Behavior of Mercury and Iodine During Vitrification of Simulated Alkaline Purex Waste

L. K. Holton

September 1981

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1.0 SUMMARY

Current plans indicate that the high-level wastes stored at the Savannah River Plant (SRP) will be solidified by vitrification. The behavior of mercury and iodine during the vitrification process is of concern because: mercury is present in the waste in high concentrations (0.1 to 2.8 wt%); mercury will react with iodine and the other halogens present in the waste during vitrification and; the mercury compounds formed will be volatilized from the vitrification process placing a high particulate load in the vitrification system off-gas.

Twelve experiments were completed to study the behavior of mercury during vitrification of simulated SRP Purex waste. Three independent variables, forming eight nodes in a 2^3 experimental design were varied for experimentation. Four experiments were repeated to improve experimental reliability. Experimental variables and bounding values were: 1) the iodide to mercury molar ratio in the simulated waste set at 0.1 and 0.9, 2) the vitrification system outlet gas temperature set at 300°C and 600°C, and 3) the oxygen content of the vitrification system atmosphere set at approximately zero volume percent and twenty volume percent. These experimental variables with bounding values are anticipated to form the bounds for process conditions in actual plant operations.

The experiments were conducted using a laboratory scale spray calciner/in-can melter system and vitrification off-gas cleanup system. The off-gas cleanup system consisted of a venturi scrubber, cyclone, downdraft condenser, off-gas heater and a HEPA filter. Simulated alkaline Purex waste was prepared by precipitation of metallic nitrates and batch washing of the resultant sludge to remove soluble salts. Simulated waste prepared by this method is believed to duplicate as accurately as possible the chemical behavior of actual alkaline Purex waste.

The mercury was completely volatilized from the vitrification system in all experiments. The mercury reacted with iodine, chlorine and oxygen to form a fine particulate solid. Quantitative recovery of mercury compounds formed in

the vitrification system off-gas was not possible due to high (37 to 90%) deposition of solids in the off-gas piping.

The behavior of mercury and iodine was most strongly influenced by the vitrification system atmosphere. During experiments performed in which the oxygen content of the vitrification system atmosphere was low (<1 vol%); iodine retention in the glass product was 27 to 55%, the mercury composition of the solids recovered from the off-gas scrub solutions was 75 to 85 wt%, and a small quantity of metallic mercury was recovered from the off-gas scrub solution. During experiments performed in which the oxygen content of the vitrification system atmosphere was high (20 vol%), iodine retention in the glass product was 3 to 15%, the mercury composition of the solids recovered from the off-gas scrub solutions was 60 to 80 wt%, and very little metallic mercury was recovered from the off-gas scrub solution.

The kinetics of reaction between iodine and mercury was concluded to be fast. However, there is competition between chlorine and iodine for reaction with mercury. The reaction between mercury and iodine was complete when there was a low ratio of iodide to mercury (0.10) in the simulated waste feed; the reaction was only partially complete (~50 to 90%) when the iodide to mercury ratio in the simulated waste was high (0.90).

From the experimental work conducted we have identified the need for further study. Areas needing attention are:

- Buildup of the mercury solids in the off-gas piping during long-term equipment operations.
- Develop processes for quantitative recovery of mercury from the alkaline Purex waste prior to vitrification.
- Separation of mercury solids from the scrub solutions and recovery of mercury from the solids.
- Assessment of corrosion by mercury and mercury compounds on the vitrification and off-gas equipment.

2.0 INTRODUCTION

Nuclear fuels reprocessed by the Savannah River Plant (SRP) over a span of 25 years have produced approximately $9.0 \times 10^4 \text{ m}^3$ of alkaline high-level radioactive wastes. These wastes consist of liquid (~58 vol%), salt cake (~29 vol%) and sludge (~13 vol%).

The stored SRP wastes, which are mainly the product of two processing schemes, can be roughly grouped into high-iron- and high-aluminum-containing wastes. A Purex process, operated in the SRP F Area, produced a waste containing high concentrations of iron. In addition, coating waste, obtained from decladding targets that were processed in F Area, added high concentrations of aluminum and mercury to the F Area waste tanks. A modified Purex process in the SRP H Area was used to process aluminum clad uranium fuel. Both the aluminum cladding and uranium were codissolved using mercury as a dissolution catalyst. The resultant HAW waste contains high aluminum concentrations while the LAW waste from the process is similar to Purex waste and has high concentrations of iron. Major chemical and radiochemical components of the F Area and H Area high-level waste sludges are summarized in Table 2.1.

Current plans indicate that these high-level wastes will be solidified by vitrification. The behavior of mercury during the vitrification process is of concern because of the high concentration of mercury in the wastes (0.1 to 2.8 wt%) and the fact that mercury and mercury compounds will be volatilized from the vitrification process thus placing a high particulate load in the vitrification off-gas.

Only limited information is presently available on the behavior of mercury and its interaction with iodine in the vitrification process. This information is limited to simple experimental studies directed towards characterization of the recombination kinetics of mercury and iodine, and thermodynamic computer studies directed towards predicting the chemical form of mercury in the vitrification system off-gas (G. B. Woolsey, Savannah River Laboratory).

TABLE 2.1. Major Components of SRP High-Level Waste Sludges(a)

Constituent	Concentration Range (wt%)	
	F Area	H Area
Al	1.5 to 2.5	7.1 to 33.5
Ca	0.6 to 2.3	0.2 to 2.9
Fe	8.9 to 32.8	3.1 to 27.9
Hg	0.1 to 0.7	0.9 to 2.8
Mn	2.0 to 10.8	1.7 to 8.8
Na	2.8 to 6.1	1.0 to 3.1
Ni	2.1 to 6.3	0.3 to 0.7
NO ₃	0.12 to 1.2	0.2 to 0.4
NO ₂	0.02 to 0.12	0.01 to 0.2
SO ₄	<0.5	<0.05
U	3.3 to 15.4	0.9 to 4.5

Radionuclide	Activity Range (mCi/g of sludge)	
	F Area	H Area
¹⁴⁴ Ce	0.21 to 30.5	0.3 to 17.4
⁶⁰ Co	1 to 1	0.01 to 0.06
¹³⁴ Cs	0.01 to <0.02	<0.01 to 0.03
¹³⁷ Cs	0.7 to 1.30	0.05 to 0.30
¹⁵⁴ Eu	<0.01 to 0.6	0.08 to 1.18
⁹⁵ Nb	<0.01 to <0.03	≤0.02
¹⁰³ Ru	<0.01 to <0.02	<0.01
¹⁰⁶ Ru	1.3 to 11.4	0.08 to 1.74
¹²⁵ Sb	0.43	0.12 to 1.27
⁹⁰ Sr	27.03 to 177.5	15.49 to 55.0

(a) Stone (1976a); Ondrejko (1974); Gray, Donnan, and Okamoto (1979); Stone (1976b); Stone, Goforth, and Smith (1979).

The purpose of this experimental study was therefore to characterize the chemical behavior of mercury during vitrification of simulated alkaline SRP waste when key process parameters are varied. The behavior of mercury, as influenced by the three process variables listed below, was studied.

- iodide-to-mercury molar ratio in the simulated SRP waste feed
- vitrification system outlet off-gas temperature
- oxygen (O_2) concentration in the vitrification system atmosphere.

3.0 EXPERIMENTAL APPROACH AND METHODS

The experimental methods and system used to conduct the mercury study are summarized in this section. Particular emphasis has been placed on the experimental methods and the experimental system to represent as completely as possible expected waste solidification plant conditions.

3.1 EXPERIMENTAL DESIGN

The experimental approach was based on a Yates 2^3 experimental design (Cochran and Cox 1957) shown in Figure 3.1. The three study variables (iodide to mercury molar ratio, temperature of vitrification system off-gas and oxygen concentration of vitrification off-gas) form eight nodes in the 2^3 experimental design. The iodide-to-mercury ratio in the simulated waste was controlled at 0.10 and 0.90 along each of two experimental planes, the off-gas outlet temperature of the vitrification system was controlled at 300°C and 600°C along each of two experimental planes, and the vitrification system

FIGURE 3.1. Yates 2^3 Experimental Design for Mercury Study

atmosphere was controlled at a condition where virtually no oxygen was present and at a condition where the oxygen concentration was approximately the same as atmospheric concentrations. Four experiments, indicated by the shaded nodes in Figure 3.1 were repeated to improve experimental certainty.

The basis for selecting each of the three experimental variables was the expected difference in chemical behavior of mercury at each experimental node.

Iodine will react with mercury in the gas phase and be condensed as a solid. This reaction pathway can be used to remove volatile iodine from the vitrification off-gas system. The other halogens, chloride and fluoride which are also present in the alkaline waste will react with mercury. Figure 3.2

FIGURE 3.2. Free Energy Versus Temperature of Various Mercury Compounds B-Boiling Temperature, M-Melting Temperature D-Decomposition Temperature, T-Transition Temperature. (Adapted from Wicks and Block 1963.)

depicts graphically the free energy of various mercury compounds as a function of temperature. This data indicates that chloride and fluoride are thermodynamically more favored to react with mercury than iodide. Based upon this data there may be competition among the various reactants. Evaluating the mercury-iodine reaction at iodide to mercury molar ratios of 0.10 and 0.90 provided information regarding efficiency and competition between reactants. Chloride and fluoride concentrations in the simulated alkaline waste were not intentionally varied for the experiments.

The equilibrium reaction between mercury and iodine is temperature sensitive. A plot of the equilibrium fraction of iodine present in the form HgI_2 as a function of temperature is shown in Figure 3.3. This plot indicates that the limiting reactant, iodine, is virtually totally reacted with mercury in the reaction:

FIGURE 3.3. Reaction Equilibrium Between Mercury and Iodine
(Adapted from data in Stull and Prophet 1971)

at temperatures below 350°C and is virtually unreacted at temperatures above 600°C. The reaction product, HgI_2 , is a covalent vapor molecule in the off gas above its saturation point. The recombination kinetics between Hg and I_2 have been shown to be fast at temperatures below 200°C (G. B. Woolsey, Savannah River Laboratory). Based upon this, it is expected that the vitrification system off-gas characteristics at 300°C and 600°C would be significantly different. However, the off-gas characteristics should be similar after quenching. This, of course, does not consider the interactions of mercury with chloride or fluoride which are also present in the simulated SRP waste. Varying the vitrification system outlet temperature at 300°C and 600°C will provide information confirming the expected reaction kinetics between mercury and iodine.

The oxygen concentration of the vitrification system atmosphere was varied from containing virtually no oxygen, to containing approximately 20 volume percent oxygen. This experimental variable is evaluated to determine if mercury metal can be formed in and condensed from the vitrification system off-gas in the absence of oxygen. This is an assumption which has been made in the development of Defense Waste Processing Facility (DWPF) flowsheet (Landon 1980).

The three experimental variables (iodide-to-mercury ratio in the simulated waste, off-gas outlet temperature and oxygen concentration of vitrification system atmosphere) are anticipated to form the bounds for process conditions during plant operations. The chemical behavior of mercury and iodine at each of these bounding cases will be evaluated providing information regarding mercury behavior in anticipated plant operations. This information will provide the basis for selection of any alternative waste processing schemes for handling mercury in the DWPF.

3.2 SOLIDIFICATION PROCESS AND EQUIPMENT DESCRIPTION

A laboratory scale spray calciner/in-can melter (SC/ICM) and gaseous effluent cleanup system was the waste solidification system used for the mercury study. A simplified schematic of this system is shown in Figure 3.4, and a photograph of the system is shown in Photograph 3.1. The SC/ICM system is comprised of the following major equipment pieces.

FIGURE 3.4. Schematic of Experimental System for Mercury Study

PHOTO 3.1. Photograph of Laboratory Scale Spray Calciner/In-Can Melter and Off-Gas Cleanup System

- liquid waste blend and feed system
- spray calciner/in-can melter
- venturi off-gas scrubber and recycle scrub tank
- cyclone separator and condensate collection flask
- downdraft condenser and condensate collection flask
- off-gas line heater
- HEPA filter

Simulated liquid waste is pumped through the spray calciner feed system and atomized by air in a commercially available spray nozzle (Spraying Systems® nozzle used) located at the top of the spray calciner. Liquid waste droplets

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(~0.1 mm dia) formed by the spray nozzle are dried and partially decomposed to metallic oxides and salts as they fall through the heated wall spray calciner chamber. The nominal operating temperature of the spray calciner is 650 to 750°C. The dried waste powder is called calcine. The calcine is mixed with glass forming chemicals as it falls from the cone section of the spray calciner into a heated receiving canister. The solid calcine/glass former mixture is heated to a temperature of 1000 to 1050°C and converted to a vitreous product.

Off-gas from the solidification process consists primarily of atomizing gas, water vapor, NO_x from nitrate decomposition, volatile waste components (Hg , HgO , HgCl_2 , HgI_2) and semivolatile components (cesium and ruthenium). This off-gas is filtered through the spray calciner filters before being decontaminated by successive stages of scrubbing, condensation, physical separation, and filtration in the off-gas cleaning system.

The design features of the SC/ICM are summarized in Table 3.1. The SC/ICM was designed to solidify liquid wastes at a rate of 1 to 4 L/h, corresponding to a glass production rate of 0.3 to 1.3 kg/h.

The venturi scrubber located approximately 50 cm from the spray calciner filter outlet cools and partially condenses water vapor from the off-gas filters and scrubs entrained particulate solid from the gas stream. The venturi scrubber (Figure 3.5) was designed to cool 130 g-moles of noncondensibles gases and 70 g-moles of condensable gases per hour from 350 to 100°C using 12 L/h of scrub solution. During experimental operations the venturi scrubber cooled the off-gas from approximately 600 to 60°C using 20 to 30 L/h of scrub solution. The flow rate of scrub solution is measured by a flowmeter and controlled by adjusting the rotational speed of the pump. The off-gas and scrub solution are separated in a cooling tank, where the scrub solution is cooled. Chilled scrub solution is recycled to the venturi scrubber. The venturi scrubber is fabricated from 304-L stainless steel bar stock. The venturi cooling tank is fabricated from 12-in. stainless steel pipe. It is equipped with cooling coils and has an nominal operating capacity of 30 L. The cooling tank is equipped with diplegs and temperature sensing instrumentation to record the weight factor, specific gravity and temperature of the scrub solution.

TABLE 3.1. Summary of Design Features of the Laboratory Scale Spray Calciner/ In-Can Melter System

Spray Calciner

Spray Chamber Diameter	5.05 in. (12.8 cm)
Spray Chamber Height	41.5 in. (105.4 cm)
Ten-Element Single-Phase Furnace Total Power	10.1 kW
Filters (three)	
Pall	Inconel 600
Diameter	1.88 in. (4.8 cm)
Length	18 in. (45.7 cm)
Surface Area	149.9 in. ² (966.9 cm ²)
Filter Heater	
Six-Element Single-Phase Total Power	7.02 kW

In-Can Melter

Furnace Diameter	5.75 in. (37.1 cm)
Furnace Height	20.25 in. (130.6 cm)
Eight-Element Single-Phase Furnace Total Power	8.6 kW

Canisters
5 in. dia x 21 in. height

System Capacity

Liquid Waste to Spray Calciner	1 to 4 L/h
Glass Production Rates	0.3 to 1.3 kg/h

The cyclone separator (see Figure 3.6) was designed for a gas flow rate of 190 L/min (6.75 ft³/min) at 350°C. The dimensions of the cyclone are those recommended by the Stairmand (Koch and Licht 1980) design for a high-efficiency cyclone. With recommended dimensions, the cyclone has an 88% efficiency for removing entrained water droplets and particulate from the gas stream. The cyclone was fabricated from 304-L stainless steel bar stock. A 2 L glass vacuum flask was used to collect condensates from the cyclone.

FIGURE 3.5. Schematic of Venturi Scrubber

The downdraft condenser is a commercially available American Standard shell and tube heat exchanger. The condenser is fabricated from 4-3/16-in. dia 316 stainless steel pipe. The tubes are 1/4 in. dia, having a total surface area of 4.3 ft². Water at a temperature of 8 to 15°C (40 to 60°F) and a pressure of 30 psig is used as a coolant on the shell side. A 4 L glass vacuum flask was used to collect condensates from the condenser. During experimental operations the condenser cooled the off-gas stream from approximately 50 to 12°C.

An off-gas heater was installed in the off-gas system to heat the gaseous effluent above its dew point before passage through a HEPA filter. The heater

FIGURE 3.6. Schematic of Cyclone Separator

was constructed by mounting, and thermally and electrically insulating Thermcraft® heaters around 2 in. dia, 304-L stainless steel pipe. The power rating on the 120-volt heaters is 10.4 watts.

The HEPA filters used were manufactured by American Air Filter Company. The filter size was used 8 in. x 8 in. x 5-7/8 in. depth. The filters are rated for a gas flow of 190 L/min (50 ft³/min).

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3.3 EXPERIMENTAL PROCEDURES

The experimental parameters varied between experiments were; iodide to mercury ratio in the simulated waste, the off-gas temperature at the filter outlet, and the atmospheric conditions within the spray calciner/in-can melter system. All other process variables including the simulated waste composition were kept as consistent as possible for each experiment.

Simulated waste was prepared by precipitation of metallic nitrates and batch washing of the resultant sludge. This feed preparation method, (described in Appendix A) was used to prepare a simulated waste that represents as closely as possible the physical and chemical properties of actual alkaline Purex waste sludge. The simulated waste for each experimental run was chemically adjusted as required. Routine chemical additions included; sodium chloride, sodium fluoride, and potassium iodide. Particular attention was given to maintaining the iodide to mercury molar ratio at the required values of 0.10 and 0.90.

The SC/ICM atmospheric conditions were changed by using two different atomizing and service gases. Compressed air was used in the experiments where the initial oxygen content of the off-gas was held at ~20 vol%. An argon/hydrogen gas mixture of 95% Ar/5% H₂ was used in those experiments where the oxygen content of the vitrification off gas was controlled to low concentrations (<1 vol%).

The off-gas outlet temperature was controlled at 300°C or 600°C by regulating power supplied to heaters located around the spray calciner filter chamber. Temperature sensing elements located in the calciner outlet gas stream were used to detect the gas temperature and provide response information for the power controller.

Prior to each experiment, a canister was weighed and placed inside the in-can melter. The canister was then connected to the spray calciner and a leak check made on the spray calciner/in-can melter system. Sources of detectable off gas inleakage into the system were identified and eliminated.

The venturi scrub solution was replaced after each experiment with approximately 10 L of water. Condensates from the cyclone and condenser collection flasks were collected after each experiment and the volume measured.

Solids or metallic mercury accumulated in the venturi scrub solution, the cyclone condensate and in the condenser condensate during all experiments. These solids were separated by vacuum filtration, dried in an oven at 30 to 50°C and weighed.

Samples collected during each experiment were initial venturi scrub solution samples, feed samples taken hourly, and off-gas samples. Samples collected after the completion of an experiment were; scrub solution and condensate filtrate samples (venturi, cyclone and condenser), glass samples and various samples of interest such as material deposits in the off-gas piping.

Off-gas samples were collected in stainless steel sample bombs after the off-gas had been passed through a glassware scrub system. This glassware scrub system consisted of a condenser, three gas washing bottles; one filled with water, one empty, and one filled with calcium carbonate, and a 10 μ m silver particulate filter. The purpose of the gas scrubbing system was to cool and remove water vapor and particulate from the off gas, providing a dry gas sample free of particulate for analysis.

3.4 SAMPLE ANALYSIS METHODS

A wide range of chemical analysis methods were used to characterize the samples collected during each experiment. The analyses methods used for each type of sample are summarized in Table 3.2. Analyses of particular interest are those for mercury and iodide. Mercury analyses for the liquid samples and glass samples were performed by flameless atomic absorption spectroscopy. Mercury analysis for solids recovered from the venturi scrub solution were performed using x-ray fluorescence, comparing the response peak areas to a known standard. Iodide analysis were normally performed using neutron activation analysis. The irradiated samples were compared against a standard after corrections for decay were made. Iodide in the feed samples was also determined by x-ray fluorescence.

TABLE 3.2. Analysis Methods for Samples Collected During Mercury Study

Analysis Method	Sample Type				
	Simulated Alkaline Feed Slurry (Liquid)	Scrub Solution and Condensate Samples (Liquid)	Glass Samples (Powder)	Venturi Solid Samples (Powder)	Calciner Off-Gas (Gas)
Induction-Coupled Plasma	X	X	X		
Flameless Atomic Absorption (Hg)	X	X	X		
Ion Chromatography	X	X	X	X	
Mass Spectroscopy					X
Neutron Activation Analysis (I)		X	X	X	
X-Ray Diffraction				X	
X-Ray Fluorescence (Hg, I)	X			X	
Scanning Electron Microscope, X-Ray Microprobe				X	

4.0 EXPERIMENTAL RESULTS

Twelve experiments were successfully completed during the mercury study project. Eight of these experiments formed the nodes in the 2^3 experimental design. Four of the twelve experiments were duplicated to increase reliability of the experimental data.

4.1 GENERAL SYSTEM BEHAVIOR

Some generalizations can be concluded about the behavior of mercury during vitrification of alkaline Purex waste. Essentially all of the mercury was volatilized from the vitrification system. Approximately 90% of this mercury reacts in the gas phase with other chemical components in the system, predominately iodine, chlorine, and oxygen to form a dense particulate. The remaining 10% of the mercury is recovered as metallic mercury. Essentially all of the mercury can be recovered from the vitrification off gas by scrubbing and condensation. However, accumulation of mercury solids within the off-gas piping prevented quantitative recovery of mercury for material balance purposes.

Essentially all of the mercury fed to the vitrification process is volatilized. Mercury was detected in the glass product, however its concentration was less than 5×10^{-4} wt%. The majority of this mercury volatilized from the vitrification process was recovered by the venturi scrubber (20 to 50%) and lesser quantities were recovered in the cyclone (0.5 to 3%) and condenser (1 to 5%). A large fraction (37 to 90% of Hg in original waste) of mercury was not recovered in the scrub or condensate solutions. The unrecovered mercury was deposited within the off-gas piping as mercury and mercury compounds formed from reaction with chlorine, iodine, and oxygen. The off-gas leaving the condenser was cooled to a temperature of 7 to 13°C. The condenser acting as cold trap (mercury vapor pressure <0.001 mm Hg) is believed to have contained all the mercury within the off-gas system. A summary of the experimental runs is found in Appendix B.

Mercury recovered from the vitrification system off-gas formed either a dense solid or mercury globules. Particulate solid recovered by the venturi and cyclone scrubbers were comprised primarily of mercury halide and oxide

compounds. Mercury recovered by the condenser was primarily metallic mercury formed by condensation of mercury vapor. These two different forms of mercury indicate that effective mercury removal from the vitrification off gas will require both particulate scrubbing and scrubbing by condensation.

The fate of iodide in the vitrification and off-gas system was strongly influenced by the oxygen content of the system. As shown in Figure 4.1 iodide retention in the glass formed varied from 27 to 55% when the vitrification system atmosphere contained a small oxygen concentration (<1 vol%). Iodide retention in the glass was reduced to 3 to 15% when the oxygen concentration of the vitrification system was approximately 20%. Uncertainties in the experimental data did not allow any conclusions to be drawn from the variation in iodide content in the glass as a function of vitrification system outlet gas temperature or iodide to mercury ratio in the alkaline waste feed. Differences

FIGURE 4.1. Percent Iodide Retention in Glass for Experiments Performed in Mercury Study

in the amount of iodide retained in the glass between the two atmospheric conditions suggests that iodide volatilization from the vitrification process is a function of oxygen content in the vitrification off-gas. Iodide and chloride, which exhibits similar behavior, react with oxygen to form volatile iodine and chlorine.

Iodide can react in basic solutions to form iodine which has a low solubility ($\sim 10^{-3}$ M) in the solution (Cotton and Wilkinson 1972). Iodine evolution from the slightly basic waste solution is therefore possible however, this does not explain the significant difference in iodide retention in the vitreous product with change in vitrification system atmosphere.

Once volatile iodine and chlorine are formed they will be removed from the process and potentially react with mercury metal also believed to be formed in the gas phase. Iodide and chloride not converted to volatile iodine or chlorine will remain in the glass as a salt, such as NaI and NaCl.

Recovery of iodine from the vitrification system off-gas was low. Iodine losses ranged from 30 to 75% dependent upon the atmospheric conditions as discussed before. It is believed that the majority of the unrecovered iodide is combined with mercury as solid deposits in the off-gas piping. The only significant iodine trapping mechanism is reaction with mercury in the gas phase to form a semivolatile compound (probably HgI_2) which can be removed from the off-gas by scrubbing. Iodine recovery efficiencies by reaction with mercury ranged from 20 to 50% based on the collected solids only. Recovery efficiencies were not significantly dependent upon the vitrification system outlet gas temperature. However, the iodine recovery efficiency was found to be dependent upon the iodide to mercury ratio in the simulated waste. Table 4.1 illustrates these results.

Iodide retention in solids recovered from the venturi scrubber tank is significantly reduced at high iodide to mercury ratios (0.90) in the simulated waste. The iodide retention in the glass did not vary significantly with iodide to mercury ratio in the waste (refer to Figure 4.1). This suggests that there is competition between iodine and other compounds for reaction with mercury.

TABLE 4.1. Recovery of Iodide by Venturi Scrubber

<u>Oxygen Concentration in Vitrification System Atmosphere (Vol%)</u>	<u>Molar Ratio I/Hg in Simulated Waste</u>	<u>Percent Recovery in Venturi</u>
~20	0.1	39 to 51
	0.9	21 to 28
~0	0.1	32 to 38
	0.9	5 to 6

These other chemical species are probably oxygen and chlorine. The lack of dependence of iodide recovery on the vitrification system temperature is important, because this confirms that the reaction kinetics between mercury and iodine are fast.

4.2 CHARACTERISTICS OF MERCURY SOLIDS

The majority of the mercury recovered from the vitrification off gas condensed to form a dense, finely divided solid. Mercury solids were formed in all experiments conducted, however the chemical composition of the solids varied between each experiment. Table 4.2 summarizes for each experiment the process conditions and the physical and chemical characteristics of the mercury solids recovered from the venturi scrub solution. Flouride was not detected in the mercury solids. The physical characteristics of the mercury solids were identified from x-ray diffraction, scanning electron microscopy, and x-ray microprobe analysis. The mercury concentration in the solids was determined by x-ray fluorescence, the iodide concentration by neutron activation analysis and the chloride concentration by ion chromatography. Unidentified material in the mercury solids is thought to be a comprised of oxygen and water.

Mercury solids were also recovered from the cyclone condensate. The quantity of these solids was small (<1 g), such that chemical analysis of these solids was not practical. The cyclone solids appeared to be very similar to the venturi solids in physical appearance. It was assumed the cyclone solids

TABLE 4.2. Characteristics of Mercury Solids Recovered from Venturi Scrub Tank

Run Number	Iodide to Mercury Molar Ratio	Outlet Off Gas Temperature (°C)	Oxygen Concentration Vittrification Off Gas (Vol%)	Mercury Solids Characteristics	Composition of Mercury Solids(g) (wt%)	
01	0.9	300	20(h)	XRD(a); Strong HgI line, weak HgCL line, estimate 80% HgI, 20% HgCl, amorphous material present MP(b); Very small Hg drop-lets present. Comprised of irregular solids characteristics of HgI. Discrete particles of HgI and HgCl present.	Hg	64.2
					I	26.3
					Cl	2.5
					Unidentified	7
02	0.1	300	20	XRD; HgI, HgCl weak to moderate approximately equal amounts MP; Platlet material present identified as HgCL, amorphous HgI present, approximately equal amounts of HgI and HgCL	Hg	67.5
					I	6.1
					Cl	3.6
					Unidentified	7
03	0.9	600	20	XRD, Strong HgI, weak to moderate HgCl, estimate 70% HgI, 30% HgCl more crystalline character than 01 MP; More amorphous character than 01 no clear differentiation between individual particles	Hg	73.8
					I	14.1
					Cl	2.2
					Unidentified	9.9
04	0.1	600	20	XRD; Strong HgI, weak to moderate HgCL similar to Experiment No. 3 except both patterns weaker less HgI more HgCL crystals than 01 MP; HgCL more prevalent than HgI solid is crystalline, small crystals cubic in shape Fe, Cr present in sample	Hg	79.5
					I	9.2
					Cl	1.6
					Unidentified	9.7
05	0.1	600	0(i)	XRD; Very weak HgI, no HgCL amorphous halo on spectrograph indicates no crystalline material present MP; Spectrograph indicates no HgCL, very weak HgI. Visually many small mercury beads present, material amorphous	Hg	86.9
					I	2.9
					Cl	0.2
					Unidentified	10
06	0.1	300	0	XRD; Weaker HgI signal than Experiment No. 5, mostly uncrystallized material MP; No HgCL observed, small amount of HgI; visually amorphous material with many small mercury beads	Hg	86.4
					I	3.0
					Cl	0.2
					Unidentified	10.4

TABLE 4.2. (contd)

Run Number	Iodide to Mercury Molar Ratio	Outlet Off Gas Temperature (°C)	Oxygen Concentration Vittrification Off Gas (Vol%)	Mercury Solids Characteristics	Composition of Mercury Solids (wt%)	
07	0.9	300	0	XRD; Moderate HgI, no HgCL, HgI intensity like 05 MP; HgI, HgCL present, discrete particles observable, a lot of crystalline HgCL present, amorphous HgI present	Hg I Cl Unidentified	81.6 8.8 0.3 9.3
08	0.90	600	0	XRD; Very strong HgI, no HgCL present amorphous material present MP; Solid very amorphous in character comprised of HgI, no HgCL present	Hg I Cl Unidentified	79.8 10.6 0.06 9.54
09(c)	0.1	300	20	MP; Solid composed of largely HgI with some HgCl. Solid amorphous in form	Hg I Cl Unidentified	71.1 17.6 0.7 10.6
10(d)	0.9	600	20	MP; Solid comprised mostly of HgI with more HgCl than 09. Crystalline solids present characteristic of HgCl	Hg I Cl Unidentified	61.5 15.1 2.0 21.4
11(e)	0.9	300	0	MP; Solid amorphous in structure, some Hg droplets present strong HgI response from solid sample	Hg I Cl Unidentified	74.2 19.0 0.2 6.6
12(f)	0.1	600	0	MP; Solid has some crystalline characteristics some mercury droplets present	Hg I Cl Unidentified	79.0 11.5 0.4 9.1

(a) XRD; Information obtained from x-ray diffraction.

(b) MP; Information obtained from Scanning Electron Microscope and Microprobe X-Ray Analysis.

(c) Repeat of experiment no. 2.

(d) Repeat of experiment no. 3.

(e) Repeat of experiment no. 7.

(f) Repeat of experiment no. 5.

(g) Analysis methods: Hg, x-ray fluorescence; I, neutron activation analysis; Cl ion chromatography.

(h) Typical gas composition leaving vitrification system; CO₂ 2.07%, Ar 0.89%, O₂ 22.1%, N₂ 74.4%, CO 0.4%, NO_x 0.13%.

(i) Typical gas composition leaving vitrification system; CO₂ 0.67%, Ar 72.4%, O₂ 0.01%, N₂ 26.3%, H₂ 0.13%, N₂O 0.47%.

had the same chemical composition as the venturi solids for material balance purposes. Metallic mercury was the primary mercury species recovered from the condenser condensate.

The chemical composition of the mercury solids for eight different experiments conducted is shown graphically in Figure 4.2 for mercury, in Figure 4.3 for iodide, and in Figure 4.4 for chloride. The axes, iodide to mercury molar ratio in the simulated waste and off-gas outlet temperature are approximate, based upon average values.

There are significant differences in the chemical composition of the mercury solids which are related to the process operating variables; the vitrification system atmosphere, the outlet gas temperature, and the iodide to mercury molar ratio in the waste. As shown in Figure 4.2 the mercury concentration of the mercury solids was 75 to 85 wt% when there is essentially no oxygen present in the vitrification off-gas. The mercury concentration was reduced to 65 to 75 wt% when atmospheric concentrations (~ 20 vol%) of oxygen are present in the vitrification off gas. The difference is due to the low oxygen concentration present in the vitrification off-gas which retains a greater fraction of iodide and chloride in the glass, being unavailable to react with mercury in the gas phase. It cannot be deduced from the chemical composition of solids whether or not there is less mercury as oxide in the solids formed, in experiments performed with very little oxygen present, as compared to the experiments performed with ~ 20 vol% oxygen present. The key to drawing this conclusion is in characterization of the unidentified solid component of the mercury solids. It is believed that the unidentified chemical species are principally oxygen and water.

The iodide and chloride concentrations in the mercury solids are greater in the experiments conducted with atmospheric concentrations of oxygen present in the vitrification system. This is the result of two phenomena. First, the iodide and chloride are converted to volatile iodine and chlorine to a greater extent when large quantities of oxygen are present. Secondly, the higher relative concentrations of iodine and chlorine in the gas phase react with mercury to produce higher concentrations of the mercury halide compounds.

- VITRIFICATION SYSTEM ATMOSPHERE, AIR
- VITRIFICATION SYSTEM ATMOSPHERE, 95% ARGON, 5% HYDROGEN

FIGURE 4.2. Mercury Composition of Off-Gas Solids Collected During Experiments

- VITRIFICATION SYSTEM ATMOSPHERE AIR
- VITRIFICATION SYSTEM ATMOSPHERE, 95% ARGON 5% HYDROGEN

FIGURE 4.3. Iodide Composition of Off-Gas Solids Collected During Mercury Study Experiments

- VITRIFICATION SYSTEM ATMOSPHERE AIR
- VITRIFICATION SYSTEM ATMOSPHERE, 95% ARGON, 5% HYDROGEN

FIGURE 4.4. Chloride Composition of Off-Gas Solids Collected During Mercury Study Experiments

Recall that the mercury halides are thermodynamically preferred over the mercury oxides as reaction products in the gas phase.

The mercury solids recovered from the scrub solution were identified as HgI (or Hg_2I_2) and HgCl (or Hg_2Cl_2) by x-ray diffraction analyses. These two compounds are relatively insoluble, and are in equilibrium with; Hg, HgI_2 and Hg, HgCl_2 , respectively. The equilibrium constants for these reactions are summarized below. (Lindsay 1979)

$$\frac{[\text{Hg}] [\text{HgI}_2]}{[\text{Hg}_2\text{I}_2]} = 2.2 \times 10^{-3}$$

$$\frac{[\text{Hg}] [\text{HgCl}]}{[\text{Hg}_2\text{Cl}_2]} = 8.3 \times 10^{-6}$$

The reaction equilibria between; Hg , Hg_2I_2 and HgI_2 or Hg , Hg_2Cl_2 and HgCl_2 is a disproportionation reaction. The mercuric form (Hg^{+2}) is readily soluble by complexation with excess chloride or iodide. However, because mercury metal is essentially insoluble in water (10^{-7} M @ 25°C) the disproportionation can occur only to a very limited extent, explaining the small equilibrium constants. It is thought that HgI_2 and HgCl_2 are the chemical species formed in the gas phase. Upon quenching the off-gas by the scrub solution or condenser, HgI_2 disproportionates to Hg_2I_2 . A similar mechanism is postulated for HgCl_2 and Hg_2Cl_2 . The HgI_2 compound is more stable than Hg_2I_2 in the gas phase, the opposite is true in the liquid or condensed phase.

Photographs of the mercury solids recovered from the venturi scrub solution for five of the twelve experiments are shown in Photos 4.1 through 4.5. These photographs were taken with a scanning electron microscope (SEM). Each photograph records characteristics of the mercury solids coincident with the experimental conditions.

Photograph 4.1 (from Experiment No. 1) displays the difference in physical structure between the HgCl and HgI particles. The HgCl compound is comprised of particles which are crystalline in character (Point 1). The HgI compound is comprised of particles which are largely amorphous in character (Point 2). The microprobe (x-ray) micrographs of each of the two particulate types are shown in Figure 4.5 and 4.6, respectively. No metallic mercury was found in the sample. The reason for this is that mercury has completely reacted with the halogens (chloride and iodide) and oxygen present in the system. Mercury is the limiting reactant in this system. HgI comprises approximately 65% of the sample and HgCl comprises approximately 22% of the solid sample.

Photograph 4.2 (from Experiment No. 4) also displays the difference in character between HgI and HgCl . This venturi solids sample is comprised of a relatively large quantity of HgCl when compared to HgI as indicated by the predominance of cubic crystalline particles present. An x-ray micrograph of the solid is shown in Figure 4.7. The mercury levels in the solid are high, suggesting that mercury oxide may also be present in the sample. Oxygen

PHOTO 4.1. Photograph of Mercury Solids Collected From Venturi Solution, Experiment No. 1 Showing HgCl and HgI particulate (10,000X)

FIGURE 4.5. X-Ray Micrograph of Venturi Solid Sample Feature (Point Number 1) from Experiment No. 1

FIGURE 4.6. X-Ray Micrograph of Venturi Solid Sample Feature (Point Number 2) from Experiment No. 1

PHOTO 4.2. Photograph of Mercury Solids Collected From Venturi Solution, Experiment No. 4 Showing Crystalline HgCl (3,000X)

FIGURE 4.7. X-Ray Micrograph of Venturi Solid Sample General Area Scan from Experiment No. 4

(molecular weight 16) cannot not be detected by the x-ray microprobe used. The solid sample is comprised of approximately 11% HgCl, 18% HgI and the remaining fraction presumed to be HgO (71%).

Photograph 4.3 is of the venturi solids sample recovered from an experiment in which the vitrification atmosphere contained essentially no oxygen, and the molar ratio of total halogen present to total mercury was low (Experiment No. 5). This sample shows that metallic mercury as round beads can be formed. The size of the mercury beads is 1 to 2 μm . The amorphous material is the

PHOTO 4.3. Photograph of Mercury Solids Collected From Venturi Solution, Experiment No. 5 Showing Mercury Metal and HgI (10,000X)

background is believed to be comprised primarily of mercury oxide (HgO) and mercury iodide (HgI). Figure 4.8 and 4.9 are x-ray micrographs of some features of the solid. These micrographs indicate that the sample is comprised primarily of mercury and HgI . The percent of HgI in the sample is approximately 53%, and the HgCl concentration approximately 2%.

Photograph 4.4 displays the difference in physical structure between HgCl and HgI . These solids were recovered from an experiment in which essentially no oxygen was present in the vitrification off gas (Experiment No. 7). The mercury iodide indicated by Point 1 is a structure having an amorphous form. The mercury chloride particle is more geometric in shape. No metallic mercury was found in this sample even though the atmospheric conditions contained essentially little or no oxygen. This may be because the mercury in the sample has evaporated in the SEM. The solid sample is comprised of approximately 17% HgI , 2% HgCl and the remainder mercury metal or mercury oxide. Figures 4.10 and 4.11 are x-ray micrographs of the same solid features of this sample.

FIGURE 4.8. X-Ray Micrograph of Venturi Solid Sample Amorphous Feature (Point Number 1) from Experiment No. 5

Photograph 4.5 shows the venturi solids recovered from an experiment in which little or no oxygen was present, the iodine to mercury ratio was 0.90, and the outlet off-gas temperature was 600°C. The x-ray micrograph (Figure 4.12) indicates that the sample is comprised primarily of HgI and Hg. The chemical composition of this sample is approximately 23% HgI, 3% HgCl and the remainder HgO or Hg metal. The amorphous character of the solid sample is due to the relatively high HgI concentration and the large yet unidentified concentration of HgO and Hg metal.

4.3 DISCUSSION OF EXPERIMENTAL RESULTS

As shown, the chemical behavior of mercury and iodine in the vitrification system is dependent upon the three process variables evaluated (I/Hg ratio in

FIGURE 4.9. X-Ray Micrograph of Venturi Solid Sample Flat Feature (Point Number 2) from Experiment No. 5

the simulated waste, off-gas outlet temperature, and oxygen content in system atmosphere). The variation in oxygen content of the vitrification system atmosphere produced the greatest difference in chemical behavior of mercury and iodine. This is a result of iodine and chlorine formation which are dependent on the gas phase composition.

Mercury is essentially completely volatilized from the vitrification system. Mercury reacts strongly with iodine formed from iodide oxidation, chlorine from chloride oxidation, and oxygen. At low ratios of iodine to mercury (0.1) the reaction between mercury and iodine is essentially complete. At high iodine

PHOTO 4.4. Photograph of Mercury Solids Collected From Venturi Solution, Experiment No. 7 Showing HgCl and HgI Particulate (10,000X)

FIGURE 4.10. X-Ray Micrograph of Venturi Solid Sample, HgI Particle from Experiment No. 7 (Point Number 1)

FIGURE 4.11. X-Ray Micrograph of Venturi Solid Sample, HgCl Particle from Experiment No. 7 (Point Number 2)

PHOTO 4.5. Photograph of Mercury Solids Collected From Venturi Solution, Experiment No. 8 Showing HgI Particulate (10,000X)

FIGURE 4.12. X-Ray Micrograph of Venturi Solid Sample and General Area Scan from Experiment Number 8

to mercury ratios (0.9), the interaction between mercury and iodine is only partially complete. This is the result of competition between chlorine and iodine for reaction with mercury.

The iodide chemical behavior is strongly dependent upon the vitrification system atmosphere. A vitrification system atmosphere containing 20 vol% oxygen tends to oxidize the majority (85 to 97%) of the iodide to iodine. The iodine volatilizes from the vitrification process. The majority of the iodine reacts with mercury and consequently is trapped as a particulate. The remainder of the iodine (10 to 30%) was estimated to be volatilized from the off-gas cleanup process based upon material balances. Iodide not oxidized, representing 3 to 15 wt% remains in the vitreous product.

Operating the vitrification system at conditions where little oxygen is present tends to keep the iodide in the reduced state. The majority (27 to 55 wt%) of the iodide remains with the vitreous product. The remainder of the

iodide is oxidized and volatilized to react with mercury in the gas phase. The mercuric iodide is recovered by off-gas scrubbing or deposited within the off-gas piping.

Scrub solution solids collected from the experiments in which there was a low oxygen content in the vitrification system atmosphere contained higher concentrations of mercury. Metallic mercury was also present in these solids in small concentrations. The exact quantity of metallic mercury could not be determined.

The majority of the mercury recovered from the scrub solution was in the mercurous or plus one oxidation state. Based on thermodynamics the mercurous state is unstable at the vitrification system temperatures of 700 to 1100°C. The following explanation may account for these observations. Mercury ion may be reduced to mercury metal by nitrate decomposition within the calcine particles (as shown in the reaction below). Iodide ion is oxidized by the oxygen present forming volatile I_2 . Mercury metal reacts directly with I_2 in the gas phase, forming HgI_2 which then volatilizes.

Upon condensation in the scrub solution, the mercuric iodide disproportionates via the following reaction, limited by the excess mercury metal (Hg^0) in the system.

The Hg_2I_2 compound is much more insoluble forming a precipitate. The disproportionation reaction is driven to the right by the low solubility of the Hg_2I_2 compound and the predominance of the mercury metal in the system. A similar mechanism is proposed for the presence of the mercurous chloride compound. Only small quantities of mercury were detected in the solution above the solids (conc ~100 ppm). This indicates that the disproportionation is essentially complete.

Recoveries of mercury and iodide in the experimental system were not quantitative. Unrecovered mercury ranged from 37 to 90 wt%. It is believed that all the mercury was contained in the vitrification system by the cold trap created with the off-gas condenser. The unrecovered mercury is deposited in the off-gas piping as solid material similar in composition to the recovered solids. Some of the iodide not recovered is tied up with the mercury. The deposition of these mercury solids may lead to off-gas plugging problems in long-term operations.

5.0 DEVELOPMENT WORK NEEDED

The experimental results have indicated the need for further development and verification testing. Areas needing study include:

- 1) Assess the buildup of the mercury solids in the vitrification system off-gas piping.
- 2) Develop methods for quantitative recovery of mercury from the alkaline Purex waste prior to vitrification.
- 3) Mercury corrosion potential in the exposed metal in the vitrification and off-gas system.
- 4) Evaluate methods to separate the mercury solids from the scrub solution, and to recover mercury from the scrub solution solids.

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APPENDIX A

SIMULATED WASTE PREPARATION

APPENDIX A

SIMULATED WASTE PREPARATION

Simulated alkaline waste for the vitrification process was prepared by precipitation of metallic nitrates and batch washing of the resultant sludge to remove Na^+ , NO_3^- , NO_2^- and SO_4^{2-} . The physical and chemical characteristics of the precipitated feed are anticipated to be similar to actual SRP waste.

The procedure for the precipitated waste preparation was based on information obtained from D. W. Jones of Savannah River Laboratory along with chemical adjustments required to more accurately represent a reference SRP alkaline waste composition.

Three, 300-L simulated waste batches were prepared for the experimental study. Each 300 L waste batch yielded approximately 100 L of alkaline waste sludge that could be used in the mercury study experiments. The procedure utilized for preparation of a 300-L batch of precipitated waste is outlined below.

A.1 PRECIPITATION OF MnO_2

2.16 L of 50% $\text{Mn}(\text{NO}_3)_2$ solution is mixed with 20.4 L of water (the resultant blend is transferred to a 300-L tank). 948 g of KMnO_4 is dissolved in 19.8 L of water. While agitating the $\text{Mn}(\text{NO}_3)_2$ solution, the KMnO_4 solution is added.

A.2 METALLIC NITRATE AND SODIUM SALT PREPARATION

The following metallic nitrates and sodium salts are added to 25.2 L of water. The solution is warmed to 35°C and agitated. The resultant chemical blend is added to the MnO_2 slurry prepared in Step A.1.

<u>Compound</u>	<u>Weight, g</u>
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	11,400
NaNO_3	3,360
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	13,800
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	1,380

<u>Compound</u>	<u>Weight, g</u>
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2,220
$\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	17,400
$\text{Hg}(\text{NO}_3)_2$	1,280

A.3 PRECIPITATION OF SLUDGE

120 kg of 50% NaOH solution is added to 78 L of water. The solution is allowed to cool and is then added to the solution formed by mixing the solutions from Steps A.1 and A.2. The combined solution is agitated and cooled, as necessary, to maintain the temperature at 35 to 40°C during caustic addition.

A.4 ADDITION OF NONREACTANTS AND FISSION PRODUCT

The following nonreactive chemicals and fission product elements are added to 22 L of water. The mixture is agitated and the chemicals are allowed to dissolve. The mixture is combined with the simulated waste blend.

<u>Compound</u>	<u>Weight, g</u>
NaNO_2	9,360
Na_2CO_3	2,520
SiO_2	1,260
$\text{Sr}(\text{NO}_3)_2$	3,360
$\text{Cs}(\text{NO}_3)$	1,260
$\text{Ru}(\text{NO})(\text{NO}_3)$	1,800 ml (70 gm Ru)
$\text{Ba}(\text{NO}_3)_2$	540
$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	3,000
TeO_2	1,740

A.5 SLUDGE WASHING

The blended chemical solution is agitated for approximately 1 h. The agitator is then turned off, and the solids formed from neutralization reactions are allowed to settle for about 48 h. A sludge layer settles to approximately 50% of the tank volume during this time. The supernate above the sludge

containing cesium, sodium, nitrate and sulphate is sampled and pumped out of the tank. The precipitated sludge was then agitated and sampled. Water was added to double the volume, and the mixture was agitated for approximately 45 min. The solution was allowed to settle, and the sampling/sludge-washing procedure continued until the sodium, nitrate and sulphate concentrations fell below limits of 5 wt%, 10 wt%, and 3 wt%, respectively on a dry-weight basis in the sludge. Six or seven wash steps were required to meet this specification.

The settling rates for the sludge mixtures are shown graphically in Figure A.1 and A.2. The sludge-settling rates increase as the difference in specific gravity between the sludge and supernate increases, which occurs with each wash step. The specific gravity of the sludge and supernate are shown graphically in Figure A.3 as a function of wash step.

FIGURE A.1. Sludge Settling During Initial and First Washing

FIGURE A.2. Sludge Settling During Second to Sixth Washing

The weight of select soluble cations and anions in the sludge are shown in Figure A.4 and A.5 as a function of wash step for a typical feed batch. Soluble chemical components are sodium potassium, sulfate nitrate, and nitrite. Slightly soluble chemical components are cesium, aluminum and tellurium. Components which are insoluble included cerium, manganese, ruthenium, mercury, nickel, barium, strontium and calcium.

The pH of the solution during sludge washing varied from 13.5 during initial separation to 12.0 during the seventh wash step. Buffering action due to the presence of carbonate in the sludge is thought to keep the pH relatively constant between each wash step.

The electrical conductivity of the supernate as a function of wash step is shown in Figure A.6. This data indicates that the use of a conductivity probe to determine the relative amount of soluble species in the supernate is possible. This technique can be used rather than chemical analysis to determine when sludge washing is sufficiently complete to meet required specifications.

FIGURE A.3. Specific Gravity of Supernate and Sludge as a Function of Wash Step

The simulated alkaline waste composition is compared with the waste composition taken from the reference Defense Waste Processing Facility Flowsheet (DWPF) (DPSTD-77-13-3) and the reference DWPF Flowsheet for Stage 1 (DPSTD 80-30) in Table A.1. In general, the concentration of each chemical constituent in the simulated feed is 40 to 60% below the reference flowsheet composition. This is due to the dilute nature of the simulated waste.

FIGURE A.4. Weight of Soluble Cation Versus Wash Step

Adjustments were made in the simulated feed composition to adjust key chemical components to reference flowsheet levels. Chemical components routinely added in these adjustment were chloride, iodide, and fluoride.

FIGURE A.5. Weight of Soluble Anion Versus Wash Step

FIGURE A.6. Electric Conductivity of Supernate as a Function of Wash Step, Sludge Washing Experiments

TABLE A.1. Comparison of Reference Alkaline Waste Compositions With Simulated Alkaline Waste Composition Range

Chemical Component	Reference ^(a,b) Composition, g/L	Reference ^(a,c) Composition, g/L	Simulated Alkaline Waste Composition Range, g/L
Al	6.6	8.6	0.35 to 0.49
Ca	3.2	4.3	1.3 to 2.9
Fe	42.7	57.1	25 to 41
Na	1.6	2.0	1.6 to 8.2
Mn	10.9	14.2	4.1 to 6.6
Ni	5.9	7.9	2.4 to 3.1
Si	1.9	--	0.15 to 0.61
Hg	6.0	3.4	3.4 to 6.2
Cl	1.2	1.3	0.02 to 4.0
F	0.13	0.16	0.001 to 0.8
I	4.5	0.60	0.09 to 3.0
NO ₃	0.60	0.46	0.25 to 4.0
NO ₂	0.20	0.17	0.10 to 0.90
SO ₄	0.12	0.096	0.10 to 0.83
Cs	0.01	0.025	0.02 to 0.18
Sr	0.06	0.01	7.2 to 9.4
Ru	0.54	0.09	0.25 to 0.30
Ba	0.006	0.014	1.6 to 2.0
Ce	0.14	0.026	7.4 to 8.8
Te	0.02	0.004	4.0 to 4.7

(a) Fission product compositions, excluding iodine, based on 5-yr aged waste.

(b) Landon, L. F. 1980. Preliminary Technical Data Summary No. 3 for the Defense Waste Processing Facility. DPSTD-77-13-3, Savannah River Laboratory, Aiken, South Carolina.

(c) E.I. duPont de Nemours & Co. 1980. Preliminary Technical Data Summary for the Defense Waste Processing Facility, Stage 1. DPSTD-80-38, Savannah River Laboratory, Aiken, South Carolina.

APPENDIX B

SUMMARY OF EXPERIMENTAL RUNS

APPENDIX B

SUMMARY OF EXPERIMENTAL RUNS

Process data from the twelve experimental runs completed during this study is summarized in this appendix. This data was included to provide the reader with information on system operating performance.

Summarized in Table B.1 is the lab-scale spray calciner/in-can melter system operating performance. Experimental tests had an averaged five hours in length, during which an average 18-L of simulated waste was solidified producing an average of 6.2 kg of glass product.

Waste feed rates varied throughout the testing due to the different spray nozzles used and modification made to the nozzles. Better overall performance in the spray calciner spraying system was achieved during the latter runs when the nozzle dimensions had been optimized. The simulated feed slurry contained many solids, resulting in frequent nozzle pluggage. An automatic cleanout needle was used to keep the feed flow as continuous as possible. However, the best performance was achieved by enlargement of the orifice on the fluid cap. Upper limits on the waste feed rate are controlled by the power output of the calciner furnace used to dry the waste. Because of this small volume atomizing nozzles are required.

The calciner furnace has five separate heating zones powered by the same power source. Temperature control was provided by a thermocouple located in Zone-4, and controlled at a temperature of 750 to 800°C. Because of this there is a wide variation in the temperature profile in the calciner barrel. The lower temperatures are at the top where the heat load due to waste drying is greatest. Controlling the temperature by the upper zone would provide excessive heating on the bottom zones limiting the heater lifetime.

There is a wide variation in temperature within the filter housing. The influence of the calciner barrel heating the filters is seen by the higher temperatures on the bottom of the filters. The filter heaters were automatically controlled by a thermocouple located in the off-gas of the filter outlet to the

required temperature. The filter material used was Inconel-600. The operating temperature limit of 600°C on the filter material was exceeded during those tests when an off-gas outlet temperature of 600°C was used. No excessive damage to the filters was noticed during the relatively short experimental project.

Table B.2 summarizes the waste compositions for each experiment. A comparison of these composition ranges with the reference SRP waste compositions was presented in Appendix A. The iodide composition was the only composition intentionally varied. This was done to adjust the iodide to mercury molar ratio.

TABLE B.2. Chemical Composition of Simulated Alkaline Purex Wastes for Mercury Study Experiments

Element ion	Average Concentrations (g/L)											
	Experiment Number											
	1	2	3	4	5	6	7	8	9	10	11	12
Al	0.44	0.39	0.44	0.49	0.44	0.42	0.48	0.49	0.45	0.35	0.46	0.49
Ba	2.0	1.9	2.0	2.06	1.81	1.72	1.9	1.9	2.0	1.6	2.0	2.2
Ca	1.6	1.5	1.8	1.91	2.27	2.81	3.0	2.9	1.7	1.3	1.74	1.8
Fe	27	25.6	28.1	40.9	36.9	35.0	39.1	37.2	25.0	20.0	26.8	27.7
Hg	6.2	4.1	4.3	5.2	4.7	4.8	5.1	5.4	4.5	3.4	4.6	4.5
K	0.40	0.70	0.46	0.09	0.04	0.06	1.0	1.0	0.13	0.64	0.8	0.8
Mg	0.09	0.07	0.07	0.09	0.08	0.08	0.09	0.09	0.09	0.07	0.08	0.09
Mn	8.1	5.7	6.4	5.9	5.6	5.4	6.2	6.6	5.2	4.1	5.4	5.6
Na	3.6	3.4	4.3	4.06	4.6	5.5	8.2	7.2	2.2	1.56	3.7	4.2
Ni	3.1	2.5	3.4	3.08	2.71	2.58	2.9	2.8	3.1	2.4	3.2	3.3
Si	0.15	0.20	0.20	0.39	0.20	0.16	0.25	0.50	0.52	0.61	0.7	1.2
Cl	1.21	0.93	0.86	0.013	0.057	0.33	3.2	3.96	2.1	0.93	1.54	0.77
F	0.082	0.067	0.067	0.001	0.003	0.006	0.14	0.18	0.80	0.40	0.080	0.055
I	1.0	0.14	0.84	0.27	0.09	0.09	2.6	2.9	0.29	1.6	2.3	0.32
NO ₃	2.5	1.47	1.47	3.4	1.9	4.3	2.9	3.0	0.50	0.25	0.34	0.80
NO ₂	0.30	NP	NP	0.41	0.32	0.90	0.90	NP	0.20	0.10	0.08	0.03
SO ₄	0.35	NP	NP	0.60	0.50	0.83	0.50	0.50	0.23	0.10	0.23	0.49
Cs	0.056	0.035	0.02	0.032	0.16	0.18	0.15	0.18	0.02	0.017	0.016	0.020
Sr	9.4	9.1	10.3	9.2	8.1	7.7	8.7	8.3	9.3	7.2	9.6	10.0

NP--Analysis not performed

TABLE B.1. Summary of Lab-Scale Spray Calciner/In-Can Melter Operating Performance

Experiment Number	LSSC-01	LSSC-02	LSSC-03	LSSC-04	LSSC-05	LSSC-06	LSSC-07	LSSC-08	LSSC-09	LSSC-10	LSSC-11	LSSC-12
Date Conducted	12/31/80	1/7/81	1/9/81	1/19/81	1/30/81	2-4-81	2-13-81	2/18/81	1/26/81	3/2/81	3/5/81	3/31/81
Waste Feed Data												
I/Hg Molar Ratio	0.9	0.1	0.9	0.1	0.1	0.1	0.9	0.9	0.1	0.9	0.9	0.1
Oxide Equiv., g/ℓ		89	82	150								
Feed Press., psig average	20	20	20	18	16	14	14	14	23	21	18	17
Temperature °C	19	20	15	28	35	34	33	36	30	19	28	24
Total Volume Consumed, ℓ	13.2	13.9	16	18.4	21.7	17.4	15.9	17.7	18.8	18.6	25.4	23.2
Average Feed Rate, ℓ/hr	2.4	2.8	4.2	3.8	4.0	3.9	3.9	4	5	4.56	5.5	4.9
Run Time	6 hr	5 hr 23 min	4 hr 35 min	6 hr 10 min	5 hr 45 min	5 hr 32 min	5 hr 15 min	5 hr	4 hr	4 hr 18 min	4 hr 25 min	6 hr
Feed Nozzle												
Manufacture Spray Systems												
Air Cap. No.	73160 SS(a)	73160 SS(a)	73160 SS(a)	73160 SS(a)	73160 SS(a)	73160 SS(a)	73160 SS(a)	73160SS(a)	67147(b)	67147(b)	67147(c)	67147(c)
Fluid Cap No.	2850 SS(d)	2850 SS(d)	2850 SS(d)	2850 SS(d)	2850 SS(e)	2850 SS(e)	2850 SS(e)	2850SS(e)	2850 SS(e)	2850 SS(e)	2850 SS(e)	2850 SS(e)
Atomizing Gas	Air	Air	Air	Air	95% Ar, 5% H ₂	95% Ar, 5% H ₂	Ar 95% H ₂ 5%	Ar 95% H ₂ 5%	Air	Air	Air	Ar 95% H ₂ 5%
Atom Air Press., psig	20	22	20	23	20	22	22	22	25	25	20	25
Atom Air Flow, scfm	0.57 - 0.68	1.1	1.1 - 1.25	0.6 - 0.8	0.65 - 0.9	0.9	0.9	0.85	0.5	0.6 - 0.8	0.5 - 0.8	0.7
Frit												
Total Frit Used, kg	2.1	1.65	1.6	5.5	2.5	2.85	4.25	2.2	2.3	1.7	2.2	2.7
Average Frit Rate, g/hr	350	306	350	892	435	515	810	440	575	395	518	450
Frit to Feed Ratio, g/ℓ	148	110	85	232	110	134	252	108	116	86	90	93
Spray Calciner												
Vacuum Normal, in. H ₂ O	6 - 10.8	5	4.5	4	6	5	1.5	4	5	4	5	3
Vacuum-During Blowback in. H ₂ O	1	1	1	1	2	1	0	0	1	0	1	0
Temperatures During Run, °C												
Zone 1, Top	480 - 575	500 - 610	520 - 620	515 - 640	470 - 570	460 - 580	400 - 475	425 - 590	450 - 580	480 - 580	490 - 555	485 - 555
Zone 2	620 - 685	605 - 700	630 - 715	615 - 710	590 - 650	510 - 665	525 - 620	500 - 670	565 - 660	565 - 650	545 - 625	540 - 620
Zone 3	710 - 740	675 - 735	715 - 750	720 - 765	705 - 745	700 - 740	705 - 720	670 - 770	720 - 735	690 - 725	660 - 710	665 - 715
Zone 4	750 - 805	705 - 750	750 - 790	735 - 770	750 - 800	750 - 780	740 - 800	735 - 805	740 - 760	730 - 780	715 - 775	710 - 790
Zone 5, Bottom	735 - 810	700 - 715	710 - 805	725 - 780	715 - 820	710 - 790	710 - 815	740 - 835	690 - 770	685 - 805	670 - 795	670 - 815
Upper Cone Temperature, °C	325 - 375	260 - 330	290 - 370	170 - 365	250 - 320	230 - 315	245 - 345	300 - 410	215 - 320	360 - 395	220 - 325	265 - 360
Lower Cone Temperature, °C	340 - 375	280 - 340	330 - 390	160 - 370	265 - 335	240 - 310	265 - 340	335 - 400	240 - 320	285 - 385	235 - 340	295 - 365
In Can Melter												
Top Zone Temp., °C	880 - 907	895 - 910	925 - 955	865 - 905	900 - 935	890 - 930	855 - 925	935 - 940	880 - 925	850 - 890	890 - 925	885 - 915
Lower Zone Temp., °C	1015 - 1040	1020 - 1050	1040 - 1060	925 - 1035	1035 - 1050	1010 - 1050	1000 - 1055	1045 - 1055	1010 - 1040	1000 - 1030	1030 - 1040	1025 - 1045

(a) Factory air cap opening 0.059 in.
(b) Factory air cap opening 0.043 in.
(c) Factory air cap drilled out to 0.052 in.
(d) Factory fluid cap opening 0.0176 in.
(e) Factory fluid cap drilled out to 0.035 in.

TABLE B.1. (contd)

Experiment Number	LSSC-01	LSSC-02	LSSC-03	LSSC-04	LSSC-05	LSSC-06	LSSC-07	LSSC-08	LSSC-09	LSSC-10	LSSC-11	LSSC-12
<u>Canister</u>												
Canister Number	1	2	3	4	5	6	7	8	9	10	11	12
Weight of Glass Produced, kg	6.48	0.98	4.0	7.85	3.96	6.01	5.67	4.19	4.43	2.98	4.41	4.9
Weight of Loose Material, kg	0.05	0.06	0.08	0.27	-	0.43	0.24	0.40	0.51	0.24	0.19	
Weight of Nonvitrified Material in - Barrel-Cone-Canister, g			166.5		735.5	712.8	242					
<u>SC Off-Gas Filters</u>												
Bottom Filter Temperature, °C	305 - 375	325 - 390	410 - 575	480 - 630	520 - 580	235 - 330	300 - 320	550 - 700	300 - 360	690 - 730	325 - 370	650 - 750
Middle Filter Temperature, °C	305 - 405	330 - 410	510 - 700	620 - 725	660 - 720	290 - 340	300 - 390	560 - 760	280 - 402	525 - 680	270 - 330	500 - 625
Top Filter Temperature, °C	195 - 240	210 - 250	300 - 450	320 - 480	380 - 470	175 - 240	200 - 220	350 - 450	190 - 235	370 - 450	220 - 250	350 - 475
Filter Outlet Temperature, °C	300	300	600	600	600	300	300	600	300	600	300	600
Filter Pressure Drop Max. in. H ₂ O	1.6	1.6	5.6	5.6	5.2	2	2	5.2	4.8	4.8	4.6	6.6
<u>Venturi</u>												
Vacuum prior to venturi in. of H ₂ O	12	8.5	8	9	8	7.5	2.5 - 4.5	9	9	10	11.5	10
Outlet Temperature, °C	59	39 - 61.5	57 - 74	42 - 55	41 - 55	49 - 53	39 - 51	50 - 59	59 - 80	42 - 56	45 - 49	50
<u>Scrub Solution (Water)</u>												
Temperature °C	16	24	25	24	18	18	19	25	29	29	35	41
Initial Volume (liters)	10.2	10	11.9	10	10	10	10	9.4	10	9.8	9.4	10.0
Volume Increase	9.6	11.9	14.5	19.4	17.6	16.2	12.3	13.3	19.8	14.6	19.4	27.7
Flow Rate to Venturi, L/h	12.3	29.1	32.9	34.8	29.1	29.1	29.1	35.0	34.0	37.1	34.8	36.7
Press of Liquid to Venturi, psig	21	20	20	20	22	22	22	22	22	23	23	23
Weight of Hg Solids Collected, g	10.3	12.4	26.4	20	25.2	17	26.5	21.8	39.4	63.6	63.1	22
<u>Cyclone</u>												
Vacuum Inlet-Outlet in. H ₂ O	11	9.5 - 10	10.5 - 11	10.5 - 11.2	10	9 - 9.5	3 - 5.5	12	10 - 17.5 11-18	15	17.5 - 18	17 - 17.50
Inlet Temperature, °C	40 - 64	40 - 61	57 - 74	58 - 76	67 - 76	66 - 71	55 - 71	71 - 78	59 - 81	58 - 71	64 - 75	72 - 81
Volume of Condensate Collected, mL	255	165	320	450	440	225	200	265	170	180	225	335
Weight of Solids, g	0.32	0.55	0.80	0.696	1.58	1.78	0.206	0.080	0.127	0.379	0.036	0.001
<u>Condenser</u>												
Inlet Vacuum in. H ₂ O	12	11	10 - 12	15	11	10	6	14	11 - 14	16	19	18
Temperature, Inlet-Outlet, °C	42 - 59, 12	37 - 53, 12	57 - 71, 11	52 - 70, 13	61 - 71, 12	63 - 67, 13	52 - 67, 8	65 - 69, 13	52 - 71, 11	54 - 65, 13	47 - 65, 13	64 - 78, 7
Volume of Condensate, mL	1700	1540	2125	3460	2690	2483	1855	2310	1960	1920	1890	3460
Weight of Solids, g	0.58	0.99	0.96	0.254	1.30	3.75	0.57	0.96	1.18	0.94	0.33	1.31
<u>Off-Gas Outlet</u>												
Flow, (SCFM)	1.3 - 1.65	1.55	0.9 - 2.2	0.75 - 1.5	0.9 - 1.4	1 - 1.1	1.2	1 - 1.2	0.9	1.2	1.2	1.2
Percent Hg Recovered by Venturi, Cyclone and Condenser, %	8.8	16.5	30.2	17.4	23.9	23.3	27.6	19.1	34.2	63.2	40.3	17.6

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