2

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RADIOACTIVE WASTE VITRIFICATION
OFFGAS ANALYSIS PROPOSAL

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Radioactive Waste Vitrification Offgas Analysis Proposal

Summary

Further validation of the Hanford Waste Vitrification Plant (HWVP) feed simulants will be performed by analyzing offgases during crucible melting of actual waste glasses and simulants. The existing method of vitrifying radioactive laboratory-scale samples will be modified to allow offgas analysis during preparation of glass for product testing. The analysis equipment will include two gas chromatographs (GC) with thermal conductivity detectors (TCD) and one NO/NO_x analyzer. This equipment is part of the radioactive forming offgas system. The system will provide real-time analysis of H₂, O₂, N₂, NO, N₂O, NO₂, CO, CO₂, H₂O, and SO₂. As with the prior melting method, the product glass will be compatible with durability testing, i.e., Product Consistency Test (PCT) and Material Characterization Center (MCC-1), and crystallinity analysis. Procedures have been included to ensure glass homogeneity and quenching. The radioactive glass will be adaptable to Fe⁺²/ΣFe measurement procedures because the atmosphere above the melt can be controlled. The 325 A-hot cell facility is being established as the permanent location for radioactive offgas analysis during forming, and can be easily adapted to crucible melt tests. The total costs necessary to set up and perform offgas measurements on the first radioactive core sample is estimated at \$115K. Costs for repeating the test on each additional core sample are estimated to be \$60K. The schedule allows for performing the test on the next available core sample.

Justification

The source of most design/design verification data for HWVP is from laboratory, bench, and pilot-scale tests using simulated waste feeds. A critical complement to these data are corresponding radioactive data, which provides a comparison between the simulant and actual feeds. The simulant preparation methods developed by HWVP must produce simulants representative of the actual waste or they are invalid for plant design.

For example, do the precipitation, decanting, and washing steps that we use to produce simulant neutralized current acid waste (NCAW) result in a feed that melts similarly to the real NCAW? The proposed work is designed to answer this question by confirming that simulants are representative of the actual waste relative to melting offgas behavior. The testing will provide a direct comparison of offgas behavior during calcination and vitrification. The testing will provide data on offgas generation rates and speciation for designing and sizing plant equipment (i.e., NO_x scrubber design and pipeline sizing), permitting, and safety.

The core sample offgas data are needed to assess safety issues related to hydrogen and ammonia evolution. Initial tests performed on crucible melts of formic acid treated NCAW showed considerable hydrogen generation. Although the hydrogen will normally combust in a melter system having plenum heaters, the hydrogen data are important to ensure safe design under all operating conditions. Ammonia in the presence of NO_x can form potentially explosive levels of ammonium nitrate in the ventilation system. The presence of organics can also act as a sensitizer for the detonation. The offgas data collected from core samples will provide information relative to these hazards.

Performing offgas analyses on the radioactive core samples provides the capability to assess the effects of actual waste composition variation on melter offgas generation. In the bench-scale radioactive melter, only a very limited number of runs with the major waste types will be performed to assess and compare offgas compositions.

Each of the HWVP waste types will produce different types and amounts of melter offgases and possible hazards. Analysis of each core sample is important to characterize offgas behavior of the different waste types during calcination and vitrification. Core samples are expensive and rare, and proper data collection is essential for each sample. If this offgas data is not collected while processing a sample, the data are lost. Delaying data collection to out-year core samples could cause permitting, safety, and economic problems because of major plant modifications.

The proposed offgas testing will provide a valid radioactive data base for permitting applications. The radioactive data will provide credible source terms as well as validate nonradioactive source terms. Certain volatiles of interest to Washington State and the Environmental Protection Agency may only be measurable on radioactive samples.

Because of the complex nature of HWVP feeds, the chemical reactions that occur during the transformation of feed into glass have only been hypothesized. Many variables govern the reaction paths: the temperature ramp rate, the oxidation state of the feed, and the atmosphere above the cold cap, etc. P. Hrma and D-S. Kim (PNL) are conducting online offgas analyses during the calcination and vitrification of simulated HWVP feeds. Their work, along with complementary radioactive testing, will lead to an increased understanding of the cold cap chemistry and justification for retaining or modifying the current hypotheses.

Background

In recent work, J. L. Ryan (PNL) has hypothesized several reactions governing the melting of formed waste. The basis assumptions and hypothesized reactions are as follows:

Assumptions of Waste Composition:

- Slurry is depleted of hydroxides, nitrites, and carbonate.
- Slurry contains nitrates, formates, and nitrates of metal salts.

Hypothesized Cold Cap Chemistry:

- When gases come off at low temperatures (i.e., 300° to 500°C), they can escape easily through the porous cold cap.
- When gases come off at high temperatures (i.e., 700° to 900°C), they cannot escape well through the viscous glass, causing foaming.
- Evidence shows that acid waste (e.g., formed waste) produces less foaming.
- As gases escape the glass, it carries H₂O with it.

Hypothesized reactions are shown in Table 1.

Table 1. Cold Cap Reactions of Formated Waste

Temperature	Sample Progress	Reaction
100°-200°C	Sample dries	Free H ₂ O is lost.
200°-300°C	NaCOOH and NaNO ₃ form eutectics.	NaCOOH melting point = 253°C NaNO ₃ melting point = 300°C
325°C	Nitrate and formate reactions complete in < 1 h.	$\text{NaCOOH} + \text{NaNO}_3 \rightarrow \frac{1}{2}\text{Na}_2\text{CO}_3 + \text{NaNO}_2 + \frac{1}{2}\text{CO}_2\uparrow + \frac{1}{2}\text{H}_2\text{O}\uparrow$ $\text{NaCOOH} + \text{NaNO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \frac{1}{2}\text{N}_2\text{O}\uparrow + \frac{1}{2}\text{H}_2\text{O}\uparrow$
~400°C	All nitrate, nitrite, and liquid are gone.	$2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}\uparrow + \text{H}_2\uparrow$ <i>be consistent on formulas</i>
580°-700°C	Some nitrate may still be present (if not enough reductant is added or it did not work effectively), which will react as batch becomes liquid. Further metal reductions	$\text{Na}_2\text{MnO}_4 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{MnO} + \text{O}_2\uparrow$ <i>Mn⁺²</i>
700°-900°C	Sodium carbonate destruction High oxidation state metals reduce (e.g., Mn ⁺⁶ to Mn ⁺⁴ as SiO ₂ goes into solution and Na ₂ CO ₃ decomposes).	$\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2\uparrow$ <i>reduction to Mn⁺² already shown above 580-700°C</i>
700°-1150°C	Further reduction of metals	For almost all elements, the higher oxidation states become less stable at higher temperatures. Reactions generate O ₂ .

The proposed offgas system will monitor for H₂O, CO₂, O₂, N₂O, H₂, N₂, NO, NO₂, CO, and SO₂, which will allow testing of these hypotheses. By comparing the stoichiometric ratios of the offgases, hypothesized reaction mechanisms can be tested.

Offgas equipment procured for analysis of radioactive core samples was used to support the first crucible melt tests performed by P. Smith and J. Vienna (PNL). During

melting of simulant NCAW, significant quantities of several gases were detected and monitored (i.e., H_2O , CO_2 , O_2 , N_2O , H_2 , CO , and NO). A preliminary look at the data indicate that additional reactions were occurring other than those stated above. Tests like these will be valuable in understanding cold cap chemistry and causes of foaming in the melter, if they are valid with respect to scaleup. The equipment used, which is the same as that proposed for radioactive testing, was functional and reliable.

Approach

Gas collection and analysis from radioactive operations in shielded facilities is a standard procedure. Recent work in laboratory-scale, radioactive forming offgas analysis and nonradioactive crucible melt offgas analysis has provided valuable experience. As a result of the radioactive offgas analysis during both types of testing, it is evident that the proposed system will perform as expected and will accurately provide the necessary information. A conceptual design for an offgas analysis system to be employed in a hot cell facility is shown in Figure 1.

Gases generated during calcination and vitrification will be swept through the system using argon with a helium tracer or other gases as justified. The flow of carrier gas will be regulated using a mass-flow controller. After the carrier gas sweeps through the crucible and mixes with the offgases, it will be mixed with an additional carrier gas to bring the dew point to below 25°C . The gases will then pass through a condenser equipped with a condensate trap. The condenser and trap are an added assurance that condensable water does not damage the high-efficiency particulate air (HEPA) filters and analytical equipment. As the gases leave the hot cell, they will pass through a HEPA filter on each side of the cell wall. Offgases will then be sampled every $1\frac{1}{2}$ min by the GCs, which separate the gases using two different columns (Mole Sieve and Pora Plot U or Q). A small amount of offgas will be vented to the fume hood just following the GCs to allow gas analysis at atmospheric pressure. A metal bellows pump will then raise the line pressure between 5 and 10 pounds per square inch (psi), which is

Figure 1. Proposed Crucible Melt Offgas System (Radioactive)

required for the NO/NO_x analyzer. Following the metal bellows pump, a mass-flow controller supplies the NO/NO_x analyzer with a constant volume of offgas, which is blended with a constant volume of argon for dilution. All of the instruments and the remaining gas will be vented to the fume hood and building ventilation, both having HEPA filtration.

The melt furnace is a high-temperature tube furnace that can easily be adapted for remote operations (see Figure 2). The furnace is equipped with a programmable controller and will be capable of accurate temperature ramp rate during the melt process. An elongated alumina crucible will be used for the melt tests. Melting, quenching, annealing, and cooling will take place within the same crucible. When annealing and cooling are complete, the glass melt will be trimmed from the alumina crucible using a wafering saw. The square geometry is preferred to enable trimming the glass/crucible interface with minimal sample loss. Because there is no need to pour the glass, there will be less wasted glass and more available for testing.

Required Equipment

The following is a list of the equipment used in the system and a record of its availability:

Gas Chromatographs (2)	Currently Available
NO/NO _x Analyzer	Currently Available
Mass-flow Controllers (3)	Currently Available
Metal Billows Pump	Currently Available
Data Acquisition Software	Currently Available
Data Acquisition/Control Computers (3)	Currently Available
Pressure and Temperature Gauges	Currently Available
High-Capacity Mass-flow Controller	To Be Procured
Custom Alumina Crucibles	To Be Procured
Melt Furnace	To Be Procured
Annealing Furnace	To Be Procured
Calibration/Carrier Gases	To Be Procured
Wafering Saw	To Be Procured

Figure 2. Melt Furnace and Crucible Setup

The designation "Currently Available" means that the equipment is part of the existing forming offgas analysis system and can be used for the vitrification offgas analysis as well. Items "To Be Procured," specifically for vitrification offgas analysis, include a high-capacity mass-flow controller, custom alumina crucible, melt and annealing furnaces, calibration/carrier gases, wafering saw, and a Pora Plot U column for the GC. A high-capacity mass-flow controller is needed to dilute offgases to sufficient levels for analysis. Alumina or other selected crucibles are not available in the desired geometry and will have to be special ordered. Furnaces capable of handling the custom crucibles and offgas apparatus are not typical and will need to be procured. Calibration and carrier gases will be restocked as necessary. A wafering saw is needed for trimming the crucible away from the glass.

Compatibility of Melting Method with Product Testing

Table 2 provides a comparison of procedural steps for the previous and proposed radioactive melting methods along with those for the Composition Variability Study (CVS) method. Previous radioactive feeds have been melted in Denver Fire Clay crucibles exposed to air and were poured into bar molds for quenching and annealing. The new method will include melting feed in alumina or other crucibles under inert or air atmosphere, air quenching, and annealing, all within the same crucible. Under the new method, the radioactive glass will be consistent with glass redox procedures used by K. Wiemers (PNL) that entail sealing the crucible and lid to eliminate oxidation of the melt from atmospheric oxygen. During recent melter experiments, the melt furnace has been more oxidizing than crucible melts exposed to air; therefore, redox measurements will not be directly comparable to melter redoxes. However, the radioactive crucible redox will provide a direct comparison with simulant crucible redoxes. The glass should be compatible with durability testing (i.e., PCT and MCC-1) and crystallinity because steps have been included to ensure glass homogeneity and quenching. Although the new method is slightly different, it is expected to produce acceptable glass. Confirmation work will be performed with simulants prior to running core samples.

Table 2. Comparison of Melt Methods

	Composition Variability Study	Previous Radioactive Method	Proposed Radioactive Method
Crucible Type:	Platinum (with platinum lid)	Denver Fire Clay (without lid)	Alumina or other (with square cross section and stainless steel lid)
Step 1	Mix raw chemicals as a batch in disk mill	Calcine by ramping melt furnace to 600°C at 225°C/h hold at 600°C for 2 h let cool	Seal lid to crucible & calcine by ramping melt furnace to 600°C at 225°C/h hold at 600°C for 2 h let cool
Step 2	Heat to 1150°C for 1 h (batch added in parts)	Grind calcine to <40 mesh using a mortar and pestle	Remove lid from crucible or cut with wafering saw
Step 3	Pour onto hot plate (high setting) let air quench	Place calcine back into crucible	Grind calcine with mortar and pestle to <40 mesh
Step 4	Hand grind and put into disk mill ≤ 1.5 min to <100 mesh	Melt at 1150°C for 2 h (batch added in parts)	Place calcine back in crucible, seal lid & melt at 1150°C for 2 h (entire batch)
Step 5	Remelt at 1150°C for 1 h	Pour onto hot plate (high setting) with bar molds (until not glowing)	Remove crucible from furnace and let air quench until not glowing
Step 6	Pour onto hot plate (high setting) with bar molds	Anneal at 500°C for 2 h and let cool in furnace overnight	Anneal at 500°C for 2 h and let cool in furnace overnight
Step 7	Anneal glass at 500°C for 2 h and let cool	Trim sides off glass bar with wafering saw prior to sample preparation	Cut or break walls of crucible away from glass bar prior to sample preparation

Location of Work

There are two locations for this testing that appear to be appropriate: 1) the 325 A-hot cell facility where radioactive formating is being performed, and 2) the 324/D-cell where radioactive melting is currently being performed. Either facility could

be used for the offgas analysis during the vitrification of the core samples; however, the 325 Building is the recommended location based on the following reasons:

1. A fume hood is currently being installed adjacent to 325A/C-cell for future forming offgas analysis. Offgas equipment will be permanently installed in the fume hood. This same equipment will already be set up as a result of the forming offgas analyses before vitrification. Performing both forming and melting in the same location will minimize the possibility of damaging equipment during transport and reduce the cost and schedule per test by decreasing setup time.
2. Either a hood or a glovebox adjacent to the hot cell is required for locating and operating the offgas analyzers. In 324/D-cell, a large glovebox was fabricated several years ago and is waiting for someone to pay for installation. The only place available for a hood is on the end of this glovebox. The cost for installation of the hood and glove box is estimated at \$100K. If a hood and glove box were installed, the hood location would necessitate a 30-to 40-ft offgas line to the analysis equipment resulting in added response time to the system. No savings will be recognized by using existing vitrification equipment in 324/D-cell because new furnaces will be needed that are compatible with the elongated crucible shape and offgas penetrations.

Simulant Testing

The system will be cold tested using available simulants to ensure that it will operate properly in a hot-cell environment. The data will be compared with previous simulant data generated in the Glass Envelope Definition crucible melt system. Simulants prepared to match each core sample will be tested as a comparison to each core sample. These simulants will be the same as those prepared for forming offgas testing.

Data Analysis and Reporting

The data from simulant and radioactive testing will be analyzed and compared. Results will also be compared with the Glass Envelope Definition simulant data. Analysis of the data will be included in the final report of the radioactive sample.

Cost and Schedule Estimates

Itemized cost and schedule estimates for these studies are provided in Table 3. The total costs shown are those necessary to set up and perform offgas measurements on the

Table 3. Itemized Estimated Costs and Schedule

	Estimated Cost
Equipment	
Custom Crucibles and Lids	\$4.0K
Melt Furnace	1.5K
Annealing Furnace	1.5K
Mass-flow Controller and Control Box	3.0K
Calibration/Carrier Gases	1.5K
Wafering Saw	5.0K
Miscellaneous/Adaptation	8.5K
Sub Total	\$25.0K
Installation	30.0K
Test Planning and Procedure Modification	15.0K
Data Analysis and Reporting	25.0K
Simulant Testing (in-cell)	10.0K
Radioactive Testing	10.0K
Total Cost	\$115.0K
Schedule for Completion of First Core Sample	6 to 7 months
Cost for Testing Additional Core Samples	\$60.0K

first radioactive core sample. The schedule shown is for completing the first radioactive test but does not include reporting, which will be a part of the overall test report. Cost information for repeating the test on each additional radioactive core sample is also provided.

11/12/93

CHUCK

I DON'T KNOW WHAT KIND OF DEAL YOU HAVE WORKED OUT W/ EUGENNE ON THIS PROPOSAL BUT YOU MIGHT WANT TO TAKE A CLOSER LOOK AT IT.

I HAVE SEVERAL COMMENTS:

1. EITHER THE CARRIER GAS OR OFF GAS LINE SHOULD EXTEND FURTHER DOWN INTO THE CRUCIBLE SO THE GAS FLOW IS NOT SHORT CIRCUITED. I BELIEVE THAT THIS IS HOW PETE SET UP THE CRUCIBLE FOR KARYN'S WORK.
2. SHOULD A COLD FINGER BE PUT IN? CAN YOU USE A COLD FINGER IN A HOT CELL?
3. HOW DOES THIS METHOD COMPARE TO THE STANDARD CRUCIBLE (SEALED) TEST? I.E. IS THIS METHOD ANY MORE OR LESS REPRESENTATIVE OF THE OXIDATION STATE IN THE MELTER THAN THE CRUCIBLE TEST METHOD? IF IT IS LESS REPRESENTATIVE, THEN CAN WE AFFORD TO LOSE THE DATA THAT WOULD BE GAINED IN THE SEALED CRUCIBLE TEST? (I DIDN'T THINK WE HAD ANY CORE SAMPLE LEFT TO PLAY AROUND WITH)

RGL

DATE

FILMED

5 / 31 / 94

END