INEEL/EXT-01-01219

"Worst Case" Simulant for INTEC Sodium-Bearing Waste Vitrification Tests

J. D. Christian

September 2001

Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

INEEL/EXT-01-01219

"Worst Case" Simulant for INTEC Sodium-Bearing Waste Vitrification Tests

Jerry D. Christian

September 2001

Idaho National Engineering and Environmental Laboratory
Idaho Falls, Idaho 83415

Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727

ABSTRACT

The Idaho Nuclear Technology and Engineering Center (INTEC) is developing technologies to process the radioactive liquid sodium-bearing waste from the waste tanks at INTEC to solidify the waste into a form suitable for disposition in a National high-level waste repository currently being considered at Yucca Mountain, Nevada. The requirement is for a qualified glass waste form. Therefore, vitrification is being developed using laboratory, research-scale, and pilot scale melters. While some laboratory experiments can be done with actual waste, the larger scale and most laboratory experiments must be done on non-radioactive simulant waste solutions.

Some tests have previously been done on simulants of a representative waste that has been concentrated and will remain unchanged in tank WM-180 until it is vitrified. However, there is a need to develop glass compositions that will accommodate all future wastes in the tanks. Estimates of those future waste compositions have been used along with current compositions to develop a "worst-case" waste composition and a simulant preparation recipe suitable for developing a bracketing glass formulation and for characterizing the flowpath and decontamination factors of pertinent off-gas constituents in the vitrification process. The considerations include development of criteria for a worst-case composition. In developing the criteria, the species that are known to affect vitrification and glass properties were considered. Specific components that may need to be characterized in the off-gas cleanup system were considered in relation to detection limits that would need to be exceeded in order to track those components. Chemical aspects of various constituent interactions that should be taken into account when a component may need to be increased in concentration from that in the actual waste for detection in experiments were evaluated.

The worst-case waste simulant composition is comprised of the highest concentration of each species of concern that will be present in current and future wastes from different tanks. Because most of the species of concern are at small concentrations relative to the bulk components that are fairly constant, maximizing them individually into a single waste composition does not substantially affect the general vitrification chemistry.

The evaluation and results are reported here. This simulant is suitable for performing laboratory and pilot-scale tests in order to develop the vitrification technology.

CONTENTS

TABLES

"Worst-Case" Simulant for INTEC Sodium-Bearing Waste Vitrification Tests

1. INTRODUCTION

The INEEL High-Level Waste Program Task Number BC42, "SIM-Waste Management Scenario," calls for preparing simulant recipes based on the Waste Management Plan. Specifically, the task is to develop a detailed procedure on how to make up chemical mixtures that will perform as satisfactory non-radioactive surrogates for waste feed material to a pilot plant vitrification facility for liquid feed and residual entrained/suspended solids. Evaluations have been made of future potential waste compositions. The objective was to identify a "worst case" composition for vitrification testing.

The compositions derived by Charles Barnes[1] provide the basis for the compositions that are evaluated. Barnes estimated future waste compositions based on two scenarios: 1) new waste tanks in which the wastes from existing tanks and future projected wastes to 2012 are blended in a way to minimize variations in compositions and 2) no new tanks, but with future wastes blended in existing tanks to assure as much uniformity as possible. In this latter scenario, the current contents of WM-180 will remain in that tank. Both scenarios were included in evaluating a single, worst-case, composition. The new tanks scenario may also be considered to represent a no-new-tanks scenario but with a feed blending tank provided in the vitrification plant that will enable similar blending of the wastes to accomplish uniformity.

The evaluations include development of criteria for defining the worst case composition. Once the composition is determined, the simulant preparation is based on that developed for WM-180 simulant.[2] That includes both a spreadsheet of reagents for calculating quantities of each and a recipe for the step-by-step procedures for preparing a solution.

2. CRITERIA FOR "WORST-CASE" WASTE COMPOSITION

Two aspects of the waste are important to development of vitrification technology. One, and the more important, is the composition that affects waste loading in and composition and properties of the glass waste form. The other is the volatile components that can affect the off-gas treatment requirements and operational design. Of the volatile (and "semivolatile") species, radionuclides are of the most interest, as their flowpath must be established and necessary removal technologies provided in the off-gas treatment system. Other potential problem volatilized species that must be evaluated are bulk chemical constituents that may challenge capacities of off-gas equipment or possibly plug off-gas piping. This latter situation is unlikely for the sodium-bearing waste (SBW). An example for fresh high-level waste processed in the past was ruthenium. It was present at high concentrations in commercial waste and was volatile under certain conditions during calcination or vitrification of the waste. This sometimes led to plugging of melter off-gas piping. Also, the high activity of ^{106}Ru resulted in difficulties in decontaminating process equipment and off-gas pipes.

2.1 Glass Formulation and Properties

The bracketing features of composition for determining vitrification limiting characteristics were determined by discussion with John Vienna of PNNL.[3] The elements or ions that are considered to be limiting for glass are S, halides (especially their sum; fluoride is the least bad), and P. A worst case simulant should have these components present at the maximum expected concentrations. The noble metals (Pd, Ru, Rh, and Ag) should also be at their highest potential concentrations. The non-volatile oxides in glass (especially Al, Cr) are important; they should not be appreciably diluted when maximizing other constituents. Since the other constituents are at very small concentrations, maximizing them will result in negligible dilution of the glass matrix.

If a substantial solids heel associated with the liquid is included that adds significantly to S, P, or Ca concentrations, it would result in a more "worst case" glass composition.

2.2 Off-Gas Constituents

While nitric acid, per se, is not identified as a component of special concern to process design considerations in terms of glass formulation, the maximum projected concentration is selected here for the "worst-case" simulant. The projected maximum concentration of 3.39 M HNO_3 in the jet-diluted waste is 2.38 molar greater than in the WM-180 waste tested so far. The additional concentration will affect sugar addition for oxidation potential control and it will increase the off-gas rate and loading of NO_x.

By selecting both the maximum nitric acid concentration and the WM-180 concentrations of aluminum nitrate and sodium nitrate (both of which are maximum for WM-180), the total nitrate is maximized. This will determine the maximum sugar addition rate, which affects the CO_2 rate and, also, the fuel rate to the noxidizer in the off-gas treatment system.

The elements of concern for off-gas characterization and treatment were determined by discussion with Ronald Goles of PNNL.[4] The volatile and semi-volatile elements of potential radiological concern are I, Cs, Tc (Re surrogate), Sb, and Te.

Ruthenium is normally a radiological concern for off-gas treatment requirements, but the SBW is sufficiently aged that radioactive ruthenium isotopes (39.27-day ^{103}Ru and 1.02-yr ^{106}Ru) have decayed to negligible levels. The total Ru concentration is also small enough so as not likely to present an operational problem in the off-gas treatment system. The total quantity of ruthenium in current and future

wastes is 194 g-atoms in 3.66 million liters that will be processed.[1] If all the ruthenium were to volatilize and then deposit as RuO_2 during processing of all the waste, the volume of deposit would be 3.7 L, based on the theoretical density of RuO_2. Of course, this is an unlikely scenario. Much of any volatilized ruthenium would be captured in a scrubber and the volatility will be substantially suppressed by the presence of a cold cap on the glass melt.

Nevertheless, ruthenium flowpath will be tracked so that operational considerations are adequately addressed in design of the plant.

As surrogates for U and Am, the elements Ce and Nd are important for tracking.

Most studies and evaluations of the volatile and semivolatile radionuclides have been concerned with Light Water Reactor (LWR) HLLW and some with defense HLLW. The former has many orders of magnitude greater concentrations of the radionuclides than does SBW. The problem volatile and semivolatile radionuclides (i.e., those discussed above) have been established based on processing those compositions of LWR waste. While it is beyond the scope of the present report to evaluate control needs for the radionuclides from the SBW, such a study is needed to provide a quantitative basis for assessing feed-to-stack control requirements and for guiding experimental characterization of elements of selected radionuclides. An evaluation would consider[5, 6] feed source terms,[1] processing rate, stack off-gas flow rate, atmospheric dispersion factors to uncontrolled areas, and regulatory concentration limits in uncontrolled areas. Additional ALARA considerations would then be taken into account and secondary waste streams evaluated. The result may be that some of the radionuclides identified above will become unimportant regarding the need to characterize their flowpaths.

Planned off-gas sampling tests[7] in the Remote Analytical Laboratory from crucible melts of WM-180 waste will provide information for evaluation, as well.

While constituents affecting the glass formulation must be incorporated at actual maximum concentrations in the simulated waste for the tests, the radionuclide elements present a different situation. Their concentrations may not be especially important, within limits, in determining the decontamination factors in the processing pilot plant system. More significantly, some are present at levels that are below detection limits for the experimental design. Thus, they must be increased in concentration above the levels in the actual waste in order to study them. Additional discussion on this point is provided in the next section.

Mercury is of special interest because its concentration in the off gas will determine whether it will need to be removed from the scrub solution as well as by the GAC bed. Mercury concentration in secondary wastes is a major issue in determining acceptable disposal sites. Therefore, if mercury is added to the simulant waste, it should be at the maximum concentration in order to determine the pertinent operating characteristics.

3. EVALUATION OF "WORST-CASE" COMPOSITION

3.1 Liquid

3.1.1 General

The projected elemental and anion compositions of wastes in the tanks for the case of no new tanks are given in Table 1, taken from Barnes.[1] Those for new tanks, also from Barnes, are given in Table 2. In both cases, charge balance is achieved by adjusting nitrate concentration. Before the wastes are prepared for vitrification, they will be transferred from the tanks to the vitrification plant by steam jetting. This will dilute the wastes by approximately 5% (possibly up to 10%). Comparisons for the purpose of selecting the worst case individual elements are made on the tank compositions directly. But, when compiling the worst case composition for simulant preparation, each element concentration will be diluted by 5% to provide the composition for the vitrification plant.

Table 1. Composition of Tank Wastes Prior to Transfer to Vitrification Plant – No New Tanks.[1]

	Stream				
	WM-180-1	WM-188-2	WM-189-3	WM-187-6	WM-181-5
Gallons	276,000	283,667	280,012	57,264	19,891
TOC, g/l	2.12E-01	4.62E-01	4.03E-01	3.78E-01	6.03E-03
UDS, g/l	2.46E-01	4.01E+00	4.16E+00	2.07E+00	5.31E-02
	Moles/liter	Moles/liter	Moles/liter	Moles/liter	Moles/liter
H+	1.06	3.56	2.43	2.73	0.05
Al	6.98E-01	5.72E-01	6.64E-01	1.81E-01	9.38E-03
Am	7.60E-08	1.33E-07	1.22E-07	3.40E-08	1.87E-09
Sb	<6.71E-05	7.31E-06	2.50E-06	1.23E-05	9.37E-08
As	5.25E-04	3.78E-05	3.38E-05	9.09E-07	1.56E-08
Ba	5.87E-05	8.64E-05	1.06E-04	2.44E-05	1.25E-06
Be	8.17E-06	1.78E-06	9.15E-07	2.09E-06	1.61E-08
B	1.29E-02	2.33E-02	2.84E-02	5.07E-03	2.70E-04
Br	1.53E-07	7.38E-06	3.62E-07	5.69E-06	3.75E-09
Cd	7.94E-04	6.32E-03	9.00E-03	8.59E-04	7.73E-05
Ca	4.97E-02	6.01E-02	7.32E-02	6.44E-03	4.61E-04
Ce	4.98E-05	2.17E-05	1.80E-05	3.15E-06	2.07E-07
Cs	8.14E-06	2.21E-05	1.73E-05	3.55E-06	2.15E-07
Cl	3.16E-02	2.30E-02	3.07E-02	3.85E-03	4.72E-04
Cr	3.53E-03	5.87E-03	6.97E-03	1.00E-03	8.17E-05
Co	2.03E-05	1.69E-04	1.12E-04	1.92E-04	2.16E-06
Cu	7.34E-04	8.77E-04	1.17E-03	1.45E-04	1.22E-05
Dy	3.15E-10	7.95E-10	6.23E-10	1.28E-10	7.73E-12
Eu	3.09E-09	9.53E-09	9.37E-09	1.05E-09	6.67E-11
F	4.99E-02	1.17E-01	1.10E-01	3.21E-02	7.84E-04
Gd	1.87E-04	4.58E-05	1.37E-05	1.80E-05	9.47E-07
Ge	4.45E-09	2.69E-08	8.93E-09	1.44E-08	1.09E-10
In	6.74E-07	1.70E-06	1.33E-06	2.73E-07	1.65E-08

Table 1. Composition of Tank Wastes Prior to Transfer to Vitrification Plant – No New Tanks.[1] (continued)

	WM-180-1	WM-188-2	WM-189-3	WM-187-6	WM-181-5
	Moles/liter	Moles/liter	Moles/liter	Moles/liter	Moles/liter
I	5.87E-07	3.69E-06	3.16E-06	1.46E-06	5.84E-08
Fe	2.29E-02	2.50E-02	2.76E-02	6.32E-03	3.18E-04
La	4.54E-06	1.14E-05	8.98E-06	1.84E-06	1.11E-07
Pb	1.38E-03	6.09E-03	1.16E-03	2.79E-03	8.12E-06
Li	3.57E-04	3.42E-04	4.72E-04	5.29E-05	4.55E-06
Mg	1.27E-02	7.79E-03	1.06E-02	1.27E-03	1.07E-04
Mn	1.48E-02	1.63E-02	2.07E-02	4.57E-03	2.10E-04
Hg	2.12E-03	6.97E-03	2.37E-03	2.90E-03	1.99E-05
Mo	2.03E-04	3.95E-04	4.80E-05	4.51E-04	3.08E-06
Nd	1.50E-05	3.79E-05	2.97E-05	6.10E-06	3.69E-07
Np	1.66E-05	2.29E-05	1.46E-05	4.61E-06	1.81E-07
Ni	1.55E-03	4.14E-03	5.81E-03	7.87E-04	7.25E-05
Nb	1.63E-05	4.74E-06	1.00E-06	1.13E-06	6.48E-08
NO3	5.59E+00	6.99E+00	6.83E+00	3.75E+00	1.02E-01
Pd	<2.47E-05	4.44E-06	3.70E-06	6.98E-07	4.35E-08
PO4	1.44E-02	4.16E-03	6.92E-03	1.77E-03	1.48E-04
K	2.07E-01	1.54E-01	2.18E-01	3.35E-02	1.84E-03
Pu	5.53E-06	7.16E-06	5.31E-06	1.72E-06	8.88E-08
Pr	4.20E-06	1.06E-05	8.29E-06	1.70E-06	1.03E-07
Pm	1.53E-09	3.86E-09	3.03E-09	6.22E-10	3.76E-11
Rh	1.84E-06	4.63E-06	3.63E-06	7.46E-07	4.51E-08
Rb	3.64E-06	9.59E-06	7.47E-06	1.59E-06	9.37E-08
Ru	1.31E-04	3.18E-05	1.90E-05	4.88E-06	2.87E-07
Sm	2.88E-06	7.27E-06	5.70E-06	1.17E-06	7.07E-08
Se	<1.54E-04	1.08E-06	1.77E-06	4.53E-07	1.76E-08
Si	<3.18E-07	3.20E-03	4.19E-03	5.81E-04	4.27E-05
Ag	<5.57E-06	2.24E-05	2.12E-05	6.02E-06	1.70E-07
Na	2.17E+00	1.29E+00	1.88E+00	3.90E-01	2.24E-02
Sr	1.25E-04	2.46E-05	1.94E-05	4.51E-06	2.55E-07
SO4	7.35E-02	4.48E-02	5.84E-02	1.08E-02	5.54E-04
Tc	2.82E-06	1.31E-05	5.76E-06	2.03E-06	8.32E-08
Te	1.45E-06	3.66E-06	2.87E-06	5.89E-07	3.56E-08
Tb	1.07E-09	2.69E-09	2.11E-09	4.33E-10	2.62E-11
Tl	<4.31E-05	9.46E-06	1.44E-05	1.68E-06	1.28E-07
Th	9.39E-11	3.74E-10	1.93E-10	6.22E-11	2.47E-12
Sn	<4.32E-05	1.17E-06	8.61E-07	3.96E-07	1.73E-08
Ti	6.08E-05	4.85E-05	6.62E-05	7.91E-06	6.65E-07
U	3.54E-04	6.52E-04	5.88E-04	7.94E-05	4.73E-06
V	<9.72E-04	1.09E-04	1.52E-04	2.21E-05	1.44E-06
Y	3.46E-06	8.71E-06	6.84E-06	1.40E-06	8.48E-08
Zn	1.10E-03	1.67E-03	1.51E-03	1.68E-03	1.82E-05
Zr	6.66E-05	1.95E-02	2.06E-02	4.30E-03	2.10E-04

Table 2. Estimate of New Tank Farm Feed Composition Variation.[1]

	VIT-1a	VIT-1b	VIT-1c	Minimum	Maximum	Max/Min
TOC, g/l	0.34	0.39	1.14	0.34	0.39	1.14
UDS, g/l	2.52	2.85	1.13	2.52	2.85	1.13
	Mol/lit	Mol/lit	Mol/lit	Mol/lit	Mol/lit	Ratio, Mol/Mol
H+	2.28	2.71	2.22	2.22	2.71	1.22
Al	5.39E-01	5.60E-01	5.74E-01	5.39E-01	5.74E-01	1.06
Am	7.52E-08	7.64E-08	7.99E-08	7.52E-08	7.99E-08	1.06
Sb	2.28E-05	2.41E-05	2.53E-05	2.28E-05	2.53E-05	1.11
As	1.62E-04	1.62E-04	1.75E-04	1.62E-04	1.75E-04	1.08
Ba	6.97E-05	7.29E-05	7.48E-05	6.97E-05	7.48E-05	1.07
Be	3.26E-06	3.42E-06	3.42E-06	3.26E-06	3.42E-06	1.05
B	1.77E-02	1.88E-02	1.91E-02	1.77E-02	1.91E-02	1.07
Br	2.94E-06	3.81E-06	2.27E-06	2.27E-06	3.81E-06	1.68
Cd	4.32E-03	4.58E-03	4.73E-03	4.32E-03	4.73E-03	1.09
Ca	4.90E-02	5.17E-02	5.36E-02	4.90E-02	5.36E-02	1.09
Ce	2.43E-05	2.48E-05	2.61E-05	2.43E-05	2.61E-05	1.08
Cs	1.29E-05	1.36E-05	1.39E-05	1.29E-05	1.39E-05	1.07
Cl	2.31E-02	2.45E-02	2.47E-02	2.31E-02	2.47E-02	1.07
Cr	4.45E-03	4.63E-03	4.80E-03	4.45E-03	4.80E-03	1.08
Co	1.09E-04	1.31E-04	1.20E-04	1.09E-04	1.31E-04	1.20
Cu	7.52E-04	7.79E-04	8.14E-04	7.52E-04	8.14E-04	1.08
Dy	4.72E-10	4.95E-10	5.06E-10	4.72E-10	5.06E-10	1.07
Eu	5.89E-09	6.26E-09	6.43E-09	5.89E-09	6.43E-09	1.09
F	7.73E-02	8.45E-02	8.40E-02	7.73E-02	8.45E-02	1.09
Gd	6.89E-05	6.75E-05	7.19E-05	6.75E-05	7.19E-05	1.07
Ge	1.27E-08	1.50E-08	1.17E-08	1.17E-08	1.50E-08	1.28
In	1.01E-06	1.06E-06	1.08E-06	1.01E-06	1.08E-06	1.07
I	2.16E-06	2.30E-06	2.17E-06	2.70E-04	2.89E-04	1.07
Fe	2.08E-02	2.18E-02	2.22E-02	2.08E-02	2.22E-02	1.07
La	6.79E-06	7.12E-06	7.29E-06	6.79E-06	7.29E-06	1.07
Pb	2.68E-03	3.48E-03	2.51E-03	2.51E-03	3.48E-03	1.39
Li	3.17E-04	3.28E-04	3.43E-04	3.17E-04	3.43E-04	1.08
Mg	8.42E-03	8.64E-03	9.11E-03	8.42E-03	9.11E-03	1.08
Mn	1.44E-02	1.51E-02	1.57E-02	1.44E-02	1.57E-02	1.09
Hg	3.44E-03	4.26E-03	3.34E-03	3.34E-03	4.26E-03	1.28
Mo	2.42E-04	2.77E-04	2.14E-04	2.14E-04	2.77E-04	1.30
Nd	2.25E-05	2.36E-05	2.41E-05	2.25E-05	2.41E-05	1.07
Np	1.23E-05	1.26E-05	1.32E-05	1.23E-05	1.32E-05	1.07
Ni	3.13E-03	3.25E-03	3.37E-03	3.13E-03	3.37E-03	1.08
Nb	6.10E-06	6.08E-06	6.45E-06	6.08E-06	6.45E-06	1.06
NO3	5.70E+00	6.25E+00	5.87E+00	5.70E+00	6.25E+00	1.10
Pd	8.94E-06	8.96E-06	9.61E-06	8.94E-06	9.61E-06	1.08
PO4	7.09E-03	7.05E-03	7.50E-03	7.05E-03	7.50E-03	1.06

Table 2. Estimate of New Tank Farm Feed Composition Variation.[1]

	VIT-1a	VIT-1b	VIT-1c	Minimum	Maximum	Max/Min
	Mol/lit	Mol/lit	Mol/lit	Mol/lit	Mol/lit	Ratio, Mol/Mol
Pu	4.34E-06	4.41E-06	4.61E-06	4.34E-06	4.61E-06	1.06
K	1.58E-01	1.64E-01	1.70E-01	1.58E-01	1.70E-01	1.08
Pr	6.28E-06	6.58E-06	6.73E-06	6.28E-06	6.73E-06	1.07
Pm	2.29E-09	2.41E-09	2.46E-09	2.29E-09	2.46E-09	1.07
Rh	2.75E-06	2.88E-06	2.95E-06	2.75E-06	2.95E-06	1.07
Rb	5.64E-06	5.91E-06	6.04E-06	5.64E-06	6.04E-06	1.07
Ru	4.96E-05	4.99E-05	5.32E-05	4.96E-05	5.32E-05	1.07
Sm	4.31E-06	4.52E-06	4.63E-06	4.31E-06	4.63E-06	1.07
Se	4.26E-05	4.19E-05	4.59E-05	4.19E-05	4.59E-05	1.09
Si	2.01E-03	2.13E-03	2.17E-03	2.01E-03	2.17E-03	1.08
Ag	1.37E-05	1.50E-05	1.52E-05	1.37E-05	1.52E-05	1.10
Na	1.47E+00	1.51E+00	1.57E+00	1.47E+00	1.57E+00	1.07
Sr	4.62E-05	4.63E-05	4.96E-05	4.62E-05	4.96E-05	1.07
SO4	4.85E-02	5.07E-02	5.27E-02	4.85E-02	5.27E-02	1.09
Tc	4.69E-06	4.95E-06	5.03E-06	4.69E-06	5.03E-06	1.07
Te	2.17E-06	2.28E-06	2.33E-06	2.17E-06	2.33E-06	1.07
Tb	1.60E-09	1.67E-09	1.71E-09	1.60E-09	1.71E-09	1.07
Tl	1.82E-05	1.83E-05	1.96E-05	1.82E-05	1.96E-05	1.08
Th	1.41E-10	1.47E-10	1.51E-10	1.41E-10	1.51E-10	1.07
Sn	1.24E-05	1.21E-05	1.33E-05	1.21E-05	1.33E-05	1.09
Ti	4.75E-05	4.90E-05	5.14E-05	4.75E-05	5.14E-05	1.08
U	3.94E-04	4.17E-04	4.31E-04	3.94E-04	4.31E-04	1.09
V	3.36E-04	3.35E-04	3.62E-04	3.35E-04	3.62E-04	1.08
Y	5.17E-06	5.43E-06	5.55E-06	5.17E-06	5.55E-06	1.07
Zn	1.40E-03	1.46E-03	1.34E-03	1.34E-03	1.46E-03	1.09
Zr	1.11E-02	1.24E-02	1.18E-02	1.11E-02	1.24E-02	1.12

Tables 1 and 2 do not include curie concentrations of radionuclides that Barnes has tabulated. The interested reader may refer to his report. For vitrification tests, the total elemental molar concentration is the parameter of interest, and those are included in the tables here. The tables are complete with some very minor components that are not included in a simulant recipe.

As is expected, the maximum concentration of all components occurs in the no-new-tanks scenario (Table 1). The maximum concentration in the five waste streams in Table 1 for each of the elements of concern discussed in Section 2 are listed in Table 3. In many cases, the WM-180 concentration is the worst. For the most important major species (especially sulfate and phosphate), WM-180 defines the worst case. For those elements that it is not the worst, the concentrations in WM-180 are provided in parentheses for comparison against the worst tank concentration. WM-180 is the one waste composition that has been characterized and a simulant waste prepared for vitrification tests through pilot scale.[2, 8] Actual WM-180 waste has been vitrified in crucibles, as well.[9] Since a single worst case recipe will be prepared, this will give a perspective of how much deviation from WM-180 occurs.

From Table 1, one sees that the major cations Na^{+}, Al^{3+}, and K^{+}, are all at the maximum concentration in WM-180. Thus, the very small deviations in the overall glass composition from that of WM-180 as a result of increasing some of the minor constituents to values in different tanks will be inconsequential, except for the properties related to changes in those minor elements. Nitrate is the major

anion. Aside from it, the major anions (and the ones that affect the glass) are, in decreasing order, F^-, SO_4^{2-}, Cl^-, and PO_4^{3-}. All but F^- are greatest in WM-180; SO_4^{2-} is the most important in challenging glass chemistry.

The worst-case waste composition is derived by picking each of the maximum values given in Table 3 for the elements that are important to the glass and off-gas properties. The balance of the waste is similarly derived from the maximum individual elemental concentrations in Table 1. Finally, the nitrate is adjusted for charge balance. As discussed in Section 3.1.1, the final composition is diluted by 5% to simulate the steam jet dilution that will occur on transferring the wastes to the vitrification plant.

Table 3. Worst-Case (Maximum) Concentrations of Species of Concern for Vitrification Tests.*

		Tank and Concentration for Worst Case			
Elements of Concern for Glass	Elements of Concern for Off Gas	WM-180 Molar †	WM-188 Molar	WM-189 Molar	WM-187 Molar
H^+	H^+	(1.06)	3.56		
Al		6.96E-1			
	Am (Nd surrogate)**	(1.15E-7)	1.33E-7		
	Sb	6.69E-5			
Br		(1.53E-7)	7.38E-6		
Ca		(4.95E-2)		7.32E-2	
	Cs	(8.12E-6)	2.21E-5		
Cl		3.15E-2			
Cr		(3.52E-3)		6.97E-3	
F		(4.98E-2	1.17E-1		
I	I	(5.87E-7)§	3.69E-6		
	Hg	(2.12E-3)	6.97E-3		
	Nd**	(1.50E-5)	3.79E-5		
Pd		2.46E-5			
PO_4^{3-}		1.44E-2			
Rh		(1.84E-6)	4.63E-6		
Ru		1.31E-4			
Ag		(5.55E-6)	2.24E-5		
SO_4^{2-}		7.33E-2			
	Tc	(2.82E-6)	1.31E-5		
	Te	(1.45E-6)	3.66E-6		
	U (Ce surrogate)***	(3.53E-4)	6.52E-4		

*Parentheses are for comparison of WM-180 with the worst case tank. Values in the tank, before jet dilution.
**Nd source concentration exceeds Am concentration in the waste.
***U concentration exceeds Ce concentration (4.98E-5 M in WM-180) in the wastes.
§A value of 1.36E-4 M I was estimated for the WM-180 report in the absence of available data.[2] However, Barnes has since compiled the value of 5.87E-7 M I.[1]
†WM-180 element concentrations in Table 3 are approximately 0.3 % less than concentration values for WM-180 provided by Barnes[1] in Table 1 due to slightly different jet dilution assumptions.

3.1.2 Special Considerations for Off-Gas Constituents

As discussed in the evaluations of WM-180 waste simulant,[2] cesium and technetium present a special situation in considerations for simulant preparation regarding off-gas behaviors. First, in order to detect and measure it in the glass during the RSM-01-1 test at PNNL,[8] cesium in WM-180 simulant was increased a factor of 209 over that of the actual waste concentration[2] to 1.65×10^{-3} M. This was required to result in 0.05 wt% Cs_2O in the glass (calculated at 25% waste oxide loading) that could be measured.[10]

Secondly, when both are present at concentrations typical of commercial HLLW, technetium can potentially affect (increase) volatility of cesium (and cesium can decrease the volatility of technetium) by forming cesium pertechnetate.[2, 11, 12, 13, 14, 15] But, halogens can also form volatile alkali halides. In commercial HLLW, the halide concentration is small compared with the major fission product concentrations and is not a factor. In the SBW, however, the halides are orders of magnitude more concentrated than the cesium and technetium. Further complicating matters, high levels of mercury concentration can strip the halogens from alkali metals and reduce the volatility of cesium.[4] However, the mercury concentration is much less than the halide concentrations in SBW and will likely not play a significant role. More significantly, the sodium and potassium ion concentrations are some five and four orders of magnitude greater than the cesium concentration and will have a major effect on availability of halides for cesium.

The pertinent concentrations in the worst-case SBW are summarized in Table 4. These concentrations of Na, K, Cs, Cl, F, and I were inputted, as well as the 0.663 M Al concentration and glass frit composition (174.01 g SiO_2, 40.16 g B_2O_3, 26.77 g Fe_2O_3, 13.386 g CaO, and 13.386 g Li_2O per liter of waste solution) for 30 wt% waste oxide loading, to the HSC program[16] to perform a simple (and incomplete) thermodynamic modeling of the system at vitrification temperatures. Mercury is at a sufficiently low concentration that it cannot have a major effect of availability of halides. The following conclusions may be drawn from the modeling. Most F and Cl (99.9+%), and all I, are tied up as the sodium, potassium, and hydrogen halides. Still, the residual F and Cl concentrations are comparable in magnitude to the cesium concentration. A substantial fraction of the cesium (about 5.1%) is volatilized as the chloride and fluoride. The balance of the cesium remains in the condensed phase as the nitrite, nitrate, and oxide. These are incomplete calculations that only predict vaporization to the extent necessary to saturate at equilibrium a volume with a total pressure of 1 atm of the major H_2O and NO_x gases at the temperature of the glass, 1160°C. Also, the glass is considered as an ideal solution, obeying Raoult's law. However, they give relative effects. Actual vaporization could exceed this in a dynamic system with a purge gas. The partial vapor pressures of the cesium halide species that are calculated by HSC could be used as input to a dynamic process model to more completely evaluate the vapor transport of the cesium.

Similar results are obtained modeling the WM-180 waste, for which 4.4% cesium volatility is predicted, both at the actual waste cesium concentration and at 209 times the actual cesium concentration. The latter was used in pilot-scale vitrification tests in which the observed cesium volatility was 13 to 20%.

Therefore, most of the halogens are tied up with the sodium, and residual cesium is available to potentially react with technetium. There are no thermodynamic data for cesium pertechnetate, so modeling cannot be done for this species, including its possible effect on enhancing the cesium volatility. Given the apparent availability of cesium aside from its volatile halides, when cesium concentration is increased in the liquid waste feed in order to measure it in the glass, the technetium surrogate, rhenium, should be proportionately increased. As shown in Table 4, the cesium and technetium are present at near comparable molar concentrations in the waste, within a factor of 1.7; that ratio ($n_{Tc}/n_{Cs} = 0.595$) should remain constant.

Selenium and tellurium may also need to be increased above actual concentrations in the waste in order to measure them in the glass and/or off gas. Ron Goles of PNNL is experienced in quantitative assessments of concentrations of the various species needed for mass balance measurements. He may be consulted for specific recommendations.

An additional aspect regarding the quantitative increases in these elements for observing them is that the limiting increases are determined by the concentration in the glass needed in order to be able to analyze them in the glass. However, an experimental approach that could be satisfactory in terms of characterizing volatilities is to measure the elements collected from the off gas and assume 1) that all of the species that escape the melter have been collected and 2) that the balance is in the melt. These measurements may be more sensitive and, therefore, smaller increases in the feed concentrations would be required. Again, Dr. Goles is the subject matter expert to consult on these types of evaluations.

Table 4. Concentrations of Species in Worst-Case Waste Potentially Pertinent to Cesium Volatilization During Vitrification.*

Species	Concentration, Molar
Na	2.06
K	0.20
Cs	2.1E-5
Cl	3.0E-2
F	1.1E-1
I	3.5E-6
Hg	6.6E-3
Tc	1.3E-5

*After 5% steam jet dilution during transfer out of waste tank. Data from Table 6.

3.2 Solids

The operational scenario considered here is that of removing only liquid from the tanks for vitrification. The solids that remain in the bottoms of the tanks will be processed separately. They are not subjects of the current development program addressed here. However, as the liquid is removed from the tanks, any suspended solids will be removed with it. Also, a small amount of solids that have settled to the bottoms of the tanks will be entrained with the liquid as it is steam jetted from the tanks through the pipes that extend to approximately 3 inches from the bottom of the tanks. Therefore, we must estimate the contribution of these solids to the total composition that will be fed to the vitrifier.

The estimate of both concentration and chemical composition of the entrained solids is difficult and very uncertain. For example, sequential liquid samples taken in 1989 and, again, in 1993 from WM-181 varied in UDS from 2.1 to 22.7 g/L in 1989 and from 0.17 to 21.6 g/L in 1993 when no changes occurred in the tank.[17] Similarly, samples from WM-185 taken from 1988 to 1991 during which the tank was only partially emptied showed variations in UDS from 0.13 to 12.2 g/L in 1988, from 0.28 to 14.6 g/L in 1990, and from 1.45 to 11.8 g/L in 1991.

Fortunately, when the final selected and compiled values are taken into account, the contribution relative to the total dissolved solids that will be vitrified and to the elemental composition of the vitrified waste is very small.

Perhaps the most thorough evaluation of entrained solids has been done for a liquid sample obtained from WM-180. An experimental determination of the quantity and elemental composition of

solids that are entrained with liquid taken from the WM-180 tank was obtained during the sampling of the liquid for characterization. Results are in the report describing the composition and simulation of the waste.[2] It was not possible to obtain an x-ray diffraction qualitative characterization of the amorphous solids. However, a thermodynamic and mass balance evaluation led to estimates of the solids chemical makeup.[2]

The concentration of the solids in the sampled WM-180 liquid was 0.225 g/L (steam-jet diluted basis). This is 0.058 wt% of the total dissolved solids (TDS) in the liquid of 388 g/L. In addition to contributing a rather negligible amount to the components that make up the glass, the solids, with the exception of silicon and traces of antimony, silver, tin, and cesium, contain the same elemental components as the liquid. When the solids elemental components are converted to an equivalent number of g-atoms element/ L (molar) in the total liquid plus solids sample, the "unique" trace element concentrations (Sb, Ag, Sn, and Cs) are all less than the detection limits in the liquid.

Because of these limiting quantities, addition of solids to WM-180 simulated waste for vitrification studies was neglected. The more interesting aspect of them was to use the bulk elemental composition to assess what the chemical constituents might be in regards to impact on tank closure activities.

Barnes has tabulated available data on concentrations of solids entrained with liquid samples taken from other tanks, using existing reports.[1] The chosen concentration varies from 0.17 to 5.05 g/L. Barnes also tabulated the modeling estimate of A. L. Olson of the chemical composition of the solids (Table 31 of Barnes[1]).

In order to assess the relative importance of solids to the total waste composition, two solids compositions are, therefore, considered: that of WM-180 solids and that of the general case (the A. L. Olson average estimate). If one takes the worst case of 5 g solids/L, which corresponds to about 1.25 wt% of the total dissolved solids in the WM-180 waste, the contributions by element, compared with the liquid dissolved solid concentration of the element for the worst-case waste (from Table 6, Section 4.1) are those shown in Table 5. In most cases, the relative contribution of an individual element is less than 5 % of the element in the liquid, in which case, it may be neglected. Those that exceed 5 % of the element in the liquid are highlighted in bold, along with potential chemical forms. These will be addressed in makeup of the simulant in Section 4.2.5.

Table 5. Solids Contributions to Composition of Liquid with Entrained Solids. Those highlighted in bold exceed 5% of the element in the liquid.

Element	General Solids[1, 18] Wt %	General Solids[1, 18] Mol/L*	WM-180 Solids[2] Wt %	WM-180 Solids[2] Mol/L*	Worst-Case Liquid Mol/L**	General Solids/ WM-180 Solids	General Solids/ Worst-Case Liq	WM-180 Solids/ Worst-Case Liq	A. L. Olson Chemical Forms (General Solids)[1, 18]	J. D. Christian Chemical Forms (WM-180 Solids)[2]
Al	2.01	0.00373	5.846	0.0108	0.6633	0.344	0.00562	0.0163	$AlPO_4$	$Al(NO_3)_3 \bullet 9H_2O$; $K_3H_6Al_5(PO_4)_8 \bullet 18H_2O$
B	3.34	0.0154	0.0511	0.000236	0.0123	65.36	**1.26**	0.0192	**B_2O_3**	
Ca	1.02	0.00127	0.430	0.000537	0.0696	2.37	0.0183	0.00771	CaF_2	$Ca(OH)_2 \bullet Ca_3(PO_4)_2$
Cr	0.26	0.00025	0.0681	0.000065	0.00664	3.82	0.0377	0.00986	Cr_2O_3	
Fe	2.79	0.00250	2.012	0.00180	0.0217	1.39	**0.115**	**0.0829**	**$FePO_4 \bullet 2H_2O$**	
Hg	0.66	0.000165	0.890	0.000222	0.00664	0.741	0.0248	0.0334	$HgCl_2$	
K	1.79	0.00229	1.471	0.00188	0.1963	1.22	0.0117	0.00958	$KNbO_3$; KCl	$K_3H_6Al_5(PO_4)_8 \bullet 18H_2O$
Mn	0.44	0.00040	0.157	0.000143	0.0141	2.81	0.0284	0.0101	MnO_2	
Na	4.88	0.0106	7.816	0.0170	2.058	0.624	0.0052	0.00826	NaCl; Na_3PO_4	$NaNO_3$; $Al(NO_3)_3 \bullet 9H_2O$
Nb	0.17	9.15E-5	1.004	0.000540	0.000016	0.169	**5.89**	**34.8**	**$KNbO_3$**	
Ni	1.64	0.00140	0.0276	0.000024	0.00147	59.42	**0.950**	0.0160	**NiO**	
Si	4.58	0.00815	2.092	0.00372	3.02E-7	2.19	**27,000**	**12,300**	**SiO_2**	**SiO_2**
Zr	15.62	0.00856	2.797	0.00153	0.0196	5.58	**0.437**	**0.0782**	**ZrO_2; $Zr(SO_4)_2 \bullet 4H_2O$**	
Cl	3.05	0.00430	0.0909	0.00128	0.0300	33.55	**0.143**	0.00427	**NaCl; KCl; $HgCl_2$**	
F	2.98	0.00784	0.0033	0.000009	0.111	903.0	**0.0704**	0.000078	**CaF_2; NaF**	
PO_4	14.07	0.00741	16.659	0.00877	0.0137	0.845	**0.541**	**0.640**	**$AlPO_4$; Na_3PO_4; $FePO_4 \bullet 2H_2O$**	**$K_3H_6Al_5(PO_4)_8 \bullet 18H_2O$**
SO_4	16.45	0.00869	1.514	0.000800	0.0540	10.87	**0.161**	0.0148	**$Zr(SO_4)_2 \bullet 4H_2O$**	
H_2O	7.97	0.0221	Balance						hydrates	
O	16.29	0.0509	to makeup 100%						oxides	
TOTAL	100.0	0.156	42.930	0.0482	3.279					

*Based on assumed suspended and entrained solids concentration of 5 g/L.
**Table 6.

4. RESULTS AND RECOMMENDATIONS

4.1 Composition and Makeup Spreadsheet

Based on the above data and discussions, the worst-case simulant solution composition is derived and provided in Table 6. Those elements of specific interest for glass composition or for off-gas characterization regarding a worst-case waste composition are indicated, with concentrations based on the maximum values identified in Table 3. The concentrations of others are taken from the WM-180 composition.[2]

The solids composition and quantities per liter of solution are discussed in Section 4.2.5 and given in Table 9.

An electronic spreadsheet is used to convert the solution ion concentrations to concentrations of reagents required to prepare a simulant solution of specified volume and is shown in Table 7. The spreadsheet is adapted from that used for the WM-180 simulant.[2] Table 7 does not show the matrix of the individual species (whose concentrations can be varied, if desired), but provides the simulant preparation reagents and amounts for 1 liter of solution. The reader will note that some elements are spread over two or more reagents such that its contribution from all the reagents sums to the value for the element in Table 6. In some cases, alternative reagents are listed, so that there are two or three entries given for the element. The spreadsheet allows one to select which reagent to use. The concentration is given in Table 7 for the primary reagent selected for use and others are listed as zero. The electronic spreadsheet, which provides for inputting the volume of simulant solution being prepared, is enclosed on diskette with this report. It is also available upon request from jerryc@srv.net or alolson@inel.gov.

The composition provided is complete. Individual experimenters will choose not to include a number of minor, hazardous components. Normally eliminating a minor component will not affect the makeup composition overall. The electronic spreadsheet enables one to calculate the new makeup composition if either a component is eliminated or an alternative reagent is selected for makeup.

4.2 Simulant Preparation

4.2.1 Reagents

The selection and preparation of reagents for preparing a simulant solution are taken from the successful WM-180 simulant preparation procedure.[2] The considerations are duplicated here.

4.2.2 Selection of Reagents

In listing reagent chemicals to use in the simulant solution makeup, available forms were determined from the Alfa AESAR catalog. In a few instances, the spreadsheet accommodates the use of alternative reagents for a component.

Most of the reagents used for the simulant preparation are nitrate salts. For those that are present at very small concentrations, one may judiciously substitute alternative salts. For example Li_2CO_3 has been substituted for $LiNO_3$ on a molar basis. Since the concentration of Li^{2+} is only 3.39×10^{-4} molar, the reaction has negligible effect on the H^+ and NO_3^- concentrations.

$Li_2CO_3 + H+(aq) \rightarrow 2\ Li^{2+}(aq) + H_2O + CO_2(g)$; $K = 6.8 \times 10^{14}$

Table 6. Worst-Case Sodium-Bearing Waste Simulant Solution Composition.*

Limiting concentration of concern for:	Species**	Concentration, Molar
	Metals:	
	H^+	3.390E+00
Glass	Al	0.663E-01
	As	4.99E-04
	Ba	5.58E-05
	Be	7.67E-06
	B	1.23E-02
	Cd	7.54E-04
Glass	Ca	6.97E-02
	Ce	4.73E-05
	Cr	6.64E-03
	Co	1.93E-05
	Cu	6.97E-04
	Gd	1.77E-02
	Fe	2.17E-02
	Pb	1.31E-03
	Li	3.39E-04
	Mg	1.20E-02
	Mn	1.41E-02
Off Gas	Hg	6.64E-03
	Mo	1.93E-04
	Ni	1.47E-03
	K	1.96E-01
Glass	Rh	4.41E-06
Glass	Ru	1.25E-04
Glass	Ag	2.24E-05
	Na	2.06E+00
	Sr	1.19E-04
	Ti	5.78E-05
Off Gas	U (Ce surrogate)	6.21E-04
	Zn	1.05E-03
	Zr	0.0196
	Anions:	
Glass	Br	7.03E-06

*Concentrations are after 5% steam jet dilution from transferring waste from tank to vitrification plant.
**Ordered alphabetically by name, not chemical symbol.
***Value is adjusted (floats) to achieve charge balance, based on H^+ being 3.39 molar.

Table 6. Worst-Case Sodium-Bearing Waste Simulant Solution Composition(continued).*

Limiting concentration of concern for:	Species**	Concentration, Molar
	Anions:	
Glass	Cl	3.00E-02
Glass	F	1.11E-01
Glass, Off Gas	I	3.51E-06
	NO_3^-	7.73E+00***
Glass	PO_4^{3-}	1.37E-02
Glass	SO_4^{2-}	6.98E-02
	Radionuclides and Surrogates:	
Off Gas	Cs	2.10E-05
	Eu	3.12E-08
Off Gas	Nd (for Am(III)	1.27E-07
	Nd (for Nd)	3.61E-05
Off Gas	Re (for Tc)	1.25E-05
Off Gas	Te	3.49E-06
	Th (for Pu(IV)	8.86E-06
Off Gas	U (Use Ce surrogate if necessary)	6.49E-04
	Elements Below Detection Limits:	
Off Gas	Sb	<6.38E-5
	Nb	<1.55E-05
Glass	Pd	<2.35E-05
	Se	<1.46E-04
	Si	<3.02E-07
	Tl	<4.09E-05
	Sn	7.52E-7 Calculated
	V	<9.23E-04

*Concentrations are after 5% steam jet dilution from transferring waste from tank to vitrification plant.
**Ordered alphabetically by name, not chemical symbol.
***Value is adjusted (floats) to achieve charge balance, based on H^+ being 3.39 molar.

Table 7. Worst-Case Sodium-Bearing Waste Solution Simulant Reagents and Concentrations. Total H^+ is 3.39 molar. Total NO_3^- floats for charge balance and is 7.73 molar.

Analyte	Amt of Reagent for		Mol Wt				
1	Liter(s)	Units	or Conc'n	Units	Form and Notes	Reagent	Moles/L
METALS - BULK ELEMENTAL ANALYSIS							
Aluminum	3.015E-01	Liter	2.2	M Al^{3+}	Solution	Al(NO3)3*9H2O	6.633E-01
Arsenic	4.936E-02	g	197.8414	g/mol		As2O3	2.495E-04
Arsenic	0.000E+00	g	389.7985	g/mol	Alternate Arsenic acid	H5As3O10[a]	0.000E+00
Barium	1.457E-02	g	261.3398	g/mol		Ba(NO3)2	5.575E-05
Beryllium	3.651E-04	g	47.00898	g/mol		BeF2	7.766E-06
Boron	7.605E-01	g	61.83302	g/mol		H3BO3	1.230E-02
Cadmium	2.326E-01	g	308.48092	g/mol		Cd(NO3)2*4H2O	7.541E-04
Calcium	1.646E+01	g	236.14892	g/mol		Ca(NO3)2*4H2O	6.970E-02
Cerium	2.053E-02	g	434.22638	g/mol		Ce(NO3)3*6H2O	4.727E-05
Chromium	2.178E+00	g	328.0871	g/mol		Cr(NO3)3*5H2O	6.640E-03
Cobalt	5.608E-03	g	291.03468	g/mol		Co(NO3)2*6H2O	1.927E-05
Copper	1.684E-01	g	241.60164	g/mol		Cu(NO3)2*3H2O	6.970E-04
Gadolinium	7.679E-02	g	433.3411	g/mol		Gd(NO3)3*5H2O	1.772E-04
Iron	8.779E+00	g	403.99922	g/mol		Fe(NO3)3*9H2O	2.173E-02
Lead	4.329E-01	g	331.2098	g/mol		Pb(NO3)2	1.307E-03
Lithium	2.339E-02	g	68.9459	g/mol		LiNO3	3.393E-04
Magnesium	3.085E+00	g	256.40648	g/mol		Mg(NO3)2*6H2O	1.203E-02
Manganese	5.046E+00	g solution	178.9478	g/mol	AlfaAesar50% soln	Mn(NO3)2	1.410E-02
Mercury	2.275E+00	g	342.61508	g/mol		Hg(NO3)2*H2O	6.640E-03
Molybdenum	1.927E-03	Liter	0.1	M MoO2(NO3)2[b]	Soln:see prep notes	Mo in HNO3	1.927E-04
Nickel	4.278E-01	g	290.79488	g/mol		Ni(NO3)2*6H2O	1.471E-03
Potassium	1.985E+01	g	101.1032	g/mol		KNO3	1.963E-01
Rhodium	1.433E-03	g	324.9508	g/mol		Rh(NO3)3*2H2O	4.410E-06
Ruthenium	2.587E-02	g	207.4281	g/mol		RuCl3	1.247E-04
Ruthenium	0.000E+00	Liter	1.48E-01	molar solution	Alternate:Solution of	Ru(NO)(NO3)3[c]	0.000E+00
Ruthenium	0.000E+00	g	237.434	g/mol	2nd Alternate for Ru	Ru(NO)Cl3[d]	0.000E+00
Sodium	1.749E+02	g	84.99467	g/mol		NaNO3	2.058E+00
Strontium	2.521E-02	g	211.6298	g/mol		Sr(NO3)2	1.191E-04
Titanium	1.096E-02	g	189.6908	g/mol		TiCl4	5.780E-05
Uranium	3.118E-01	g	502.12928	g/mol		UO2(NO3)2*6H2O	6.210E-04
Zinc	3.121E-01	g	297.49148	g/mol		Zn(NO3)2*6H2O	1.049E-03
Zinc	0.000E+00	g	136.2954	g/mol	Alternate: ZnCl2	ZnCl2[e]	0.000E+00
Zirconium	9.800E-03	Liter	0.05	M ZrF4 in 9.8M HF[f]	Soln:see prep notes	ZrF4	1.960E-02
ANION ANALYSES							
Chloride	2.449E-03	Liter	12	molar solution		HCl	2.938E-02
Fluoride	3.995E-4	Liter	28.9	molar solution		HF[g]	1.154E-02
Fluoride	0.00000	g	48	wt% HBF4 solution	Alternate for F	HBF4[g]	0.000E+00
Iodide	5.827E-04	g	166.0028	g/mol		KI	3.510E-06
Nitrate	2.201E-01	Liter	15.4	molar solution		HNO3	3.112E+00
Phosphate	9.384E-04	Liter	14.6	molar solution		H3PO4	1.370E-02
Sulfate	3.877E-03	Liter	18	molar solution		H2SO4	6.979E-02
RADIONUCLIDE ANALYSES AND SIMULANTS.[h]							
TOTAL ELEMENTAL CONCENTRATION CALCULATED FROM RADIONUCLIDE ANALYSES.							
Cesium	1.507E-03	g	194.91035	g/mol		CsNO3	2.10E-05
Cesium	0.000E+00	g	168.3582	g/mol	Alternate: CsCl	CsCl	0.000E+00
Europium	1.393E-05	g	446.0705	g/mol		Eu(NO3)3*6H2O	3.123E-08
Rhenium[i]	2.328E-03	Liter	0.00537	M Re, 0.814MHNO_3	Aqueous solution of	Re in 5% HNO_3	1.250E-05
Neodymium[j]	5.567E-05	g	438.346			Nd(NO3)3*6H2O	1.270E-07
Thorium[k]	2.055E-03	Liter	0.00431	M Th, 0.814MHNO_3	Aqueous solution of	Th(NO3)4 in 5% HNO_3	8.857E-06

Table 7. Worst-Case Sodium-Bearing Waste Solution Simulant Reagents and Concentrations (continued).

ELEMENTS LOOKED FOR BUT NOT DETECTED[l]							
CONCENTRATIONS GIVEN ARE DETECTION LIMITS EXCEPT WHEN INDICATED AS A CALCULATED LIMIT THAT							
IS LESS THAN THE DETECTION LIMIT. IF ANY OF THESE IS NOT ADDED, ENTER ZERO IN ITS RESPECTIVE CELL IN ROW							
71 TO ELIMINATE THE SMALL EFFECT ON CALCULATED ANION CONCENTRATIONS. NOTE VALUE DELETED FOR FUTURE.							
Antimony	1.454E-02	g	228.115			SbCl3	6.375E-05
Niobium (Calcd)	1.443E-03	Liter	0.01076	M Nb, 0.998 M HF	Aqueous solution of	NbCl5 in 2% HF	1.553E-05
Palladium[m]	2.938E-02	g solution[m]	8.5	wt% Pd=7.99E-4 mol/g solution. Solution		Pd(NO3)2	2.347E-05
Selenium	1.155E-02	Liter	0.01266	M Se, 0.814MHNO$_3$	Aqueous solution of	Se in 5% HNO$_3$	1.462E-04
Silicon	8.475E-06	Liter	0.03561	M Si, 0.814MHNO$_3$	Aqueous solution of	Si in 5% HNO$_3$	3.018E-07
Silver	3.618E-03	g	169.873			AgNO3	2.130E-05
Thallium	8.359E-03	Liter	0.004893	M Tl, 0.814MHNO$_3$	Aqueous solution of	Tl in 5% HNO$_3$	4.090E-05
Tin (Calcd)[n]	0.000E+00	g	156.7068			SnF2	0.000E+00
Vanadium	4.704E-02	Liter	0.01963	M V, 0.814MHNO$_3$	Aqueous solution of	V in 5% HNO$_3$	9.233E-04

FOOTNOTES: Comments include references to spreadsheet use for modifying inputs.

[a]If using $H_5As_3O_{10}$ instead of As_2O_3, delete the value in column L for As_2O_3 (cell L10), and enter it in the row for $H_5As_3O_{10}$ (cell L11) as = L71. The spreadsheet will automatically adjust the reagent additions.

[b]0.100 M $MoO_2(NO_3)_2$ in 6.8M HNO_3. See prep notes in simulant letter.

[c]If using $Ru(NO)(NO_3)_3$ solution instead of $RuCl_3$, delete the value in column AM for $RuCl_3$ (cell AM32) and enter it in the row for $Ru(NO)(NO_3)_3$ (cell AM32) as =AM71. (the total Ru). Enter the Ru molar concentration of the reagent in cell D33. If the solution contains excess HNO_3, enter its molar concentration in cell H83. The spreadsheet will automatically adjust the HCl and HNO_3 additions. Note: If you later go back to $RuCl_3$ or $Ru(NO)Cl_3$, reenter 0 in cell AM33).

[d]If using $Ru(NO)Cl_3$ instead of $RuCl_3$, delete the value in column AM for RuCl3 (Cell AM32) and enter it in the row for $Ru(NO)Cl_3$ (cell AM34) as = AM71 (the total Ru).

[e]If using $ZnCl_2$ instead of $Zn(NO_3)_2*6H_2O$, delete the value in column AY for $Zn(NO_3)_2*6H_2O$ (cell AV39) and enter it in the row for $ZnCl_2$ (cell AV40) as = AV71 (the total zinc). The spreadsheet will automatically calculate mass to add and adjust the other nitrate and chloride balances.

[f]If using ZrF_4 solutions of different ZrF_4 and HF concentration, enter the new Zr molarity in cell D41. Enter the initial HF concentration into which the Zr was dissolved in cell H91. The new residual HF concentration will be automatically calculated as $[HF]_0$-4*[Zr] in cell I41. If the solution also contains HNO_3, enter its concentration in cell H93. If it contains boric acid, enter the boron concentration in cell H95. CAUTION: Be careful that Zr concentration is not too low or initial HF concentration is too high such that the fluoride added with the solution will exceed total fluoride in the simulant. This would be displayed as a negative concentration for HF in cell H44 (or of HBF4 in cell H45 if HBF4 is being used as an alternate to HF).

[g]If using HBF_4 solution instead of HF, enter 0 in cell BB44. Enter the wt % HBF_4 reagent in cell D45 if different from the default 48%. This will recalculate the amount of H3BO3 to add, line 14. Later, if you return to the use of HF reagent instead of HBF_4 set cell BB44 = BB72. This will automatically set HBF_4 to 0 and adjust HF and H_3BO_3 appropriately.

[h]Isotopes and total elemental composition of the following radionuclides are included in and bracketed by the bulk chemical analysis and makeup reagents: Ba, Ce, Co, Gd, I, Mo, Ru, Zr, Sr. Cerium is normally used as a surrogate for plutonium. Its concentration in the bulk reagents encompasses the plutonium content. Uranium, if added for the bulk uranium content, brackets and may serve as a surrogate for neptunium.

[i]Rhenium is a surrogate for Tc-99.

[j]Neodymium is a surrogate for Am(III).

[k]Thorium is a surrogate for Pu(IV). The Pu speciation at 100°C is estimated to be 70% Pu(III), 30% Pu(IV). In glass, it will be 100% Pu(IV). IF ONE CANNOT WORK WITH THORIUM, THE CE(IV) FROM CERIUM ADDED FOR THE BULK ANALYZED REAGENTS IS ADEQUATE AND AT SUFFICIENT CONCENTRATION FOR A SURROGATE FOR PLUTONIUM. If thorium is NOT added, enter 0 in cell AT71 to eliminate the small effect on calculated nitrate. If you later add thorium, reenter 8.857E-6 in cell AT71.

[l]Cesium was analyzed for in bulk elemental analyses and not detected at 7.343E-6 M. Calculated total cesium from Cs-137 radiochemical analysis is 7.884E-6 M. The detection limit value is used here for the estimate of cesium and it is included with the radionuclides, above..

[m]Add Pd(NO3)2 solution after nitric acid has been added.

[n]Default for tin is zero, based on the assumption that zirconium reagent is prepared from dissolution of Zircaloy, which provides the tin. If zirconium reagent is prepared from pure Zr, then enter tin concentration 8.0E-7 M in cell **AU71**.

$RuNO(NO_3)_3$ solution excess HNO_3 molar concentration:	**3**
Initial HF molarity used for Zr dissolution(total fluoride):	**10.00**
HNO_3 molarity in the Zr solution:	**0.0**
Boron molarity in Zr solution:	**0**

4.2.3 Notes on and Preparation of Specific Reagents

1. Arsenic. Thermodynamic calculations (HSC) indicate that arsenic will exist in solution as As(III) in the form of the associated aqueous species $HAsO_2$ and H_3AsO_3. Therefore, As(III) hydrolyzes to produce 3 H^+ and the effect on charge remains +3. The available form of arsenic acid is $H_5As_3O_{10}$, which is As(V). The trichloride and trifluoride are liquids and could be weighed for adding to the waste simulant solution. According to the CRC Handbook, As_2O_3 is soluble in water to 0.046 molar and in HCl; the kinetics of dissolution is not known. Dissolution in H_2O would produce $HAsO_2/H_3AsO_3$. Arsenic acid, if used, ought to adjust the valence in the solution.

   The INEEL chemical inventory database lists only arsenic oxide. Therefore, the makeup is based on its use. If other reagents as described above are available, they may be substituted with appropriate adjustments to anions or (in the case of arsenic acid) H^+ (the effect on acid is sufficiently small to be ignored, however). If As_2O_3 dissolves with difficulty in H_2O, heat the solution. When it is added to the acid simulant, the dissolution will likely be completed.

2. Boron. Boric acid, H_3BO_3, titrates one mole of base per mole of boron: $OH^- + H_3BO_3 \rightarrow B(OH)_4^-$ or $OH^- + H_3BO_3 \rightarrow BO_2^- + 2H_2O$. Therefore, its presence increases the H^+ concentration by boron concentration in the mass balance calculation.

3. Molybdenum. Molybdenum is amphoteric. It exists as the molybdate ion, MoO_4^{2-}, at pH > 6.5. As the solution is acidified, molybdenum makes transitions to polymeric species, e.g., $[Mo_7O_{24}]^{6-}$. At pH 0.9, ($[H^+]$ = 0.126 M), the isoelectric point* of molybdic acid is reached, and the neutral species H_2MoO_4 precipitates. At lower pH, the molybdenyl cation, MoO_2^{2+}, forms. However, as one goes through the isoelectric point, if H_2MoO_4 precipitates, experience shows that it is difficult to redissolve. Therefore, rather than dissolving molybdic acid (i.e., molybdate) into nitric acid, our approach is to prepare the molybdenyl species directly by dissolving molybdenum metal in nitric acid.

   The dissolution procedure is based on experience. For a 1 L simulant recipe, prepare an excess in order to be able to measure quantities. If desired, you could scale this back to 10 mL. Dissolve 0.9593 g Mo metal in 100 mL 7 M HNO_3. If using sponge or solid metal, heat to near boiling (~95-100°C). The dissolution rate will be approximately 36 mg/cm^2-min (penetration rate 0.21 cm/h). If using powdered Mo, slowly heat until you observe adequate dissolution rate. This will result in a solution of approximately 0.1 M Mo (as MoO_2^{2+}), 6.8 M H^+, and 7 M NO_3^-. To the 1 L simulant, add 1.819 mL of this stock solution to result in 0.000182 M Mo, added H^+ of 0.0124 M H^+, and added NO_3^- of 0.0127 M.

* The isoelectric point is the pH at which a substance or system is electrically neutral.

4. Ruthenium. Ruthenium exists in nitric acid solutions as complexes of nitrosyl ruthenium cation, $Ru(NO)^{3+}$, with varying degrees of NO_3^-, NO_2^-, and H_2O species occupying the five coordination positions. Ideally, one would add $Ru(NO)(NO_3)_3$ (either solution or crystalline hydrated salt). Alfa AESAR lists 1.5% w/v ruthenium nitrosyl nitrate solution (presumably 1.5 g Ru per 100 mL) and crystalline $Ru(NO)(NO_3)_3 \bullet xH_2O$, 28% Ru (corresponding to x = 2.435). Excess nitric acid for the solution is not specified. Since the INEEL chemical database lists $RuCl_3$, and the chloride associated with the ruthenium is less than the total chloride content of the waste, the formulation is based on adding $RuCl_3$. The solution should be allowed to equilibrate for 24 hours so that the ruthenium will be converted to $Ru(NO)^{3+}$. If one has access to the nitrosyl solution or crystal and use it, reduce the number of moles of HCl by 3 times the Ru moles and increase the nitric acid moles by 3 times the Ru moles (actually negligible in both cases). If the solution contains excess nitric acid, adjust the HNO_3 addition accordingly. The specific procedure for doing so is specified in the footnote of the spreadsheet.

5. Zinc. The primary makeup is based on using $Zn(NO_3)_2 \bullet 6H_2O$. However, $ZnCl_2$ may be used, if desired. If so, follow the instructions on the makeup spreadsheet so that it will adjust calculations for nitrate and chloride from other species. Specifically, enter 0 for the $Zn(NO_3)_2 \bullet 6H_2O$ cell in column AY (cell AY 39) and set the $ZnCl_2$ cell in column AY (cell AY 40) equal to AY71 (the total Zn). Then, the spreadsheet will calculate the quantity of $ZnCl_2$ to add in place of $Zn(NO_3)_2 \bullet 6H_2O$ and will adjust HCl and HNO_3 additions for the change.

6. Zirconium. Zirconyl nitrate solution could be prepared from dissolving zirconyl carbonate in nitric acid. However, waters of hydration lend uncertainty. The preferred approach is to dissolve zirconium metal (or Zircaloy) in HF as follows. The quantities and concentrations are designed to be compatible with fluoride in the simulant. For the 1 L simulant, dissolve 18.24 g Zr in 100 mL 10 M HF. If using Zircaloy instead of Zr metal, the quantity to weigh is 18.64 g (Zircaloy II) or 18.60 g (Zircaloy IV). The zirconium dissolution will be exothermic and rapid. If using Zircaloy, tin will require heating overnight to effect its dissolution.

   This will result in a solution that is approximately 2.0 M Zr, 2.0 M H^+, and 10 M F. For the 1 L simulant, add 9.80 mL of this stock reagent to result in 0.0196 M Zr, added H^+ of 0.0196 M.

4.2.4 Radionuclide Surrogates

The selection of non-radioactive substitutes for the radioactive species is based on simulating as closely as possible the phase behavior in the vitrified waste. This leads to different selections than if one were to simulate the aqueous behavior. Discussions with J. D. Vienna of PNNL led to the following selections for the transuranics.[19] For the transuranium elements, simulants used for surrogates are selected to represent the coordination number, valence, and ionic radius of the actinide in glass. Information from Vienna is summarized in Table 8. Data for the properties were taken from Shannon.[20]

4.2.4.1 Americium

Both Eu(III) and Nd(III) have been used for surrogates for Am(III) in aqueous solutions. Choppin[21] suggests Eu(III). Recently, Felmy and Rai[22] determined that the $Nd^{3+} - Cl^-$ Pitzer ion interaction parameters were successful in representing $Pu^{3+} - Cl^-$ and, thus, is a suitable surrogate for

An(III) ions (the An symbol represents actinides in general). The fact that the Nd(III) ion size is closer to that of Pu(III) than is Eu(III) and that it cannot be oxidized to the (IV) state favors the use of Nd(III) as a surrogate for Am(III) in glass.

Table 8. Properties of Transuranic Cations and Alternative Potential Surrogates in Glass.

Species	Valence	Coordination Number	Crystal Radius
Am in glass	**(III)**	**6**	**1.115**
Eu	(III)	6	1.086
Nd	(III)	6	1.123
Sm	(III)	6	1.098
Pu in glass	**(IV)**	**8**	**1.10**
Hf	(IV)	8	0.97
Th	(IV)	8	1.19
Ce	(IV)	8	1.11
Ce	(III)	8	1.283
Np in glass	**(V)**	**6**	**0.89**
U	(V)	6	0.90
U	(IV)	6	1.03
U	(VI)	6	0.87

4.2.4.2 Plutonium

Plutonium exists as Pu(IV) in glass. Hafnium provides the closest simulant for plutonium in terms of solubility in glass. However, the glass from the waste solution will be much below saturation in plutonium and solubility is not an issue. Ce(IV) is the more suitable overall simulant for Pu(IV), based on its ionic radius. However, the cerium oxidation state in glass is distributed approximately 50:50 between Ce(III) and Ce(IV).[23] Thorium is also a good simulant for Pu(IV) in terms of radius, and it only exists in the (IV) state. Thus, if one can work with the slightly radioactive thorium, Th(IV) is the substitute of choice for plutonium. However, if one is not able to work with thorium, cerium may be substituted by doubling its concentration over the plutonium concentration (if not otherwise present at greater concentration), on a molar basis. Its behavior and distribution in the glass can be used as an indicator for plutonium. The Ce(III) that forms is acceptable, given that the waste contains cerium at a molar concentration approximately 20 times the plutonium concentration, by calculation. By measurement in the WM-180 waste, the concentration ratio is 5.3. Since cerium is added already at the bulk analysis concentration, it is not necessary to add any more for plutonium substitute.

4.2.4.3 Neptunium

Neptunium forms Np(V) in glass. In aqueous solutions, Np(V) is the most suitable surrogate for An(V) species, in general. The most suitable substitute for Np(V) in glass, otherwise, is U(V) according to Vienna. However, no U(V) oxide exists in thermodynamic databases. Those listed are UO, UO_2, U_4O_9, U_3O_7, U_3O_8, and UO_3. U(VI) has suitable properties, as well. Uranium will be converted to the prevailing stable oxide when vitrified. In air, U_3O_8 is the stable form at glass temperature; in the presence of a reducing agent, such as FeO, it is reduced to UO_2. Thus, uranium may be present as a mixture of U(+5.33) and U(+4), no matter what aqueous valence is the starting species. Therefore, uranyl nitrate in the nitric acid solution that is already present in the waste is selected.

If one is unable to work with uranium, neptunium cannot be simulated. If uranium is, in fact, a suitable substitute, that added for the uranium content of the waste will bracket and encompass the neptunium content.

4.2.4.4 Cesium and Technetium

Rhenium is a suitable substitute for technetium-99. Their chemical features are very similar.

When radioactive waste is evaporated and vitrified, the cesium and technetium interact to form cesium pertechnetate. This both enhances cesium volatility and diminishes technetium volatility from what each would be in the absence of the other. See Section 3.1.2 for discussions on considerations for these elements in preparing the simulant solution.

The cesium and rhenium (for technetium) concentrations provided in the simulant makeup procedure correspond to the actual waste composition. If an experiment is tracking the cesium in the glass, the cesium concentration must be increased as indicated in Section 3.1.2 to 1.65×10^{-3} molar for 30 wt% waste loading. When this is done, the concentration of the rhenium surrogate for technetium should be increased by the same factor of 78.6, to 9.82×10^{-4} molar for 30 wt% waste loading.

4.2.5 Solids

The elements in Table 5 for which the solids contribution at 5 g solids/L exceeds 5% of the liquid concentration for the element are included in formulating a solids composition. Both the WM-180 and the general solids are included in the evaluation; the larger quantity of each element from the two is selected.

The resulting suggested composition is given in Table 9. It is only a "guess" at what may represent the solids, based on prior thermodynamic and mass balance modeling, but without qualitative identification of solids in actual waste. The combined solids make up 4.72 g/L (anhydrous basis), which is 94.4% of the total solids in Table 5. Some of the salts will likely dissolve upon addition to the liquid waste. However, the contribution to the overall composition of the waste vitrified will be representative.

4.2.6 Makeup Procedures

The makeup procedures are adapted from those used to prepare the WM-180 simulant solution,[2] which are duplicated here.

The following is a step-by-step recipe for preparing the worst-case simulant solution described in the Table 7 and the Excel spreadsheet that calculates the reagent quantities for 1 liter of simulant. The procedures are written for additions of water to result in a final volume. If one is preparing the simulant by weighing the solution, the density for the complete simulant is needed in order to determine the final weight to achieve upon adding the final water diluent. This may be measured on a small batch of prepared simulant. The density is estimated to be 1.35±0.01 g/mL.

If you are preparing a small quantity that can be prepared in a beaker that can be stirred and heated, reagents can be inserted directly into the makeup vessel. If you are preparing a large quantity, e.g. 20 L, that utilizes a vessel that cannot be well mixed nor heated, a modification is made to enable dissolution of individual components in smaller vessels prior to adding to the makeup vessel contents.

In the procedures, all analyzed constituents are included. If, for a specified experiment, it is desired to eliminate specific reagents or to substitute different reagents, adjust accordingly. This is

accomplished by entering zero for the eliminated element in the Excel Simulant Makeup Spreadsheet line for total element molar concentration, row 71. The spreadsheet will adjust the calculated quantities of reagents as necessary to reflect the change. (For most of the minor components, of course, that do not include extra acid dissolvent, effect on overall composition may be generally ignored.) It may be preferable to prepare a side stock solution of hazardous/RCRA reagents that can be added to the complete the simulant on a case-by-case experimental basis.

Table 9. Worst-Case Solids Composition and Concentrations Added to Liquid Waste.

	Concentration Added to Liquid Waste	
Compound	Mol/L	g/L
B_2O_3	0.0770	0.536
$FePO_4 \bullet 2H_2O$	0.00250	0.377
$KNbO_3$	0.00054	0.0972
NiO	0.00140	0.105
SiO_2	0.00815	0.490
ZrO_2	0.00422	0.519
$Zr(SO_4)_2 \bullet 4H_2O$	0.00435	1.231
KCl	0.00175	0.130
NaCl	0.00255	0.149
CaF_2	0.00127	0.0992
NaF	0.00530	0.223
$AlPO_4$	0.00627	0.765
TOTAL		5.124 (hydrated); 4.720(anhydrous) 4.721 (anhydrous basis)

The following steps are for preparing 1 L of simulant in a single vessel. The quantities can be scaled to the volume actually being prepared, up to about 4 L in a glass beaker. Modifications are given, also, for preparing larger batch quantities.

The following procedure is based on the assumption that the hazardous and RCRA constituents can be handled and added without difficult controls along with the other reagents. However, an Independent Hazards Review (IHR) has not been processed. Until it has, some of the reagents cannot be included in the makeup at INTEC. The specific elements that may be affected are As, Ba, Be, Cd, Cr, Hg, Pb, and U. An approved IHR is in place (for D. R. Peterman) that accommodates working with Ba, Cr, Hg, and Pb and it may be considered for providing an umbrella for preparations.

Likely, it will be expedient to prepare the hazardous constituent dissolutions separately by making up one or two fairly concentrated solutions of sets of them in the correct relative concentrations that can be used as stock reagent(s) to pipette in the required quantities to the rest of the simulant solution. In that way, cumbersome controls for weighing would only have to be dealt with once and subsequent simulant solution preparations would be simpler. The procedure, controls, and approvals are being developed. This includes identifying which specific reagents are affected. For example, chromium, being Cr(III), may not be the concern as if it were Cr(VI).

PREPARATION OF 1 L WORST-CASE LIQUID SIMULANT

1. Calibrate the makeup vessel at the target simulant volume. Either transfer an accurately measured volume of water from a volumetric flask or weigh 1000×(H_2O density, g/cm^3) g of H_2O per liter. Assuming approximately 20°C, weigh 998.23 g H_2O per liter. Mark the level. Alternatively, calibrate an Erlenmeyer flask that will be used for the final dilution. This will be more accurate, since the necked-down region of the flask provides more sensitivity to volume. Or, for the 1 liter of simulant, the final dilution could be done in a volumetric flask.

2. Weigh out and place into the beaker the specified quantities of $Ba(NO_3)_2$, BeF_2, $Cd(NO_3)_2 \bullet 4H_2O$, $Ca(NO_3)_2 \bullet 4H_2O$, $Ce(NO_3)_2 \bullet 6H_2O$, $Cr(NO_3)_3 \bullet 5H_2O$, $Co(NO_3)_2 \bullet 6H_2O$, $Cu(NO_3)_2 \bullet 3H_2O$, $Gd(NO_3)_3 \bullet 5H_2O$, $Fe(NO_3)_3 \bullet 9H_2O$, $Pb(NO_3)_2$, $LiNO_3$, $Mg(NO_3)_2 \bullet 6H_2O$, $Hg(NO_3)_2 \bullet H_2O$, $Ni(NO_3)_2 \bullet 6H_2O$, KNO_3, $NaNO_3$, $Sr(NO_3)_2$, $TiCl_4$, $UO_2(NO_3)_2 \bullet 6H_2O$, $Zn(NO_3)_2 \bullet 6H_2O$ (or the alternate, $ZnCl_2$), and KI. If necessary, break up large chunks into a powder prior to weighing.

3. Add approximately 300 mL demineralized H_2O. Stir and heat as needed to effect dissolution. This will result in a (molar) ion product of $[Na][NO_3^-]$ of approximately 46, within the calculated solubility product at 25°C of 59 (from the CRC Handbook solubility), which should result in the dissolution of the limiting salt, $NaNO_3$. To assure that $NaNO_3$ remains soluble, the increase in nitrate from addition of $Al(NO_3)_3$ and HNO_3 solutions will be done later only after most of the diluent water has been added.

4. In a small beaker (50 mL for a 1 L simulant), weigh in the specified amount of H_3BO_3. Add approximately 40 mL H_2O. Pipette in the specified amount of HF reagent. Stir. The HF will cause most of the boric acid to readily dissolve, forming HBF_4, though it is in slight stoichiometric deficiency. Heat gently, if needed, to effect complete dissolution of the boric acid. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.

5. In a small beaker (30 mL for a 1 L simulant), weigh in the specified amount of As_2O_3 (or the alternate, $H_5As_3O_{10}$). Add 15 to 20 mL H_2O. Stir and heat as necessary to effect dissolution. If dissolution does not occur, add the specified volume of HCl stock solution. This should cause the arsenic to dissolve. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.

6. Add the specified mass of 50 wt% $Mn(NO_3)_2$ solution.

7. Add the specified volume of ZrF_4 stock solution, prepared as instructed in Footnote 1. Stir.

8. See step 9 for comment about dilution volume at this point. Add dilution H_2O to about 500 mL per 1 L simulant. Stir.

9. Add the specified volume of $Al(NO_3)_3$ stock solution. This will be 285.5 mL for a stock solution concentration of 2.2 M Al^{3+}. If the stock concentration is less than 2.2 M Al^{3+}, subtract the additional required volume from the 500 mL dilution volume in step 8. Stir.

10. In a separate beaker (250 mL for 1 L simulant) place 50 mL H_2O. SLOWLY add the specified volumes of H_2SO_4, HCl (only if not added in step 5), and HNO_3 stock solutions to the water (do not add the water to the acids – it will splatter). Stir. Slowly add this solution to the makeup vessel. Stir.

11. Add specified quantities of $Pd(NO_3)_2$ and $Rh(NO_3)_3 \bullet 2H_2O$.

12. Add the specified volume of $MoO_2(NO_3)_2$ stock solution that has been prepared as instructed in Footnote 2. Stir.

13. Add the specified quantity of $RuCl_3$ (or, if using alternate $Ru(NO)(NO_3)_3$ solution – preferred if available – , its specified volume). Stir.

14. This solution should now be at approximately 900 mL for a 1 L simulant preparation. Transfer it to a 1 L calibrated Erlenmeyer or 1 L volumetric flask. Rinse the beaker with a small volume (approximately 50 mL) of H_2O to the flask. Do not fill to the fill line at 1 liter.

15. Seal and store the flask contents until ready to use. At that time, you will add the specified volume of H_3PO_4 stock solution and then add H_2O to the 1 liter fill line. Mix well. By adding the phosphoric acid just before the experiment, precipitate formation may be retarded. Phosphate precipitate may slowly form after the H_3PO_4 addition.

MODIFICATION OF MAKEUP PROCEDURE FOR LARGE VOLUMES

The following modifications are based on the consideration that the primary makeup vessel cannot be adequately heated and/or stirred to effect dissolution of individual components and is a variation of the approach used by D. R. Peterman. The example is provide for preparing 20 L of simulant; it can be scaled as desired.

FOR 20 L SIMULANT*:*

1. Place 2.7 L deionized H_2O into the primary makeup vessel that is calibrated for final volume.

2. Into a 4 L beaker, weigh in the specified quantities of $NaNO_3$ and KNO_3. If necessary, grind the salts to size-reduce large chunks.

3. Add 3.3 L H_2O to the salts in the 4 L beaker. Stir and heat as necessary to effect dissolution.

4. Transfer this solution to the primary makeup vessel. Stir.

5. Remove approximately 3 L of solution from the makeup vessel to the 4 L beaker. Add to this the specified amounts of $Ba(NO_3)_2$, BeF_2, $Cd(NO_3)_2 \bullet 4H_2O$, $Ca(NO_3)_2 \bullet 4H_2O$, $Ce(NO_3)_2 \bullet 6H_2O$, $Cr(NO_3)_3 \bullet 5H_2O$, $Co(NO_3)_2 \bullet 6H_2O$, $Cu(NO_3)_2 \bullet 3H_2O$, $Gd(NO_3)_3 \bullet 5H_2O$, $Fe(NO_3)_3 \bullet 9H_2O$, $Pb(NO_3)_2$, $LiNO_3$, $Mg(NO_3)_2 \bullet 6H_2O$, $Hg(NO_3)_2 \bullet H_2O$, $Ni(NO_3)_2 \bullet 6H_2O$, $Sr(NO_3)_2$, $TiCl_4$, $UO_2(NO_3)_2 \bullet 6H_2O$, $Zn(NO_3)_2 \bullet 6H_2O$ (or the alternate, $ZnCl_2$), and KI. If necessary, break up large chunks into a powder prior to weighing. Allow sufficient time for each salt to dissolve before adding additional salts. Stir and heat as necessary to effect dissolution.

6. Transfer this solution back into the makeup vessel. Mix well.

7. In a 1 L beaker, weigh in the specified amount of H_3BO_3. Add approximately 800 mL H_2O. Pipette in the specified amount of HF reagent. Stir. The HF will cause most of the boric acid to readily dissolve, forming HBF_4, though it is in slight stoichiometric deficiency. Heat gently, if needed, to effect complete dissolution of the boric acid. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.

8. In a 600 mL to 1 L beaker, weigh in the specified amount of As_2O_3 (or the alternate, $H_5As_3O_{10}$). Add 300 to 400 mL H_2O. Stir and heat as necessary to effect dissolution. If dissolution does not occur, add the specified volume of HCl stock solution. This should cause the arsenic to dissolve. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.

9. Add the specified mass of 50 wt% $Mn(NO_3)_2$ solution to the makeup vessel and stir.

10. Add to the makeup vessel the specified volume of ZrF_4 stock solution, prepared as instructed in Footnote 1. Stir.

11. See step 12 for comment about dilution volume at this point. Add dilution H_2O to about 10 L. Stir.

12. Add the specified volume of $Al(NO_3)_3$ stock solution. This will be 5.71 L for a stock solution concentration of 2.2 M Al^{3+}. If the stock concentration is less than 2.2 M Al^{3+}, subtract the additional required volume from the 10 L dilution volume in step 11. Stir.

13. In a separate 4 L beaker place 1 L H_2O. SLOWLY add the specified volumes of H_2SO_4, HCl (only if not added in step 8), and HNO_3 stock solutions to the water (do not add the water to the acids – it will splatter). Stir. Slowly add this solution to the makeup vessel. Stir.

14. Add specified quantities of $Pd(NO_3)_2$ and $Rh(NO_3)_3 \bullet 2H_2O$.

15. Add the specified volume of $MoO_2(NO_3)_2$ stock solution that has been prepared as instructed in Footnote 2. Stir.

16. Add the specified quantity of $RuCl_3$ (or, if using alternate $Ru(NO)(NO_3)_3$ solution – preferred if available – , its specified volume). Stir.

17. This solution should now be at approximately 18 L. Seal and store the contents until ready to use. At that time, you will add the specified volume of H_3PO_4 stock solution and then add H_2O to the 20 liter fill line. Mix well. By adding the phosphoric acid just before the experiment, precipitate formation may be retarded. Phosphate precipitate may slowly form after the H_3PO_4 addition.

FOOTNOTES:

1. Dissolve zirconium metal (or Zircaloy) in HF as follows. The quantities and concentrations are designed to be compatible with fluoride in the simulant. Dissolve 0.456 g Zr in 100 mL 10 M HF. If using Zircaloy instead of Zr metal, the quantity to weigh is 0.466 g (Zircaloy II) or 0.465 g (Zircaloy IV). The zirconium dissolution will be exothermic and rapid. If using Zircaloy, tin will require heating overnight to effect its dissolution. The concentration of tin in the worst-case waste is less than that associated with zirconium in Zircaloy. Because of this, use of zirconium metal is preferred. However, the use of Zircaloy would result in only 0.00028 M Sn, an acceptably low concentration.

2. Preparation of stock molybdenum solution. Dissolve 0.9593 g Mo metal in 100 mL 7 M HNO_3. If using sponge or solid metal, heat to near boiling (~95-100°C). Keep a watch glass over the beaker to minimize evaporation. The dissolution rate will be approximately 36 mg/cm^2-min (penetration rate 0.21 cm/h). If using powdered Mo, slowly heat until you observe adequate dissolution rate. This will result in a solution of approximately 0.1 M Mo, 6.8 M H^+, and 7 M NO_3^-. (Note: Because the solution may evaporate a bit during the heating, it may be necessary to transfer the cooled solution to a 100 mL volumetric flask, add a small amount of rinse water to the beaker, and transfer it to the volumetric flask to bring the volume to 100 mL.)

   To assure that the acidity of the simulant solution is at a pH below 0.9, the isoelectric point of molybdenum, this stock solution will be added after nitric acid has been added to the simulant solution. To the 1 L simulant, add 1.819 mL of this stock solution to result in 0.000182 M Mo, added H^+ of 0.0124 M H^+, and added NO_3^- of 0.0127 M.

5. REFERENCES

1. C. M. Barnes, Feed Composition for Sodium-Bearing Waste Treatment Process, INEEL/EXT-2001-01378, July 2001.

2. J. D. Christian, Composition and Simulation of Tank WM-180 Sodium-Bearing Waste at the Idaho Nuclear Technology and Engineering Center, INEEL/EXT-2001-00600, May 2001.

3. J. D. Vienna, Battelle Pacific Northwest Laboratory, Richland, Washington, personal communication, July 10, 2001.

4. R. W. Goles, Battelle Pacific Northwest Laboratory, Richland, Washington, personal communication, July 10, 2001.

5. J. D. Christian and T. R. Thomas, "Treatment of Off-Gases from Process Operations," in Separation Techniques in Nuclear Waste Management, T. E. Carleson, N. A. Chipman, and C. M. Wei, Editors, CRC Press, New York, 1995.

6. J. D. Christian and D. T. Pence, Critical Assessment of Methods for Treating Airborne Effluents from High-Level Waste Solidification Processes, PNL-2486, June 1977.

7. C. R. Edinborough, "Evaluation of Radioactive Offgas Sampling Methods," INEEL Engineering Design File No. EDF-2711, June 29, 2001.

8. R. W. Goles, J. M. Perez, B. D. MacIsaac, D. D. Siemer (INEEL), and J. A. McCray (INEEL), Test Summary Report INEEL Sodium-Bearing Waste Vitrification Demonstration RSM-01-1, PNNL-13522, May 2001.

9. L. G. Olson, Radioactive Crucible-Scale Glass Melts Using INTEC Tank WM-180 Sodium-Bearing Waste, INEEL/EXT-01-01029, September 2001.

10. R. W. Goles, Battelle Pacific Northwest Laboratory, personal communication, January 10, 2001.

11. S. J. Rimshaw and F. N. Case, “Volatilities of ruthenium, iodine, and technetium on calcining fission product nitrate wastes, in Proc. 16th DOE Nuclear Air Cleaning Conference, San Diego, California, October 20-23, 1980, Report CONF-801038, U.S. Department of Energy, February 1981.

12. S. J. Rimshaw, F. N. Case, and J. A. Tompkins, Volatility of Rhenium-106, Technetium-99, and Iodine-129, and the Evolution of Nitrogen Oxide Compounds During the Calcination of High-Level, Radioactive Nitric Acid Waste, Report ORNL-5562, February 1980.

13. St. Halaszovich, S. Dix, and E. R. Merz, “Studies of radioelement volatilization in the course of HLLW vitrification,” in Spectrum ’86, Proc. Am. Nucl. Soc. Int. Topical Meeting on Waste Management and Decontamination and Decommissioning, Niagara Falls, New York, September 14-18, 1986, Report CONF-860905, 1986.

14. P. W. Cains, “Semi-volatile radionuclides in high-level waste calcination and vitrification off-gases,” in Proc. U.K. Filtration Conference on Gas Cleaning in the Nuclear Industry, Manchester, England, March 12-12, 1987.

15. P. W. Cains, K. C. Yewer, and S. Waring, “Volatilization of ruthenium, cesium and technetium from nitrate systems in nuclear fuel processing and waste solidification,” Radiochim. Acta, 56, 99 (1992).

16. Roine, Outokumpo HSC Chemistry® for Windows, Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database, Version 4.1, Outokumpo Research Oy Information Service, P O Box 60, FIN-28101 Pori, Finland; available from ESM Software, Hamilton, Ohio.

17. M. D. Staiger, C. B. Millet, R. A. Nickelsen, R. A. Wood, and A. Chambers, Tank Farm Facility, Tank and Waste Data, Engineering Design File EDF-1598, Rev. 0, March 2001.

18. M. C. Swenson, Historical Tank Farm Sample Results, Westinghouse Idaho Nuclear Company letter MCS-27-92, December 17, 1992.

19. J. D. Vienna, Pacific Northwest National Laboratory, personal communication.

20. R. D. Shannon, “Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halide and Chalcogenides,” Acta Cryst., A32, 751 (1976).

21. G. R. Choppin, American Chemical Society seminar, Idaho Falls, ID, October 10, 1994.

22. A. Felmy and D. Rai, J. Solution Chem., 28, 533 (1999).

23. J. G. Darab, H. Li, and J. D. Vienna, "X-ray absorption spectroscopic investigation of the environment of cerium in glasses based on complex cerium alkali borosilicate compositions, "J. Non-Crystalline Solids, 226, 162-174 (1998).