.114
Ru	0.060	RuNO(NO <sub>3</sub> ) <sub>3</sub>	317.09	0.395	0.152
Sb	0.150	Sb <sub>2</sub> O <sub>3</sub>	291.50	1.00	0.150

Element	Batched Oxide Wt%	Source Chemical	Formula Wt. (incl. water)	Oxide Factor (or elem equiv.)	Chemicals g/L (100 g oxide)
Se	0.200	SeO <sub>2</sub>	110.96	1.00	0.200
Si	16.120	SiO <sub>2</sub> (quartz)	60.09	1.00	16.120
Sr	0.080	Sr(NO <sub>3</sub> ) <sub>2</sub>	211.63	0.490	0.163
SO <sub>3</sub>	0.470	Na <sub>2</sub> SO <sub>4</sub>	142.04	0.564	0.833
Tc	0	subst. Re <sub>2</sub> O <sub>7</sub>	484.40	1.00	0
Te	0.140	TeO <sub>2</sub>	159.60	1.00	0.140
Ti	0.060	TiO <sub>2</sub>	79.90	1.00	0.060
Tl	0	subst. Nd(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	438.35	0.384	0
U	0	subst. Nd(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	438.35	0.384	0
V	0	deleted	0	0	0
Zn	0.040	Zn(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	297.47	0.274	0.146
Zr	3.910	ZrO(NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	267.26	0.533	7.336
Total	100.000				

Table 2. Nitrogen and Carbon Components of the RFP Simulant

Component	g/100g WO	Source Chemical	Anion Equivalent	Source Chemical
			g/g	g/100g WO
NO <sub>2</sub> <sup>-</sup>	2.588	NaNO <sub>2</sub>	0.667	3.880
NO <sub>3</sub> <sup>-</sup>	1.540	NaNO <sub>3</sub>	0.729	2.112
TOC	0.732	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0.179	4.089 as carbon
TIC	5.988	Na <sub>2</sub> CO <sub>3</sub>	0.566	10.580

While this procedure is written to produce a specific blended waste simulant, it can be used as a template to produce a wide range of waste type simulants. Of course, if the simulant composition is very different from that presented here, the procedure may require significant adjustments, but the general philosophy remains the same.

Previous HLW simulants have been prepared with a neutralized current acid waste (NCAW) composition or an "all-blend" composition of the Hanford tanks; both exclude acutely toxic and radioactive elements (PNNL 1995). The specification for the RFP blended waste simulant uses a procedure similar to that of NCAW simulant. Acutely toxic and radioactive species are either substituted or eliminated from the composition (see Table 1). The aluminum source in the NCAW simulant was precipitation of  $\text{Al}(\text{OH})_3$  by addition of  $\text{NaOH}$  to  $\text{Al}(\text{NO}_3)_3$ , whereas the blended waste simulant contains aluminum as the mineral boehmite. In both simulants, the organic component is added as oxalate. This decision was based on the prediction that organic complexants in the waste tanks break down into oxalate (Agnew 1994). The carbon in the washed and blended waste is expected to be mainly in the form of carbonate.<sup>(a)</sup>

One of the characteristics of the final blended waste simulant is a low nitrate concentration. Achieving the target nitrate level in the blended waste simulant requires several water washes of the solids. If the ionic strength or pH in the blended waste simulant becomes too low, the suspended-solids state becomes the stable condition and the settle-decant wash method becomes ineffective. The target nitrate level should not cause this effect. However, if the slurry is made too dilute or overwashing occurs, it may occur. If this condition is observed, adding small amounts of sodium nitrite back to the blended waste simulant will cause it to settle.

The blended waste simulant specification is written for the preparation of 1000 liters at 100 g waste oxide/L and is summarized as follows. A stock simulant is prepared by first coprecipitating a hydroxide slurry from a nitrate solution containing the major waste elements (Fe, Ni, Nd, Zr, and Mn). The soluble/ slightly soluble salts (halides, hydroxides, nitrates, nitrites, sulfates, borates, phosphates, oxides, and oxalates) are added dry to the major element slurry. Three other slurries are added to the major element and soluble/slightly soluble slurry: 1) minor components as an insoluble compound slurry (oxides, fluorides), 2) an optional coprecipitated noble metals (Rh, Pd, Ru) slurry, and 3) a mineral slurry. Excess nitrate and sodium are removed by washing with water. A small amount of sodium nitrite may be added to the wash water if the slurry solids settling rate becomes too sluggish. Sodium and nitrate were added in various amounts with other elements, and appropriate additions are made after washing to bring these components to nominal levels. Figure 1 is a flowchart of the simulant preparation steps.

The blended waste simulant 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 within the programmatic funding and schedule constraints. An actual blend of the Hanford tank waste combines wastes resulting from many process streams. The simulant preparation does not mimic each process stream, only the final composition of the blended waste. The blended waste specification includes the minor components except those which are acutely toxic. The omission of these elements was carefully considered with regard to properties which may influence catalytic behavior or the glass properties. If additional omissions are considered

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(a) MacClean, Graham, Westinghouse Hanford Company, Personal Communication.

A.5

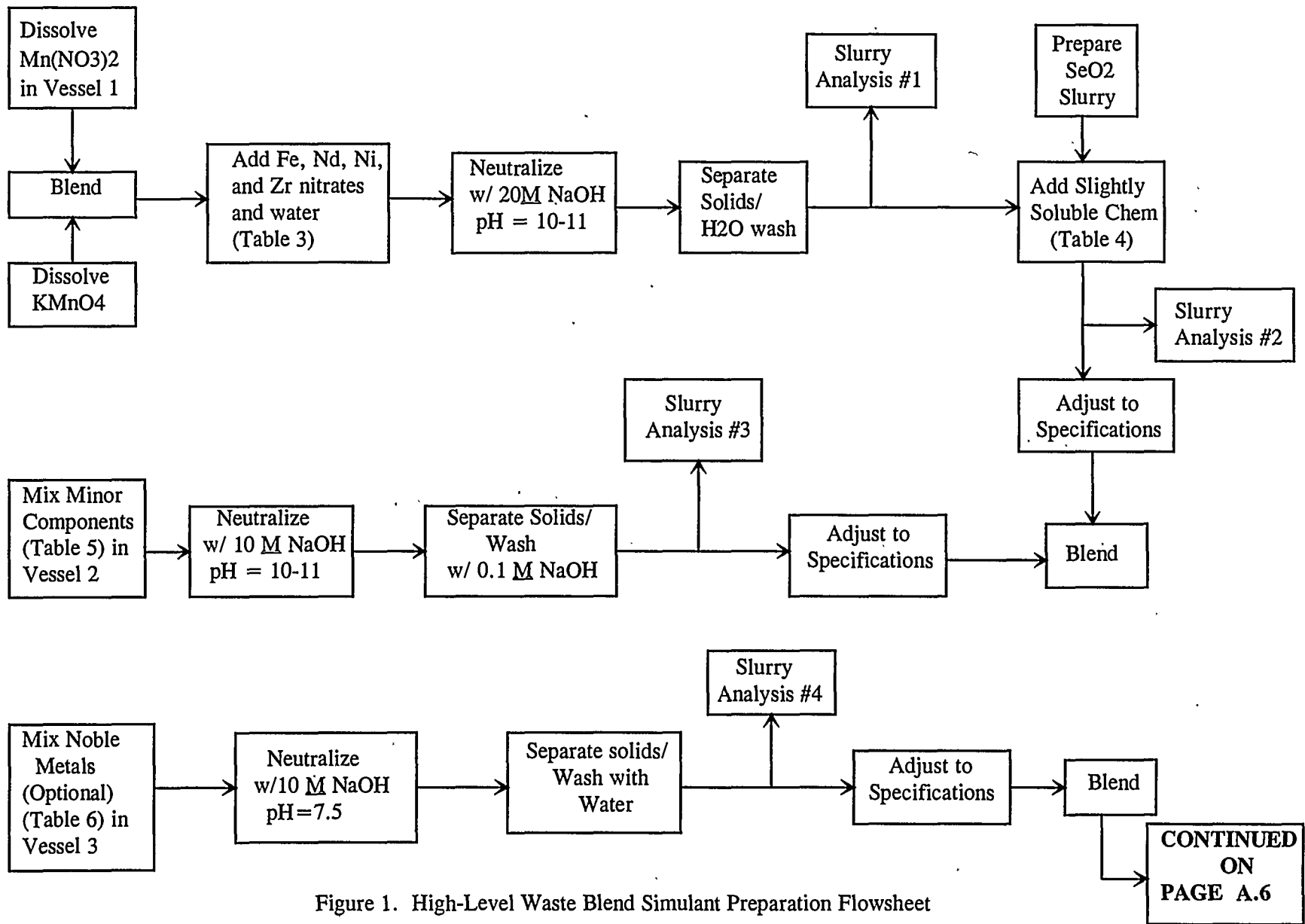


Figure 1. High-Level Waste Blend Simulant Preparation Flowsheet

A.6

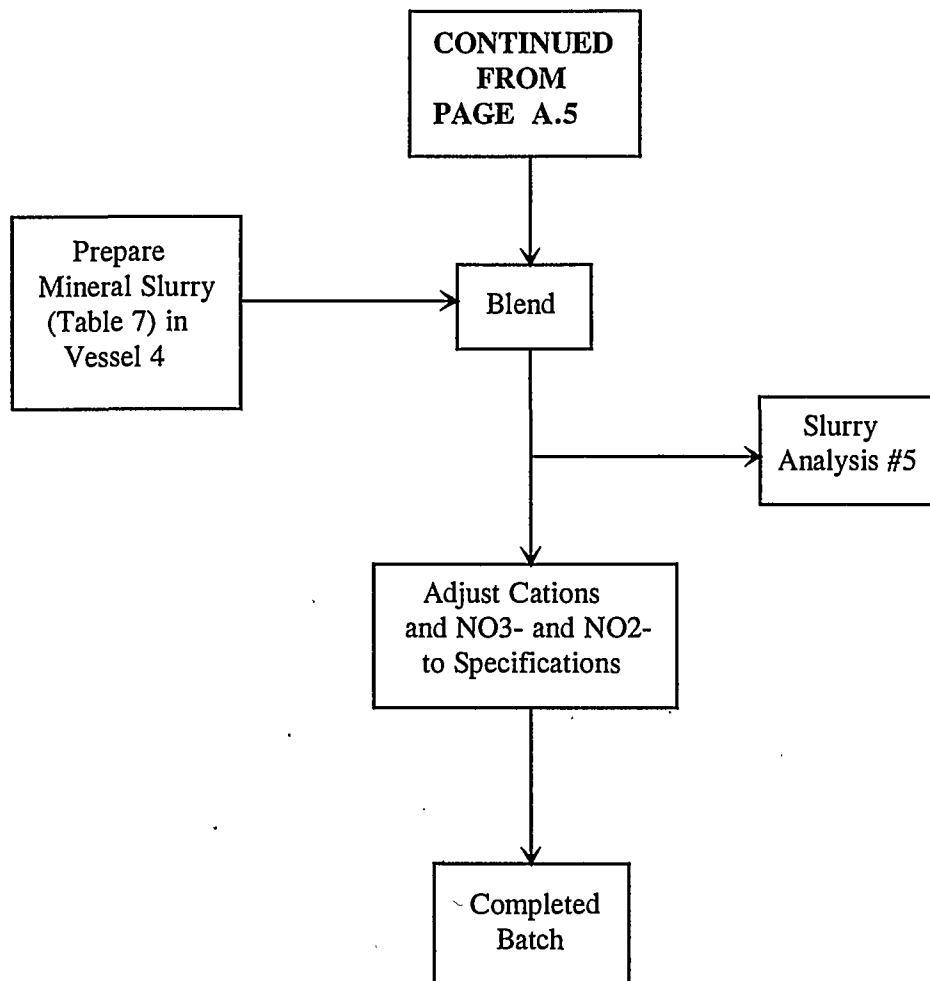


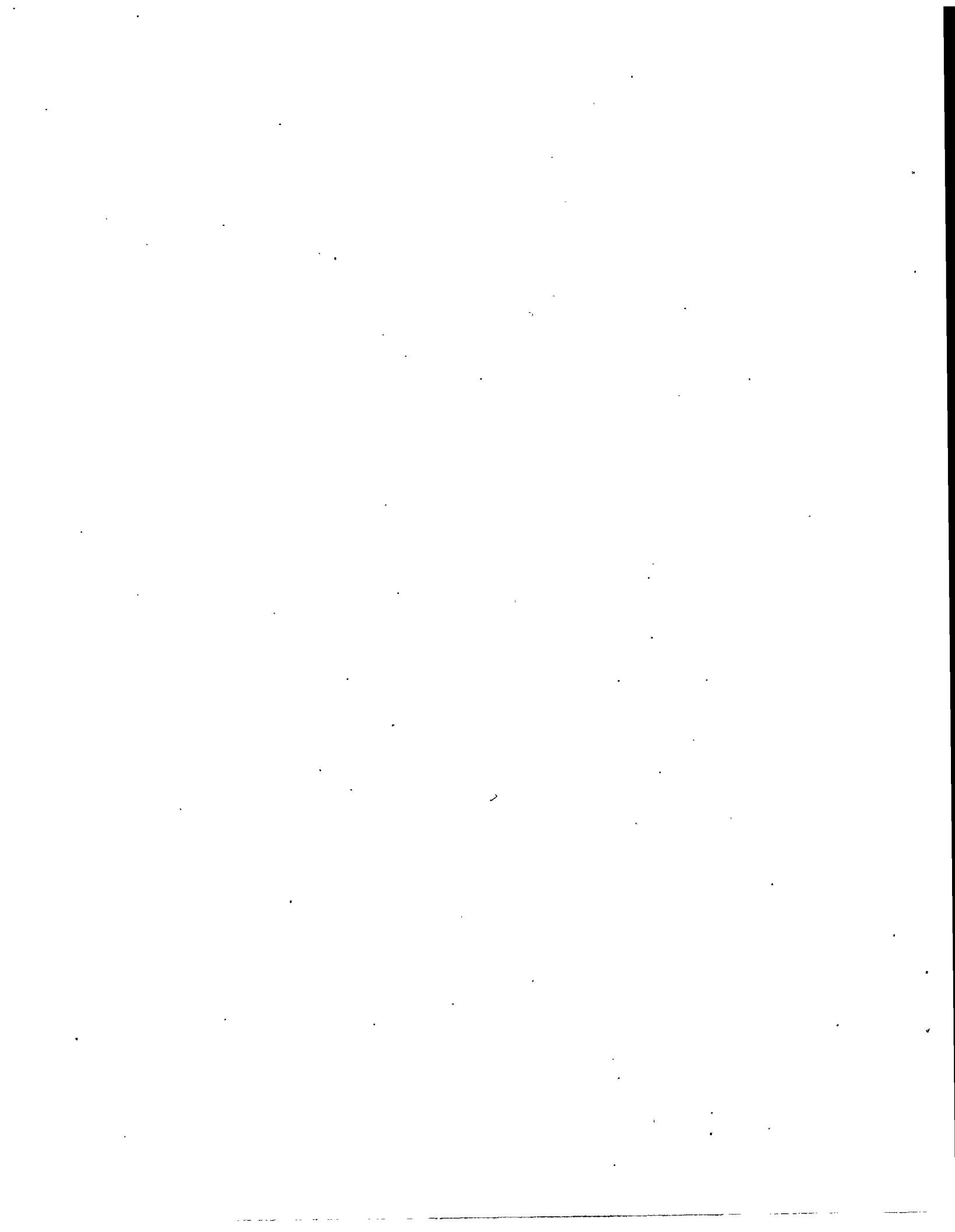
Figure 1(cont.). High-Level Waste Blend Simulant Preparation Flowsheet



for melter evaluation testing because of batch size, expense of minor components (i.e. noble metals), and safety issues; their effects should be carefully evaluated. Radioactive elements are deleted or substituted. Neodymium is the surrogate element for U, the major radioactive component (~1.3 wt %) in the waste. These limitations need to be considered with respect to the application for which the simulant specification is used.

A waste simulant made by this procedure will be characterized by the following laboratory tests: grain size analysis, rheology measurements as a function of time (7 and 30 days) and concentration (150, 300, 450 gWO/L), dry-out, low temperature (to 400°C) calcination tests.

The grain size distribution allows an implied comparison to actual wastes with respect to rheological properties. Slurries with similar grain size distributions of the same phases are expected to exhibit similar rheological properties (Morrey 1995). Rheological properties may also change as the slurry's particulate supernate chemistry changes with age. Low temperature calcination predicts the potential for hazardous gas generation.



## 2.0 Blended Waste Simulant Preparation Procedure

Chemicals added as insoluble solids are to be in the form of fine powders (< -325 mesh) so that complete dispersion and homogeneity will occur. The use of a grinder pump or other shearing device to make sure that solids are finely divided is acceptable. Highly toxic and carcinogenic materials (see appropriate MSDS) are indicated in the tables by shading. These materials should be handled in well ventilated areas with appropriate personnel protection.

The vessels used in this procedure should be equipped with cooling capabilities, a mixing impeller, and tank ventilation. During the preparation, slurry temperatures should be maintained below 40°C to control exothermic reactions during the hydroxide precipitation steps. Mixing times should be sufficient to guarantee complete dispersion and homogeneity of the slurries. The user or producer determines the appropriate agitation times.

The capacity of the tanks used to prepare a 1000-L batch will determine the number of washing steps required to remove excess sodium nitrate. Analysis steps are to be used only to verify that all the chemicals were added and added in the correct amounts. Uncertainties in the analytical data should be considered before basing chemical adjustments on the analytical measurements.

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 or chemical species of components. A settle/decant separation method should be used with caution because 1) the suspension may gel and 2) the method requires large quantities of dilution water and extended settling times. If possible, centrifugation is recommended. The use of a basic nitrite wash solution may facilitate the settling of the simulant by preventing suspensions from forming.

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 Tables 3-8. Highly toxic or carcinogenic components (see appropriate MSDS) are shaded, and no radioactive constituents are added. Feed-stock chemicals should be technical grade quality or higher. Certification by the vendor of such e.g., copies of supplier certification, is recommended.

### 2.1 Preparation of Major Component Slurry

This part of the procedure provides instructions to precipitate  $MnO_2$  and neutralize, precipitate, and wash the major component hydroxide slurry. Quantities of the components can be found in Table 3.

- A. Fill vessel 1 with [A] L of water.
- B. Add [B] g of 50% 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.
- 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 between 35°C and 40°C to make sure 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). During this step, insoluble  $MnO_2$  will form.
- E. With continued mixing, add [E] L of water, [F] g of ferric nitrate nonahydrate  $\{Fe(NO_3)_3 \cdot 9H_2O\}$ , [G] g of zirconium nitrate pentahydrate  $\{Zr(NO_3)_2 \cdot 5H_2O\}$ , [H] g of nickel nitrate hexahydrate  $\{Ni(NO_3)_2 \cdot 6H_2O\}$ , and [I] g of neodymium nitrate hexahydrate  $\{Nd(NO_3)_3 \cdot 6H_2O\}$  to vessel 1.

Table 3. Major Components<sup>(a)</sup>

Item	Component	Unit	Quantity
[A]	Dilution Water	L	100
[B]	$Mn(NO_3)_2$ (50% solution)	g	$1.90 \times 10^3$
[C]	$KMnO_4$	g	$5.60 \times 10^2$
[D]	Dilution Water	L	100
[E]	Dilution Water	L	300
[F]	$Fe(NO_3)_3 \cdot 9H_2O$	g	$1.24 \times 10^5$
[G]	$ZrO(NO_3)_2$	g	$7.34 \times 10^3$
[H]	$Ni(NO_3)_2 \cdot 6H_2O$	g	$4.01 \times 10^3$
[I]	$Nd(NO_3)_3 \cdot 6H_2O$	g	$2.66 \times 10^3$
[J]	20 M NaOH	L	100
[K]	Wash Solution <sup>(b)</sup>	L	700

(a) Highly toxic or carcinogenic components are shaded.

(b) Wash with 0.01M NaOH solution with 0.69 g/L  $NaNO_2$  added to maintain the ionic strength of the solution and to maintain the basicity so that the nitrite does not decompose.

- F. Mix until the nitrates are completely dissolved. Precipitated  $\text{MnO}_2$  will not dissolve during this step. When the nitrates are completely dissolved, the solution will be clear with fine black specks of  $\text{MnO}_2$  floating throughout.
- G. In a separate vessel, prepare approximately [J] L of a 20 M NaOH solution by dissolving 800 g of NaOH per liter of water.
- H. Stirring constantly, slowly add approximately [J] L of 20 M NaOH solution to the solution in vessel 1 until the pH is 10 to 11 and stable (a variation of not more than  $\pm 0.2$  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  $40^\circ\text{C}$ .
- I. Continue to mix 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 a wash/solids-separation sequence (such as settle/decant) and leave final volume so that solids are less than 20 wt% and total soluble nitrate is less than 0.97 g per liter of final total volume (1000 L). Past preparations indicate that 2 to 3 equivalent volumes, a total of [K] L of wash solution, will be needed to bring the amount of nitrate below the maximum allowable limit. SOLIDS CONCENTRATION MUST BE MAINTAINED BELOW 30 wt% DURING THE SEPARATION PROCESS so that Zr and Fe species are not exposed to air.
- K. Mix 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 that washing was sufficient to decrease the nitrate and that major cationic species have not been lost (except for sodium). Major cations, excluding Na, should be within  $\pm 10\%$  of target values listed in Table 3. The amount of nitrate retained should be less than 0.97 g for every liter of the final total volume (1000 L).

## 2.2 Addition of Soluble and Slightly Soluble Components

This part of the procedure provides instructions for adding the soluble and slightly soluble components to the major hydroxide slurry. Quantities of the components can be found in Table 4.

- A. While continuously mixing the slurry in vessel 1, add the soluble and slightly soluble components to the vessel in the order and amounts shown in Table 4. *The carcinogenic and highly toxic components should be pre-slurried with water in a ventilation hood using the appropriate respiratory precautions and then poured into vessel 1.*
- B. Based on the analytical results from Section 2.1 for potassium, add KOH to adjust the potassium level of the simulant to  $1.37 \times 10^{-2}$  mol/L.

- C. Mix 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  $\pm 10\%$  of target values listed in Table 3, and the soluble/slightly soluble components should be within  $\pm 15\%$  of the values specified in Table 4.

### 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 are found in Table 5.

- A. To a second vessel (vessel 2) add approximately [A] L of water. Add components [B] through [N] from Table 5 in the order and amount shown. Any insoluble components should be ground to a maximum diameter of 0.1 mm.

Table 4. Soluble and Slightly Soluble Components<sup>(a)</sup>

Item	Component	Unit	Quantity
[A]	NaCl	g	$1.53 \times 10^2$
[B]	Na <sub>2</sub> SO <sub>4</sub>	g	$8.33 \times 10^2$
[C]	CuSO <sub>4</sub> · 5H <sub>2</sub> O	g	$2.19 \times 10^2$
[D]	H <sub>3</sub> BO <sub>3</sub>	g	$2.47 \times 10^2$
[E]	Na <sub>3</sub> PO <sub>4</sub>	g	$2.40 \times 10^3$
[F]	Na <sub>2</sub> CO <sub>3</sub>	g	$1.06 \times 10^4$
[G]	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	g	$4.09 \times 10^3$
[H]	Ba(OH) <sub>2</sub> · 8H <sub>2</sub> O	g	$1.26 \times 10^3$
[I]	CsNO <sub>3</sub>	g	$8.53 \times 10^2$
[J]	MoO <sub>3</sub>	g	$1.00 \times 10^1$
[K]	Sb <sub>2</sub> O <sub>3</sub>	g	$1.50 \times 10^2$
[L]	ReO <sub>2</sub>	g	$5.70 \times 10^2$
[M]	Sr(NO <sub>3</sub> ) <sub>2</sub>	g	$1.63 \times 10^2$
[N]	SeO <sub>2</sub>	g	$2.00 \times 10^2$

(a) Highly toxic or carcinogenic components are shaded.

Table 5. Minor Component Nitrates and Insolubles<sup>(a)</sup>

Minor Components				Insolubles			
Item	Compound	Unit	Quantity	Item	Compound	Unit	Quantity
[A]	Dilution Water	L	355	[J]	La(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	g	1.29x10 <sup>3</sup>
[B]	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	g	3.10x10 <sup>3</sup>	[K]	NdF <sub>3</sub>	g	3.18x10 <sup>2</sup>
[C]	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	g	1.73x10 <sup>3</sup>	[L]	TeO <sub>2</sub>	g	1.40x10 <sup>2</sup>
[D]	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	g	3.15x10 <sup>2</sup>	[M]	TiO <sub>2</sub>	g	6.00x10 <sup>1</sup>
[E]	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	g	8.44x10 <sup>3</sup>	[N]	AgNO <sub>3</sub>	g	8.80x10 <sup>1</sup>
[F]	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	g	7.61x10 <sup>3</sup>	[O]	10 M NaOH	L	50
[G]	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	g	1.46x10 <sup>2</sup>	[P]	0.1 M NaOH	L	200
[H]	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	g	1.25x10 <sup>2</sup>				
[I]	Pb(NO <sub>3</sub> ) <sub>2</sub>	g	5.04x10 <sup>2</sup>				

(a) Highly toxic or carcinogenic components are shaded.

- B. In a separate vessel, prepare approximately [O] L of a 10 M NaOH solution by adding 400 g NaOH per liter of water.
- C. Stirring constantly, slowly add approximately [O] L of 10 M NaOH solution 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. Continue to mix the slurry for 1 hour. If the pH has dropped below 10, add additional NaOH to return the pH to between 10 and 11.
- E. In a separate vessel, prepare approximately [P] L of 0.1 M NaOH solution adding 4 g NaOH per liter of water.
- F. Perform a wash/solids-separation sequence (such as settle/decant) and leave final volume so that solids are less than 20 wt% and total soluble nitrate is less than 0.97 g per liter of final total volume (1000 L). Use of a 0.1 M NaOH wash solution will preserve the high pH of the

solution. Past preparations indicate that 2 to 3 equivalent volumes, a total of [P] L of wash solution, will be needed to bring the amount of nitrate below the maximum allowable limit.

- G. Mix the vessel contents thoroughly and collect a representative sample for analysis. Analyze the sample (slurry analysis 3) and determine the amount of nitrate and cations retained in the slurry to confirm sufficient washing has occurred to decrease the nitrate and that cationic species (except sodium) have not been lost. The amount of nitrate retained should be less than 0.97 g for every liter of the final total volume (i.e. 1000 L). The minor and insoluble components should be within  $\pm 15\%$  of the values specified in Table 5.
- H. Transfer the washed slurry to the blend in vessel 1 as shown in Figure 1.

## 2.4 Preparation and Addition of Noble Metals (OPTIONAL)

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 6.

- A. Prepare the noble-metals solution in vessel 3 by placing [A] g of  $\text{Rh}(\text{NO}_3)_3$ , [B] g of  $\text{RuNO}(\text{NO}_3)_3$ , and [C] g of  $\text{Pd}(\text{NO}_2)_2$  in [D] L of 4 M  $\text{HNO}_3$ .
- B. Add approximately [E] L of 10 M NaOH to the noble-metals slurry until the pH reaches  $7.5 \pm 0.5$ . A brown precipitate will form around pH 6.
- C. Boil the slurry for 10 minutes or until the supernate becomes clear.
- D. Perform a wash/solids-separation sequence (such as settle/decant) and leave final volume so that solids are less than 20 wt% and total soluble nitrate is less than 1 g per liter of final total volume (1000 L). Use of a 0.1 M NaOH wash solution which will preserve the high pH of the solution. Past preparations indicate that 2 to 3 equivalent volumes, a total of [F] L of wash solution, will be needed to bring the amount of nitrate below the maximum allowable limit.
- E. Mix the vessel contents thoroughly and collect a representative sample for analysis. Analyze the sample (slurry analysis 4) for retained nitrate and cations to confirm that washing was adequate and that cationic species have not been lost. The amount of nitrate retained should be less than 1 g for every liter of the final total volume (1000 L). The concentrations of noble metals should be within  $\pm 15\%$  of the values specified in Table 6. Document the composition of the product slurry.
- F. Transfer the washed slurry to the blend in vessel 1 as shown in Figure 1.



**Table 6. Noble Metals Slurry Components<sup>(a)</sup>**

Item	Component	Unit	Amount
[A]	Rh(NO <sub>3</sub> ) <sub>3</sub>	g	1.14x10 <sup>2</sup>
[B]	RuNO(NO <sub>3</sub> ) <sub>3</sub>	g	1.52x10 <sup>2</sup>
[C]	Pd(NO <sub>3</sub> ) <sub>2</sub>	g	3.80x10 <sup>1</sup>
[D]	4 M HNO <sub>3</sub>	L	25
[E]	10 M NaOH	L	5
[F]	Wash Solution	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 minerals slurry. Quantities of the components are shown in Table 7.

- A. Add approximately [A] L of water. Add components [B] and [C] from Table 7 in the order and amount shown. This slurry should be prepared in a hood and personnel should wear respiratory protection because SiO<sub>2</sub> is carcinogenic. Any insoluble components should be ground to a maximum diameter of 0.1 mm before being introduced into the tanks.
- B. Transfer the slurry to the blend in vessel 1 as shown in Figure 1.

**Table 7. Mineral Phase Components<sup>(a)</sup>**

Item	Compound	Unit	Amount
[A]	Dilution Water	L	250
[B]	AlOOH (boehmite)	g	2.10x10 <sup>4</sup>
[C]	SiO <sub>2</sub>	g	1.61x10 <sup>4(b)</sup>

(a) Highly toxic or carcinogenic components are shaded.

(b) Value assumes 100% of oxide is supplied by that phase. Fine silica is the first choice material.

## 2.6 Final Blend Adjustment

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

- A. Mix the vessel contents thoroughly and collect a representative slurry sample of the final blend. Analyze the sample (slurry analysis 5) to determine the concentration of the components in the blended waste simulant. Major oxides, excluding sodium, should be within  $\pm 10\%$  of the values listed in Table 3. All other components should be within  $\pm 15\%$  of the values specified in Tables 4 through 7. The weight percent solids should be between 15% and 20%.
- B. Adjust the nitrate, nitrite, and sodium concentrations to 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 because sodium will have been added with the nitrate and nitrite.
- C. Adjust the wt% solids by adding or evaporating water as appropriate.
- D. 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

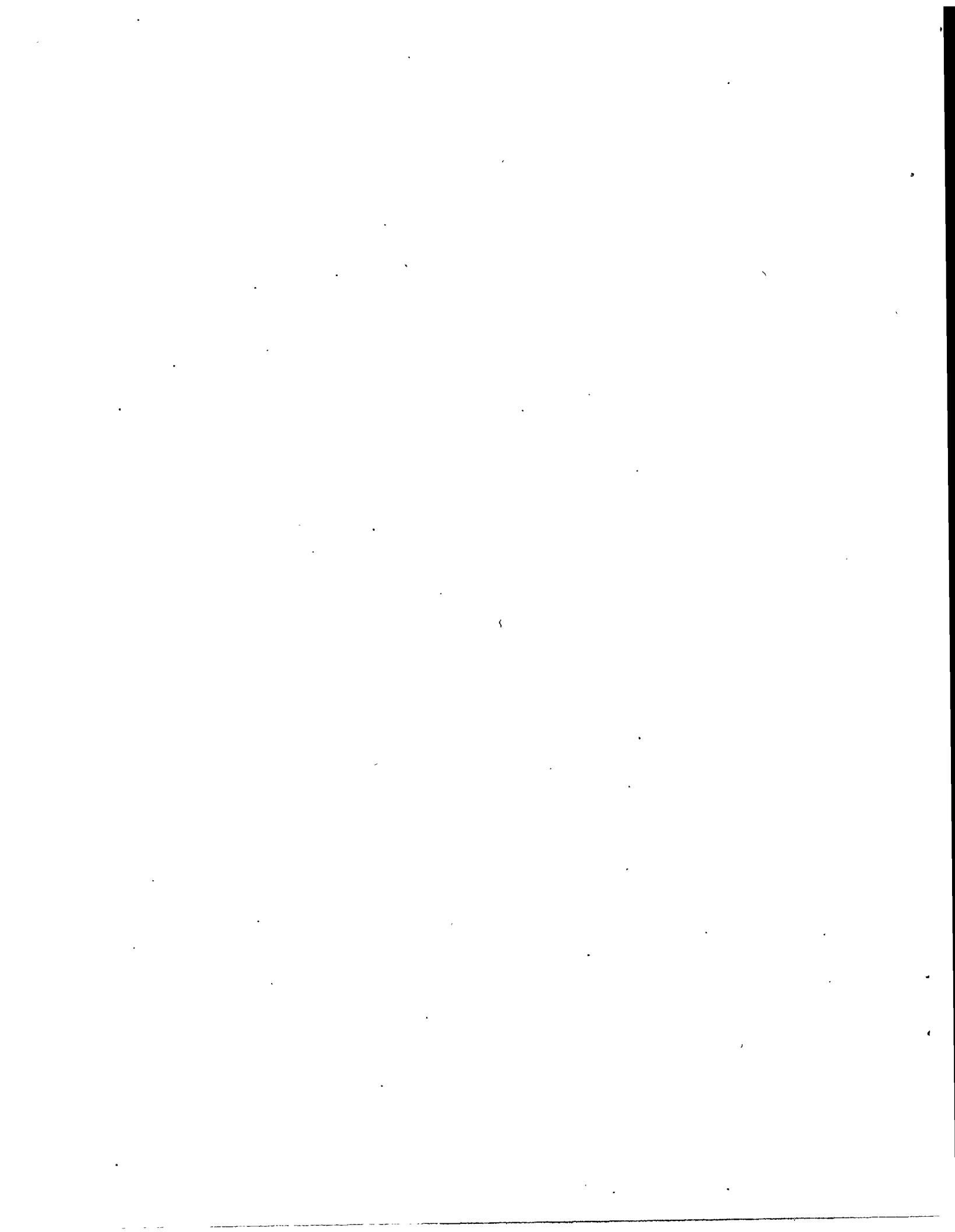
Item	Ion	Source	Target Concentration (g ion/L)
[A]	NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	2.112
[B]	NO <sub>2</sub> <sup>-</sup>	NaNO <sub>2</sub>	3.880
[C]	Na <sup>+</sup>	NaOH	17.673

### 3.0 Requirements and Specifications

1. Meeting the following specifications for the chemical composition is recommended:

Weight Percent Solids	15 to 20 wt%
Major Oxides (excluding Na):	$\pm 10\%$ of values in Table 3
Other Oxides	$\pm 15\%$ of values in Tables 4, 5, 6, and 7
Anions (excluding $(NO_2^-)$ and Total Organic Carbon	$\pm 15\%$ of values in Tables 4 and 5
Sodium (before final adjustment):	$< 17.67$ g/L
Nitrite (before final adjustment):	$< 3.88$ g/L
Nitrate (before final adjustment):	$< 2.11$ g/L

2. Feed-stock chemicals should be technical grade quality. Certification by the vendor of such (e.g., copies of supplier certification) is recommended, and copies should be included with the shipping documentation.
3. When storing the blended waste simulant, care should be taken to prevent the slurry from losing water content and drying out because the chemical species of iron and zirconium can be affected by exposure to air. To prevent this, store the simulant in a sealed container.



## 4.0 References

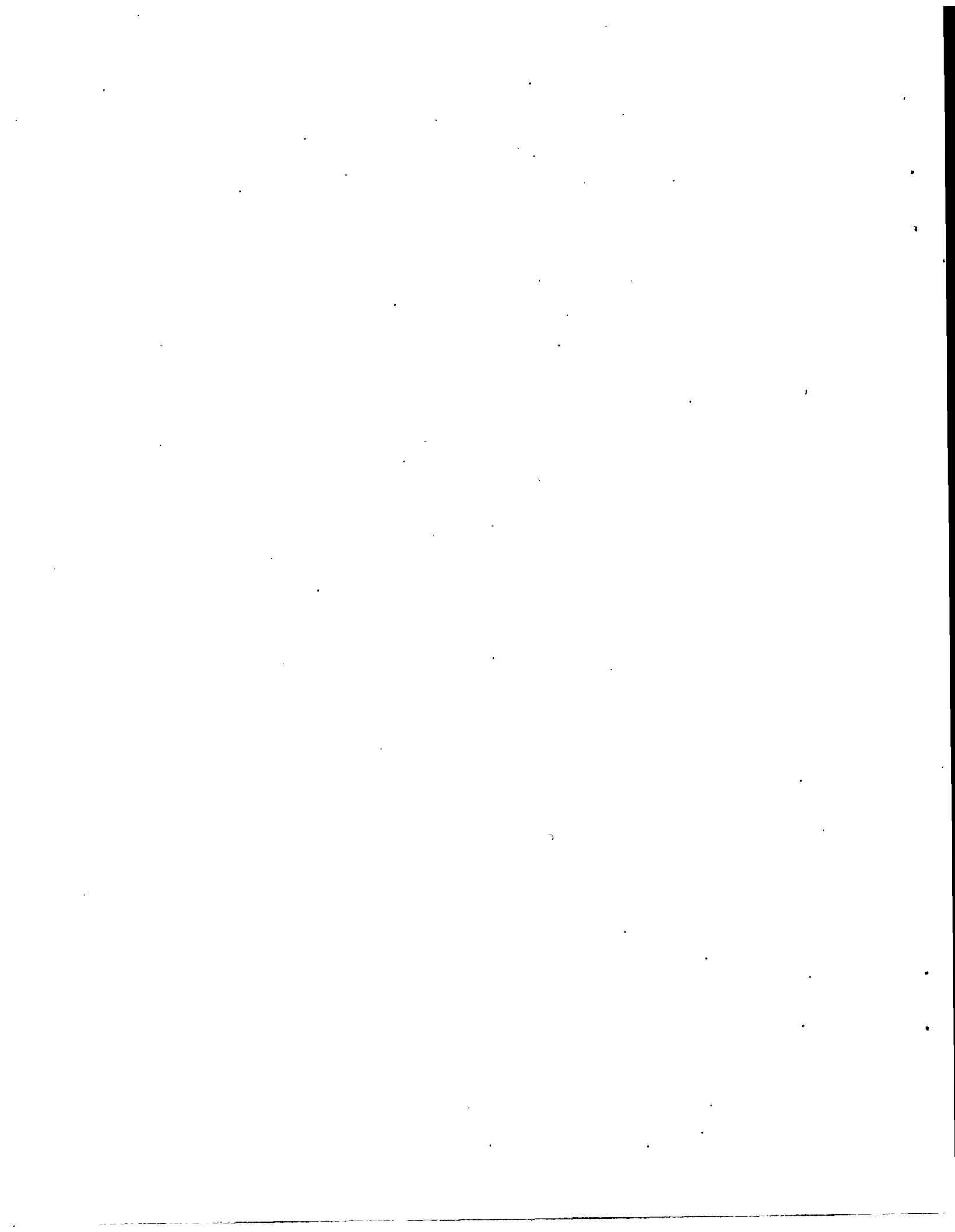
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## Appendix A.1

RFP Simulant Composition at 31 g oxide/L in Terms of Elements

Element	g/L Element	Element	g/L Element	Element	g/L Element
Ag	0.018	K	0.110	Ru	0.017
Al	2.931	La	0.135	S	0.049
As	0.000	Mg	0.223	Sb	0.039
B	0.013	Mn	0.151	Se	0.044
Ba	0.169	Mo	0.002	Si	2.336
Bi	0.017	Na	5.478	Sr	0.021
Ca	0.443	Nd	0.270	Tc	0.000
Cd	0.350	Ni	0.250	Te	0.034
Ce	0.030	P	0.140	Ti	0.011
Cl	0.028	Pb	0.097	Tl	0.000
Cr	0.070	Pd	0.005	U	0.000
Cs	0.181	Pu	0.000	V	0.000
Cu	0.018	Re	0.151	Zn	0.010
F	0.028	Rh	0.013	Zr	0.897
Fe	5.339				

Nitrogen and Carbon Components of the RFP Simulant at 31 g oxide/L

Component	g/31g WO	Source Chemical	Anion Equivalent	Source Chemical
			g/g	g/31g WO
NO <sub>2</sub> <sup>-</sup>	0.802	NaNO <sub>2</sub>	0.667	1.202
NO <sub>3</sub> <sup>-</sup>	0.477	NaNO <sub>3</sub>	0.729	0.654
TOC	0.227	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0.179	1.268 as carbon
TIC	1.856	Na <sub>2</sub> CO <sub>3</sub>	0.566	3.279



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