WSRC-MS-98-00038
CONF-980905--

Off-Gas Analysis During the Vitrification of Hanford Radioactive Waste Samples

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A document prepared for SPECTRUM '98, NUCLEAR AND HAZARDOUS WASTE MANAGEMENT INTERNATIONAL TOPICAL MEETING at Denver, CO, USA from 9/13/98 - 9/18/98.

DOE Contract No. **DE-AC09-96SR18500**

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WSRC-MS-98-00038X

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Extended Summary of a Paper Proposed for Presentation at "Spectrum '98," Nuclear and Hazardous Waste Management International Topical Meeting, September 13-18, 1998, Denver, CO, and for Publication in the Proceedings.

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy.

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INTRODUCTION

As part of the Tank Waste Remediation System (TWRS), the United States Department of Energy (DOE) issued a Request for Proposal (RFP)[1] to vendors interested in building and operating a privatized facility for immobilizing radioactive waste currently being stored in tanks at the DOE site in Hanford, Washington. British Nuclear Fuels Limited (BNFL), responded to the RFP and was awarded a contract[2] to perform the initial phase of this work. BNFL has teamed with SAIC, Bechtel National Inc., GTS Duratek and the Vitreous State Laboratory (VSL) at Catholic University to develop and demonstrate technology needed to meet the terms outlined in the TWRS RFP. In collaboration with the BNFL team, the Savannah River Technology Center (SRTC) was asked to perform radioactive demonstrations with four samples of the actual radioactive waste from Hanford. SRTC has produced and characterized three Low-Activity (LAW) glasses and a single High-Level Waste (HLW) glass from actual radioactive Hanford waste samples. This paper describes the off-gas analysis of samples collected during the radioactive vitrification experiments. Production and characterization of the Hanford waste-containing LAW and HAW glasses are presented in related reports from this conference.

WORK DESCRIPTION

The radioactive demonstration was performed remotely in the SRTC Shielded Cells. Vitrification of the Hanford LAW and HLW samples was performed in three steps. First, water was evaporated from the sample and collected in one of the off-gas system traps. Then, the mixture was calcined. This removed the semi-volatile species that were in the waste form, e.g. nitrate and nitrite. Finally, the material was brought to the melt temperature and held there before the resulting glass waste form was taken from the furnace and sampled.

At the start of the experiment, the glass-forming chemicals and waste streams were mixed. Then, the off-gas system was set up. The off-gas system included a condenser, a dry-ice trap, charcoal filters, and a vacuum pump. The off-gas system was developed to keep hazardous species from the shielded cells environment. The crucible was put in the furnace, and the off-gas system was connected. The temperature of the furnace was then slowly increased 10 °C every 30 minutes, from the initial 50 °C, until water was collected below the condenser. When water started to accumulate in the condenser trap, the temperature was held constant until the condensation stopped. Then, the temperature was increased at the same rate until water started condensing again. This was continued until the furnace reached 200 °C.

Next, the furnace temperature was increased to 900 °C (at a nominal rate of 100 °C per hour) during which time the volatile species, e.g. nitrate and nitrite, were driven from the mixture. The temperature was increased slowly to avoid foaming or "splattering" of the material in the crucible. During this temperature ramp, brown vapor (NO_2) was typically seen in the off-gas system. Once the furnace reached 900 °C, it was held at this temperature for thirty minutes. The off-gas system was disconnected. Material was finally brought to the melt temperature of between 1120 °C and 1150 °C and held there for 2 hours. The resulting glass waste form was taken from the furnace, quenched and sampled.

The condensate trap and the cold trap were sampled after the experiment and the mass of the charcoal filters was measured to determine whether anything was adsorbed on the filters. The mass of the filters increased from 81 grams at the start of the tests to 86 grams after vitrifying the last glass indicating that 5 grams of material (organic carbon and perhaps some moisture) had been adsorbed on the activated charcoal. Off-gas samples were transferred to Analytical Development Section (ADS) for analysis by gamma PHA, ICP-ES and mass spectroscopy to determine what was volatilized from the mixture during vitrification.

ANALYSIS OF THE OFF-GAS SAMPLES

Analysis of samples taken from the condenser and the cold trap indicated that very little other than water was collected in the condenser or cold trap. The charcoal filters were not analyzed.

Table 1 gives the radionuclide composition of the condensates from the LAW vitrifications. Although very little of the radionuclides appear to have volatilized, a larger than expected fraction of the volatile Cs passed through the condenser into the dry-ice cold trap before it was condensed and collected. Sr/Y-90 could not be determined for the cold trap samples because of limited sample volumes.

Table 1. Radionuclide Composition (μCi/mL) of Off-Gas Samples Collected during Vitrification of Envelope A, B, and C LAW Waste Streams

Radionuclide	Envelope A		Envelope B		Envelope C	
	Condensate	Cold Trap	Condensate	Cold Trap	Condensate	Cold Trap
Am-241	$< 6 \times 10^{-4}$	$< 6 \times 10^{-4}$	$< 6 \times 10^{-4}$	$< 6 \times 10^{-4}$	$< 6 \times 10^{-4}$	1.4×10^{-3}
Cs-137	1.4×10^{-3}	8.2×10^{-4}	1.2×10^{-2}	3.7×10^{-4}	1.0×10^{-3}	3.5×10^{-3}
Sr/Y-90	3.1×10^{-5}	No Analysis	No Analysis	No Analysis	3.1×10^{-4}	No Analysis

Table 2 gives the radionculide composition of the condensate and cold trap samples collected during the HLW vitrification demonstrations. Although the Cs-137 and Tc-99 concentrations were between two and three orders of magnitude greater in the samples than in the LAW samples, they were two to three orders of magnitude lower than the concentrations in the HLW glass. Sr-90 was not detected in these samples. Concentrations of Cs-137 and Tc-99 were much higher in the dry-ice cold traps than initially expected.

Table 2. Radionuclide Composition (μCi/g) of Off-Gas Collected during Vitrification of HLW Samples

Radionuclide	Envelope D			
	Condensate	Cold-Trap	Condensate	Cold-Trap
Cs-137	3.89	1.38	6.38	0.82
Tc-99	2.88×10^{-4}	5.86×10^{-5}	5.56×10^{-4}	4.5×10^{-5}

A comparison can be made of the major Cs-137 and Sr-90 radionuclides detected in the glass to the amounts of these species added in the HLW glass formulation. Table 3 shows the results of such a comparison. Cs-137 was added predominately from the treated supernate stream and the HLW filtered sludge solids. A total of approximately 1.4×10^5 μCi of Cs-137 was present in the feed streams used to produce the 60 grams of HLW glass. The concentration of Cs-137 in the HLW glass was in the range of (1.9 to 2.1) $\times 10^3$ μCi/g of glass. Therefore, a total of 60 grams of glass contained (1.1 to 1.3) $\times 10^5$ μCi of Cs-137. Relatively low levels of Cs-137 were detected in the HLW glass off-gas condensate and cold-trap samples. A total of only about 300 μCi of Cs-137 is estimated from

analyses of the off-gas samples. Thus, the calculated amounts of Cs-137 in the feed streams is close to the amount found in the HLW glass.

Table 3. Comparison of Radionuclides in the Feed Streams to Radionuclides in the HLW Glass and Off-Gas Samples

	Source	Total Microcuries	Sum Total Microcuries
Cs-137			
Feed Stream	Treated Supernate HLW Filtered Solids	1.1×10^5 2.6×10^4	1.4×10^5
After Vitrification	HLW Glass HLW Off-Gas Streams	$(1.1\text{-}1.3) \times 10^5$ 3×10^2	$\sim 1.2 \times 10^5$
Sr-90			
Feed Stream	Treated Supernate HLW Filtered Solids	1.3×10^4 4.2×10^4	5.5×10^4
After Vitrification	HLW Glass HLW Off-Gas Streams	$(6.6\text{-}7.2) \times 10^4$ -	$\sim 6.9 \times 10^4$

Table 3 also shows the results of a comparison for Sr-90. Sr-90 was added predominately from the treated supernate stream from Envelope C pretreatment and the HLW filtered sludge solids. A total of approximately 5.5×10^4 µCi of Sr-90 was present in the HLW feed streams. Of this Sr-90 source, about 1.3×10^4 µCi was in the TRU/Sr/Fe solids and about 4.2×10^4 µCi was in the HLW filtered sludge solids. The concentration of Sr-90 in the HLW glass was $(1.1 \text{ to } 1.2) \times 10^3$ µCi/g of glass. Therefore, a total of 60 grams of glass had $(6.6 \text{ to } 7.2) \times 10^4$ µCi of Sr-90. Sr-90 was not detected in the HLW glass off-gas condensate or cold-trap samples. Therefore, the amount of Sr-90 measured in the feed streams was within 20% of the Sr-90 detected in the product HLW glass.

REFERENCES

1. United States Department of Energy, "TWRS Privatization Request for Proposals," **DE-RP006-96RL13308**, February 1996.
2. British Nuclear Fuels Limited, Incorporated, "Tank Waste Remediation System Privatization Technology Development and Demonstration Program," August 1995.