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To the Graduate School:

This thesis entitled "Vitrification of Cesium-Contaminated Organic Ion Exchange Resin" and written by Thomas N. Sargent, Jr. is presented to the Graduate School of Clemson University. I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Environmental Systems Engineering.

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DISCLAIMER

Accepted for the Graduate School:

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VITRIFICATION OF CESIUM-CONTAMINATED ORGANIC ION EXCHANGE RESIN

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Systems Engineering

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by
Thomas N. Sargent, Jr.
August 1994

ABSTRACT

Vitrification has been declared by the Environmental Protection Agency (USEPA) as the Best Demonstrated Available Technology (BDAT) for the permanent disposal of high-level radioactive waste. Savannah River Site currently uses a sodium tetraphenylborate (NaTPB) precipitation process to remove Cs-137 from a wastewater solution created from the processing of nuclear fuel. This process has several disadvantages such as the formation of a benzene waste stream. It has been proposed to replace the precipitation process with an ion exchange process using a new resorcinol-formaldehyde resin developed by Savannah River Technical Center (SRTC). Preliminary tests, however, showed that problems such as crust formation and a reduced final glass wasteform exist when the resin is placed in the melter environment. The newly developed stirred melter could be capable of overcoming these problems. This research explored the operational feasibility of using the stirred tank melter to vitrify an organic ion exchange resin. Preliminary tests included crucible studies to determine the reducing potential of the resin and the extent of oxygen consuming reactions and oxygen transfer tests to approximate the extent of oxygen transfer into the molten glass using an impeller and a combination of the impeller and an external oxygen transfer system. These preliminary studies were used as a basis for the final test which was using the stirred tank melter to vitrify nonradioactive cesium loaded organic ion exchange resin. Results from this test included a cesium mass balance, a characterization of the semi-volatile organic compounds present in the off gas as products of incomplete combustion (PIC), a qualitative analysis of other volatile metals, and observations relating to the effect the resin had on the final redox state of the glass.

DEDICATION

This thesis is dedicated to my wonderful wife, Heather, who in the last eighteen months has taught me the true definitions of love, patience, and support.

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I could not have finished if it were not for the support I received from each member of my family back in Stone Mountain, GA. It was obvious they wanted me to finish as much as I did. Thanks Mom, Dad, Rebecca, and Jonathan!

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CHAPTER 1

INTRODUCTION

Vitrification, the conversion of a material or materials into a glass or glass-like substance, has been declared the Best Demonstrated Available Technology (BDAT) for the treatment of high-level radioactive waste (HLW) (FR, 1990). It has also been chosen for treatment of high level wastes in Germany, France, Great Britain, and Japan (Wicks, 1989). It involves subjecting materials capable of forming a glass or glass-like substance to temperatures above 1000° C so that they may form a glass. One way this is done is in an electrically heated glass melter with either alloy or ceramic lining. This is known as *ex situ* vitrification. The original waste can be bound into a glass matrix which is extremely leach resistant and has usually undergone an extremely beneficial volume reduction from a practical and economic standpoint.

High-level radioactive waste (HLW) is the waste product resulting from the processing of nuclear fuel. Currently, there are approximately 120,000 m^3 of HLW stored in two tank farms with a total of 51 carbon steel tanks at the Savannah River Site (SRS). After ten to twenty years of aging, one of the major sources of beta and gamma radiation is cesium-137. Because of it's alkali nature, cesium-137 is soluble in water which can result in a cesium-contaminated waste salt solution. The current method used by SRS to remove this radioactive ion from solution is precipitation using sodium tetraphenylborate (NaTPB) (Wallace, 1988). This process, however, produces a large amount of organic material which puts a burden on a glass melter. A process step performed prior to melter processing is used to decrease the amount of organic compounds in the melter feed. This step incorporates the hydrolysis of the TPB with formic acid to yield benzene which can be removed through steam distillation. Although the process is able to remove approximately 90 percent of the organic material, it is very complex and has several disadvantages. These disadvantages include the presence of large amounts of sodium, potassium, and titanium that are fed to the melter, and the regulatory and safety concerns of handling the benzene waste stream.

Although ion exchange was proposed to replace the sodium tetraphenylborate precipitation process, it was discarded due to major additions in processing space required for the operating equipment. A new resin has been developed, however, which is capable of removing cesium under SRS HLW storage conditions (Wallace, 1988). This proposed process carries several advantages which could outweigh the necessary modifications in the tank farm program. Two of these advantages are a lower amount of alkali metals fed to the melter, which would increase the reliability of the glass making process, and the absence of boron in the resin which would allow the boron content of the glass to be more easily regulated. One method suggested for disposal of the used resin is to feed it along with frit and other necessary additives directly into the existing Defense Waste Processing Facility (DWPF) melter at the SRS. Preliminary tests, however, (Bibler, 1991) showed that problems exist when the resin is placed in the melter environment. First, the resin has the tendency to accumulate on top of the melt in a crust. This increases the time for the feed to become incorporated in the melt and allows more time for cesium to volatilize instead of becoming immobilized in the melt. Second, the organic resin causes significant reducing conditions in the melt which could increase the volatility of alkali metals such as cesium and can result in a less durable glass.

The newly developed stirred tank melter may be capable of overcoming both of these problems. The melter used for these experiments is the Stir-Melter™ WV-0.25 designed and fabricated by Stir-Melter, Inc. It's design includes an impeller that enters the melt from the top. Since the entire melt is agitated by the impeller, the crust formation is decreased by continuously drawing the surface into the melt. The impeller agitation can also ameliorate the negative effects of a reduced melt by constantly refreshing the surface layer and thereby increasing oxygen exchange between the melt and vapors above the melt. A more oxidized melt could lower the amount of cesium volatilized as well as other metals (Bickford, 1994).

This research focused on the vitrification of the ion exchange resin developed at the SRS. The goal of this research was to provide a basis for determining the feasibility of vitrifying the organic ion exchange resin proposed to decontaminate aqueous solutions containing cesium-137. The research was conducted in four phases. The first phase involved several crucible level experiments. This phase investigated the effects of organic compound additions on the formation of a glass wasteform. These effects included oxidation/reduction shifts and cesium retention. It also examined the reducing effectiveness of the ion exchange resin in comparison to elemental carbon. The goal of the second phase was to establish nominal melter operation parameter values. This phase determined acceptable values for operational parameters such as impeller height, impeller rotational speed, and melter temperature which needed to be maintained in order to sustain satisfactory melter production rate and operating conditions which indicate successful operation of the melter. The third phase was oxygen transfer tests. This phase examined the rate of oxygen transfer into the molten glass through combinations of impeller agitation, an external air sparger, and water in the feed. The fourth and final phase was the actual vitrification of the resin using the stirred melter. The primary goal of this phase was to approximate a cesium mass balance around the melter including the feed, exit glass, and off gas streams. The test program for this phase also included gas sampling for semi-volatile organic compounds, other volatile metals in addition to cesium, and total particulate matter.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

The Vitrification Process

Vitrification is the process of turning a material or materials into a glass or glass-like substance. It is a general term covering all glass making operations from the creation of bottle glass to the treatment of radioactive, hazardous, and mixed wastes. Mixed wastes are those which have both a hazardous element or compound and the radioactive elements and are often the most difficult to treat successfully. In the environmental engineering realm, the term vitrification specifically covers the process in which a wide variety of waste streams are converted into a durable glass wasteform (USEPA, 1992).

Glass melter designs combine many of the characteristics of flash boilers, calciners, incinerators, and electrically heated glass melters (Bickford, 1986). The melter acts as a flash boiler when a slurry feed containing organic compounds is exposed to the 500° C to 900° C surface of the glass pool. Volatile organic compounds present in the feed can be considered to boil off at the same temperature as water. These compounds can be collected in an off gas treatment system and destroyed effectively (Bickford, 1986). Calcination occurs as the solids in the feed settle into the melt pool and are further heated. The formates and hydroxides of cations such as Al, Na, and Ca are converted to oxides which are then incorporated in the glass matrix. Several of these cations are common components in hazardous waste streams and thus decrease the amount of additives needed for successful vitrification (Bickford, 1986). When organic contaminants are subjected to typical vitrification temperatures of over 1000° C, they are destroyed either by pyrolysis or combustion. Some of the heavier organic compounds are pyrolyzed within the melt. The majority of the combustion generally occurs in the plenum above the melt or in a secondary combustion chamber. Destruction efficiencies of over 99.999 percent have been reported in vitrification systems for compounds such as chlorobenzene, phenol, and carbon tetrachloride (Armstrong, 1985; USATHMA, 1988; Klingler, 1989).

The melters are electrically heated by passing a current through electrodes submerged in the molten glass. The heat caused by the resistance of the glass to the current allows the molten glass to maintain a melting temperature. Resistance heaters are also used in some cases to provide extra heat when needed (Bickford, 1986).

Savannah River Site High Level Waste Program

At the SRS, the high-level radioactive waste (HLW) residue of over 30 years of reprocessing irradiated nuclear fuels for national defense purposes is currently stored in 51 carbon steel tanks located in two tank farms and totals approximately 120 thousand cubic meters. This HLW at SRS is the residue of chemical reprocessing of uranium fuel and targets after irradiation in nuclear reactors. HLW contains most of the fission products of irradiation, including the intense beta and gamma radiation emitters Cs-137 and Sr-90 (Pearson, 1991).

The HLW produced is first transferred from the separation facilities, where it was generated, to waste receipt tanks. While in these tanks, the waste divides into three parts. First, a metal oxide sludge settles out. This sludge consists of metal oxides of aluminum, iron, and manganese. It makes up approximately 10 percent of the waste volume and has the majority of the radioactivity since it includes most of the fission products and some actinides that were not recovered in the reprocessing facility. The overlying layers are a salt solution and a salt cake. The salt solution and cake are primarily sodium nitrate, sodium nitrite, and sodium hydroxide. It is also highly radioactive because it contains cesium-137 (Pearson, 1991).

The metal oxide sludge, salt solution, and salt cake are allowed to remain in the receipt tanks undisturbed for at least one year in order for the short-lived isotopes to decay and for the metal oxides to settle. After one year, the salt solution and salt cake are decanted off and concentrated into a salt cake. This cake is allowed to decay for several more years before further processing (Pearson, 1991).

Tank sludges high in aluminum are leached with NaOH to dissolve most of the aluminum. Approximately 75 percent of the hydrated aluminum is dissolved resulting in a volume reduction of about 50 percent (Pearson, 1991). All sludges are washed with water to decrease the volume by removing the soluble salt content. It is currently thought that this washed sludge will be stored at 10 to 19 weight percent solids and fed to the Defense Waste Processing Facility (DWPF) melter. The DWPF is a treatment facility designed for the processing and immobilization of High-Level Radioactive Waste (Pearson, 1991).

The current method to remove the radionuclides from the salt solution and salt cake is through the addition of sodium tetraphenylborate solution (Bibler, 1991). This produces insoluble tetraphenylborate salts of cesium, ammonium, and potassium. A small amount of sodium titanate slurry is also added to adsorb any residual plutonium or strontium. The resultant slurry, composed of tetraphenylborate salts and used sodium titanate, is then processed under continuous filtration until it is 10 weight percent solids. It is then washed to a low soluble salt level and pumped to the DWPF (Pearson, 1991).

Before vitrification, the tetraphenylborate salts are processed to remove most of the organic carbon. This is accomplished by the addition of formic acid which converts the phenyl groups to an immiscible benzene phase. The benzene is removed through steam distillation and incinerated. The remaining aqueous phase solution contains the cesium and other metals as formate salts, boric acid, formic acid, phenol, and phenylboric acid. This solution is known as Precipitate Hydrolysis Aqueous (PHA) product. The solution along with the insoluble titanate is collected and fed to the Sludge Receipt and Adjustment Tank (SRAT) (Pearson, 1991).

The SRAT is fed by the washed sludge slurry and the precipitate hydrolysis product. Mercury is reduced to its elemental state in the SRAT through the addition of formic acid and removed with steam distillation. The SRAT slurry is then mixed with borosilicate glass frit and concentrated to 45 weight percent by boiling. It is transferred to the Melter Feed Tank and then fed to the melter (Pearson, 1991).

The decontaminated salt solution from the waste processing steps will be mixed with cement, flyash, and slag to produce saltstone which will be disposed of as a Low-Level Radioactive Waste (LLW) at SRS (Pearson, 1991).

The Ion Exchange Process

A cation exchange resin has been developed recently by SRS whose cesium capacity was four times greater than the best commercial resin (Wallace, 1988). It can potentially reduce the complexity of the decontamination process. The Cs removal could occur in the tank farm area, the Sr removal in a sodium-titanate (Na-Ti) column, and mercury removal in a resin column. Spent Sr titanate could be fed with the Cs resin to the melter.

The potential advantages of the ion exchange process are (Wallace, 1988)

1. The need for the acid hydrolysis process would be eliminated;
2. The alkali elements going to the melter as part of the PHA product would be eliminated. This would greatly increase the reliability of the glass making process;
3. The amount of titanium going to the melter would be decreased by about a factor of 10. This will significantly reduce the possibility of devitrification in the glass product, and of spinel formation in the melter;
4. No boron is introduced to the glass making process by the spent resin. Thus, the boron content in the glass can be controlled by regulating borosilicate glass additions;

5. The volume of waste sent to the Saltstone facility, where decontaminated salt solution is immobilized by mixing with cement, slag, and flyash, should be less for the ion exchange process (Pearson, 1991);

6. Problems associated with the generation of organic compounds in the TPB precipitate process would be eliminated;

7. The need for a holding tank regulated under the Resource Conservation and Recovery Act (RCRA), an incinerator, and mercury removal processes to handle the benzene waste stream created through the formic acid hydrolysis would be eliminated.

The possible disadvantages of the ion exchange process are (Wallace, 1988)

1. The cost and schedule of the tank farm program would be impacted;
2. Engineering aspects of the ion exchange process, such as resin transport have not been evaluated in detail.

The Ion Exchange Resin

The resin which is being proposed to replace the tetraphenylborate process for cesium removal is a resorcinol-formaldehyde cation exchange resin (Bibler, 1987). It is prepared by condensing the potassium salt of resorcinol with formaldehyde in an aqueous solution. This results in a gel which is dried at approximately 100° C. The sample can be prepared in three separate forms distinguished by the exchangeable cation. Initially, the resin is present in the potassium form. The hydrogen form is prepared by washing the resin present in the potassium form in a dilute solution of nitric acid. A combination potassium/sodium form is prepared by rinsing the potassium resin with 2 M NaOH solution.

Studies of Vitrification of Ion Exchange Resin

Bibler (1991) used a ceramic-lined joule heated melter with a capacity of 18 kg of glass for their demonstrations of the vitrification of the same organic ion exchange resin used in this study. The melter was fed with a 58 wt% slurry containing ground borosilicate glass, sludge, and resin. The ground glass was frit 165 developed at SRS.

The sludge was a "typical" composition for sludges which will be processed at SRS. The anions in the sludge were primarily nitrates, nitrites, and formates. The resin was 0.95 weight percent cesium. The melter operating temperature was 1150° C. It was reported that during the feeding phase, the slurry "fell on the top surface of the melt, water was flashed off, any organic present was incinerated, sludge was dissolved in the melt, and the frit was melted." The molten product was collected in stainless steel beakers through an overflow drain. The off gas system was able to collect condensate from the water fed to the melter as well as particulate matter entrained in the off gas.

Three runs were performed using this melter. The first run used a combination of sludge and frit, while the second and third runs used a mixture of frit, sludge, and resin. The schedule for the first two runs consisted of pouring for sixteen hours during the first two days and eight hours during the third day with the melter idling for the remaining hours of each day. The schedule for the third run was one run with a duration of fifty-three hour (2.2 days). Each run collected 12 cans of glass with each can holding approximately 12 kg.

Bibler concluded that no effects on melter operation were caused by resin addition to the feed. This included no shorting out of the melt due to conductive species, no pluggages in the off gas system, and adequate pourability of the melt. The resin did, however, have an effect on the final glass compositions. The sample for each run had very similar compositions except for the relative amounts of Fe(II) and Fe(III). Whenever resin was present, the Fe(II) concentration was higher, indicating the glass was in a more reduced state. The amount of Fe(II) was highest during the third run. This was because the other two run schedules included an idling time where oxygen had a chance to diffuse into the melt and reoxidize the melt. Samples were taken several times during the course of the runs. In all cases, the glass became more reduced and less durable as time passed during resin feeding. This inverse relationship between durability and redox state is due to the fact that Fe(II) acting as a network modifier reduces durability while Fe(III) is a network former. However, the glass is still an "acceptable waste form" when "compared to the preliminary results with the DWPF Environmental Assessment (EA) glass."

Vitrification with Organic Compounds

One possible problem with organic compounds in the melter environment is the formation of soot and tar. Both of these can cause pluggages in off gas system equipment. More importantly, these carbon deposits can cause sulfidization or carburization of melter equipment. Depending on the type of redox environment, alloys can be attacked moderately or severely. Inconel-690 placed in a reducing environment showed "catastrophic" sulfidization (Bickford, 1986).

Redox Control of Glass

Redox control of the glass melt is an important process operation. It is done by balancing the amount of reducing agents and oxidizing agents in the feed and plenum. For a complex feed which includes organic compounds, the redox state of the waste glass is found by balancing the reducing potential of feed organic compounds and the oxidizing potential of the gases above the melt as well as any nitrates or polyvalent elements in the waste (Bickford, 1991). One of the primary tests for excessive amounts of organic compounds in the melter feed is determining the ratio of Fe(II) to Fe(III) or Fe(II) to total iron (Bickford, 1986). Accurate control of the redox state can lead to better metal retention within the melt, a more durable final glass product, more efficient heat transfer within the melt, and a better Destruction and Removal Efficiency (DRE) of organic compounds in the feed.

Cesium Volatility

Cesium is a semi-volatile metal. This is of concern at nuclear sites because it is primarily present as a radioactive isotope such as Cs-137. There have been several efforts to lower the volatility of cesium in a melt. One method was to add soda ash or sodium oxide to the melt to decrease the melting temperature. However, the increased evolution of off gas offset the benefits of the new melt temperature (Spalding, 1989). Current trends in cesium control include either controlling process feed or recycling off gas components. Controlling process feed involves monitoring the constituents in the feed and how they affect cesium volatility, while recycling off gas components such as HEPA filters or scrubber water, minimize the amount of cesium in the secondary off gas system waste stream (USEPA, 1992).

Kamizono (1986) examined the volatility of cesium within a stainless steel canister. The purpose of his study was to look into the safety aspects of HLW vitrification storage. In this experiment, HLW was placed into a canister which was heated in a furnace to 1000°C in steps of 25°C. It was noted that the decay heat did not play an important role in the temperature control of the glass. During the course of heating, air samples were taken into a bottle with a volume of approximately 7 cm^3. The normalized concentration of cesium (taken by dividing the airborne concentration by the glass concentration) approached it's maximum value in less than one hour. Kamizono divided the complex release mechanism into two pathways. First, the radionuclide must migrate from within the melt to the melt surface. Second, the radionuclide at the surface reacts with other elements. Cesium has been reported to volatilize as $CsBO_2$ (Asano, 1985). This means that the volatility of cesium at the surface has some relation to the interaction between cesium and boron. The volatility of cesium also increases with increasing temperature with the activation energy equal to approximately 140 kJ/mol. The temperature range of this study was from 400°C to 1000°C.

When alkali metals are bound in a glass matrix, they begin to act in a non-ideal manner. For example, the activity of cesium oxide when incorporated in a glass is several orders of magnitude lower than when it is existing as a pure element. This decreases the volatility of cesium from a glass matrix significantly. If cesium does volatilize, it quickly disassociates into Cs^+ and O_2 (Sanders, 1977). After volatilizing, the vapor pressure of Cs^+ is approximately 10 times higher than that of Cs_2O (Odoi, 1979).

CHAPTER 3

EXPERIMENTAL OBJECTIVES

The goal of this research was to provide a basis for determining the feasibility of vitrifying a cesium-contaminated organic ion exchange resin. In order to meet this goal, the following research objectives were established:

1. using crucible studies to determine some of the effects such as changes in Fe(II)/Fe(total) ratio and cesium retention that the addition of organic compounds have on the formation of a glass;
2. determining a range of acceptable values for several operating parameters such as melter temperature and also determining the relative importance of the operating parameters;
3. approximating oxygen transfer rates into a glass melt using different combinations of operating conditions;
4. using pilot scale demonstrations to perform a cesium mass balance around the melter including the feed, off gas, and exit glass streams;
5. characterizing semi-volatile products of incomplete combustion (PIC) found in the off gas resulting from the vitrification of the resin.

CHAPTER 4

MATERIALS AND METHODS

A pilot-scale stirred tank glass melter fabricated by Stir-Melter, Inc. was used to investigate the potential application of vitrification in the treatment of organic ion exchange resin (Richards, 1991). The experimental system consisted of the melter, two related feed systems, an oxygen sparger, and an off gas treatment system. Three phases of preliminary studies were performed prior to the actual use of a pilot-scale glass melter for the vitrification of the cesium-contaminated ion exchange resin. These preliminary studies included crucible studies and oxygen transfer tests.

Experimental Plan

The research was divided into four phases. The first phase was a crucible study. This phase examined the effect that the addition of an organic material had on the resulting glass wasteform. These effects included cesium retention and final redox state of the melt. The goal of the second phase was to set a range of operational parameters that would allow for successful operation of the melter. A matrix with 12 different combinations of operating parameters was established in order to determine a range of acceptable operating parameters and also to distinguish the relative importance of the operating parameters. The third phase was oxygen transfer tests. Approximate values of the oxygen transfer rate into the molten glass under different combinations of impeller agitation, oxygen sparging, and feed water were calculated based on temporal changes in the Fe(II)/Fe(total) ratio. The fourth phase of research was the vitrification of actual cesium-contaminated ion exchange resin. The results from each of the first three phases of research were used in establishing conditions for the fourth phase.

Research Equipment

Stirred Tank Melter

The stirred tank glass melter used in this research was the Stir-Melter model WV-0.25. A cutaway of the melter is shown in Figure 1 (Richards, 1991). It is a Joule-heated melter with a power supply rated at 50 V maximum, 300 Amperes maximum, or 10 kW total power. The vessel is constructed of Inconel™ alloy 601. It is 15.24 x 15.24 x 30.48 cm (6 x 6 x 12 in). The vessel is surrounded by exterior 7 kW heating elements which are used for startup and to assist in maintaining melter temperatures if necessary. An impeller extends into the molten glass from above. The height and rotational speed of the impeller can be controlled. Feed components are fed into the melter through ports located above the melter vessel. The feed materials fall into the vessel and on the molten glass bath where they are rapidly incorporated into the melt through impeller agitation. When the molten glass level reaches 6 inches from the bottom of the vessel, the glass drains from an overflow spout. The molten glass exits from the bottom of the tank, upwards through a channel in the corner of the vessel, over an overflow point located 15.24 cm (6 in) from the bottom of the vessel, and then downward to an outlet located at the bottom of the melter. There is also an additional water-cooled drain plug located in a lower corner of the vessel adjacent to the overflow channel. This is used when emptying the melter vessel (Richards, 1991).

The melter used in these experiments was also equipped with a drain tube heater. Occasionally, the glass exiting the melter through the overflow drain cooled while passing down the exit tube and caused blockages. A heated rod, placed adjacent to the exit tube, kept the local environment inside the tube at approximately 1000° C to aid in maintaining a steady flow of glass. The rod heated the entire drain tube except for the lower two to three inches. In addition to the drain heater, a propane

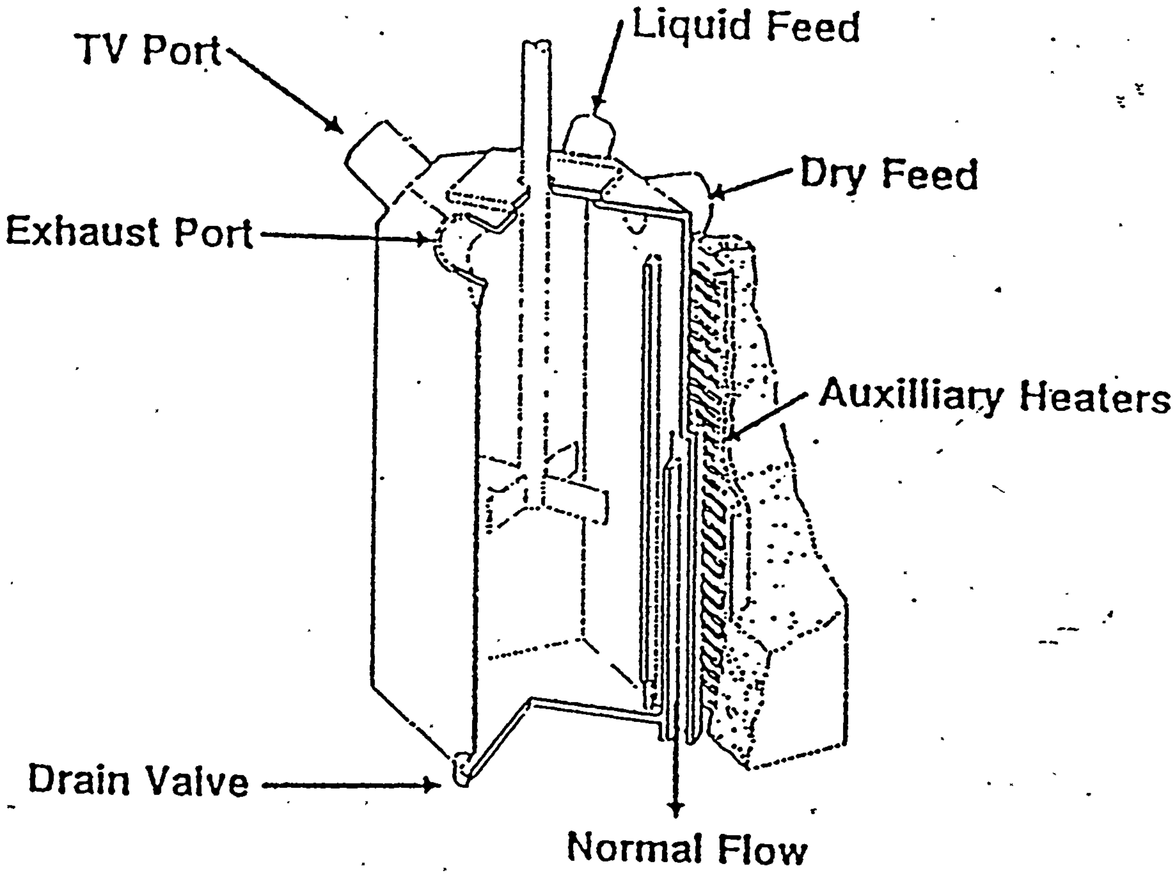

Figure 1. Cutaway of Stir-Melter WV-0.25 (Richards, 1991)

burner was used to heat the lower few inches of the drain tube so that the exiting glass did not cool as it left the tube.

Feed System

The feed system used during Phases II and III of the research is shown in Figure 2. It consisted of a large stainless steel mixing tank, a secondary stainless steel vessel, a diaphragm pump, and a peristaltic pump. The slurry mixture was stored in the large mixing tank capable of holding over 55 gallons. This tank was equipped with a large impeller and baffles in order to keep the slurry in suspension. The mixture was pumped with a diaphragm pump into the secondary vessel which was elevated above the large mixing tank on a small stand. The operating volume of the secondary vessel was approximately 3 liters. The slurry entered the secondary vessel tangential to the walls of the vessel creating a swirling motion in the secondary vessel which kept the slurry in suspension. The secondary vessel had two exit ports. The first port was a tube which entered from the bottom of the vessel and ended approximately 3.5 inches from the bottom. When the slurry reached the height of the tube, it would overflow into the tube and drain through a hose back into the large mixing tank. It was installed so that a constant level of slurry was maintained in the vessel to assist in maintaining a steady flowrate. The second port was a small hole in the side located approximately 2.75 inches from the bottom of the vessel. The slurry was pumped from this port using a Cole Parmer peristaltic pump with a Masterflex controller through the water-cooled slurry feed nozzle and into the melter vessel.

The feed system shown in Figure 3 was used during Phase IV research. It was much simpler than that used in Phases II and III. The previous system was not used during Phase IV research because it would have involved either allowing the resin to mix in the large mixing tank or using an auger feeder to feed the resin as a separate feed stream. Both of these circumstances were unacceptable. If the resin was allowed

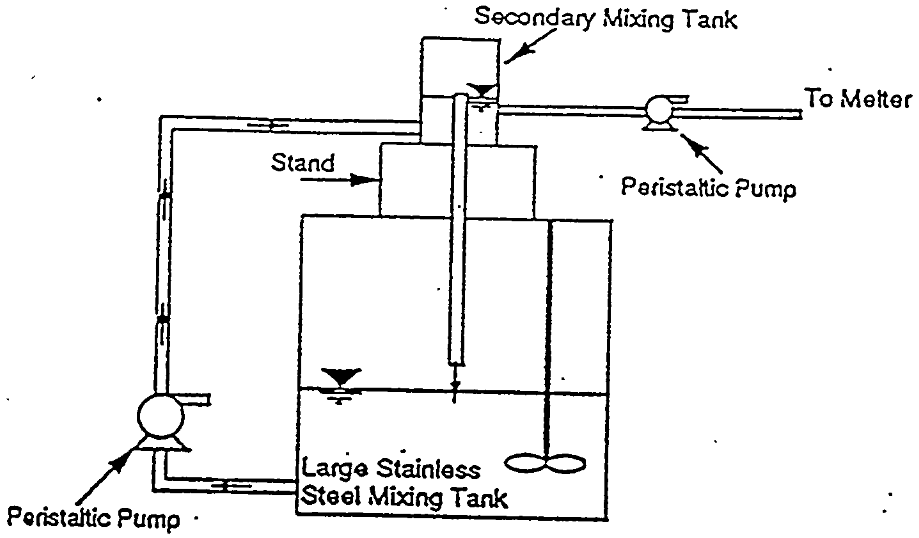

Figure 2. Feed System Used in Phases II and III

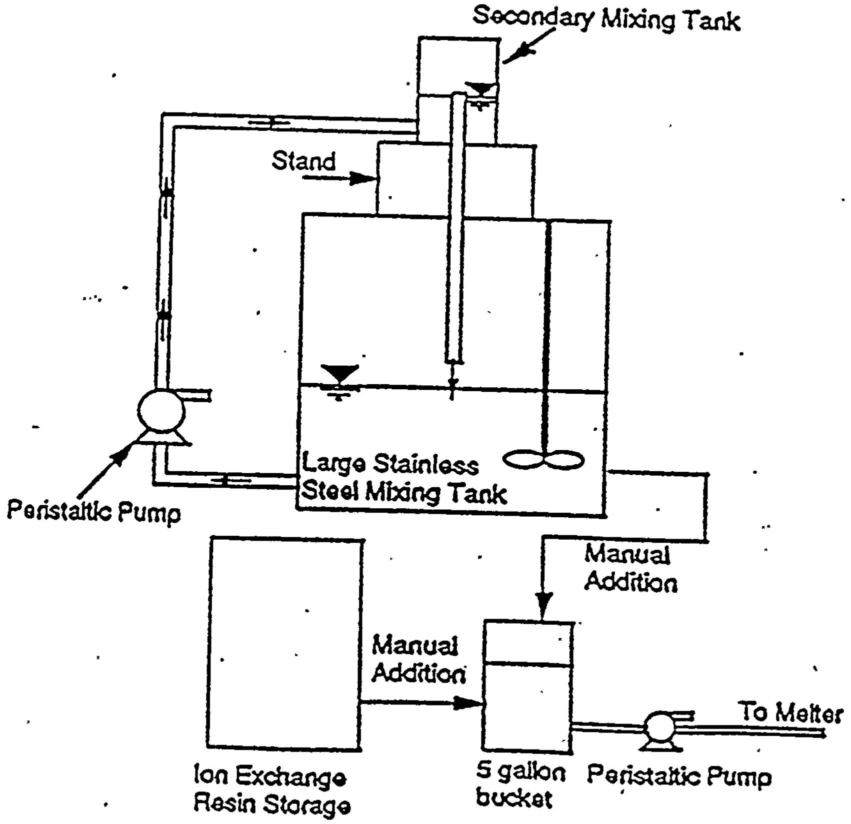

Figure 3. Feed System Used in Phase IV

to mix in the large mixing tank, the cesium might have disassociated from the resin into the slurry and behaved differently in the melter. Auger feeding of the resin was attempted unsuccessfully. When it was fed in this manner, it became swept up in the off gas before it could reach the melt surface. Therefore, the slurry from the large tank and cesium-contaminated ion exchange resin were mixed in a 5 gallon bucket. The feed to the melter was pumped directly from this bucket into the melter using a Cole Parmer peristaltic pump with a Masterflex controller.

The water-cooled slurry feed nozzle fit directly into the slurry feed port of the melter assembly. The nozzle consisted of two concentric 304 stainless steel tubes. The outer diameters of the two tubes were 0.25 inches and 0.75 inches, respectively. The slurry travelled down the 0.25 inch tube into the melter. The 0.75 inch diameter tube surrounded the smaller tube and was sealed around both ends forming a jacket. This jacket was fed with ambient temperature cooling water so that the nozzle and slurry did not become too hot and cause a blockage.

Gas Sparging System

The melter used in this study was also equipped with a gas sparging system consisting of a 0.50 inch I.D. Inconel 601 tube inserted into the molten bath. The gas was supplied from an ordinary gas cylinder. The gas travelled from the cylinder through a calibrated Gilmont flowmeter before being expelled directly under the impeller. The flowrate of the gas was controlled using a needle valve.

Redox Probe

The redox probe was a hollow ceramic probe with a zirconium oxide pellet at the tip. It was manufactured by C.S.I.R.O. in Australia under U.S. Patent # 4,046,661 (Arculos, 1981). Inside the ceramic probe was a type R thermocouple consisting of platinum and rhodium wires. Another platinum wire ran down the outside of the ceramic probe and wrapped around the zirconium oxide pellet. Redox measurements were taken by reading the voltage across the two platinum wires. Temperature measurements were made simultaneously by reading the voltage across the thermocouple wires and using a thermocouple table specific to the R type thermocouple (Burns, 1993).

Off Gas Treatment System

The off gas treatment system is shown in Figure 4. A 5 hp blower (not shown in figure) created a negative pressure in the headspace of the melter and pulled gases evolved from the feed and air inleakage through a 2 inch riser pipe. The gas then passed through a combination venturi scrubber/sqpray quencher. Approximately one liter per minute of water was added through the quench in order to decrease the temperature and scrub some of the larger particles. The gas then was bubbled into a bubbler tank with an operational volume of approximately 92 liters through a perforated pipe. The water level in the tank was controlled to approximately 15 inches using a tube which entered through the top and was connected to a continuously operating peristaltic pump. The tube stopped approximately 15 inches from the bottom of the tank as shown in the figure. Thus, when the water level in the tank reached 15 inches, it was pumped from the tank. The gas then travelled through a countercurrent scrubber packed with 0.50 inch Raschig rings. The scrubber column contained 5 feet of packing and was 6 inches in diameter. The scrubber solution was continuously pumped from a reservoir at a rate of approximately 1 to 2 gallons per minute which had an operational volume of approximately 325 liters through the column and back into the reservoir.

Temperature Control

Watlow brand temperature controllers were used to control the power supplied by the glass melter. Both the melter heating circuit (Joule) and the auxiliary heating circuit

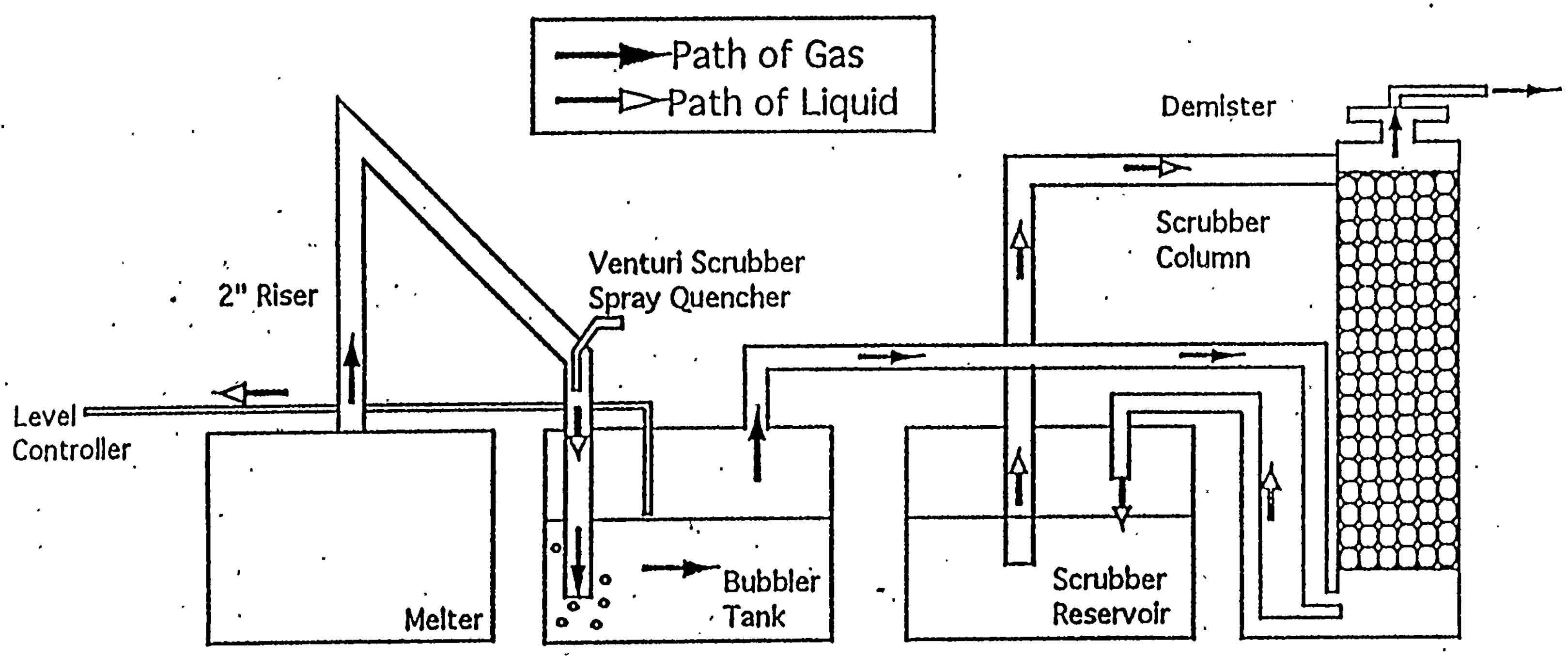

Figure 4. Off Gas Treatment System

were controlled by a Watlow controller to a user defined temperature setpoint. In addition to the setpoints, the user could also define the percentage of the maximum power available to be used by the melter in each heating circuit. Type S thermocouples were used in controlling each heating circuit. The thermocouples were placed so that they measured the temperature next to the vessel wall. The thermocouple used by the melter controller measured the temperature near the bottom of the vessel. The thermocouple used by the auxiliary controller measured the temperature approximately 6 inches above the melter thermocouple. Typically, the melter controller was supplied with a higher setpoint than the auxiliary controller so that the glass was predominantly heated using Joule heating.

Research Chemicals

Slurry

The slurry provided by SRS used in Phases II, III, and IV of this research was a HLW surrogate of what would actually be fed to DWPF melter. The slurry was approximately 35 to 40 weight percent solids. It was made of three components. The first component was a surrogate metal oxide sludge similar to what would be found at the bottom of the waste tanks at SRS. The second component was frit 202, which is a borosilicate glass frit designed by SRS for the vitrification of HLW. The third component was simulated PHA material. If the ion exchange process actually replaced the NaTPB precipitation process, the simulated PHA material would not be present in the slurry. PHA was present because an existing surrogate containing the PHA material was available, and it was decided that the small amount of PHA material existing in the slurry would not significantly affect this study. No external organic material such as carbon or resin was present in the slurry except for the small amount of formic acid contributed by the simulated PHA material. An approximate oxide composition of each of the three primary components of the slurry is shown in Table I (Schumacher, 1991).

During Phase IV the slurry was premixed with the resin before being fed to the melter. This mixture was analyzed by Corning Engineering Laboratory Services (CELS). Results of these analyses are provided in Chapter 5.

Ion Exchange Resin

The ion exchange resins used in the study were provided by SRS. It was made available in two forms. The first form was ion exchange loaded with elemental cesium. The mass ratio of cesium in the loaded form of resin was 0.16 grams of cesium per gram of clean dry resin. It was approximately 38.4% solids but had no free standing water in the container. This resin was used in both Phases I and IV. The second resin was not loaded with cesium and was basically dry. This resin was used in Phase III.

Miscellaneous Chemicals

The carbon used in Phase I and Phase III was granulated activated carbon supplied by Calgon (CAS# 7440-44-0). The ferric oxide used in the crucible study was 99+% pure and supplied by Harcross Pigments (Lot number F8090). The sodium carbonate used in the crucible study was technical grade, mined. It was supplied by General Chemical. The glass frit used in the crucible study was supplied by Bassichi's Co. (Lot number CBF-230). The anhydrous borax used in the crucible study was 99.5% pure on a metals basis and supplied by Johnson Matthey (Lot number H10C05). The cesium carbonate used in the crucible study was 99% pure on a metals basis and supplied by Johnson Matthey (Lot number I29C06).

Phase I: Crucible Study

Sample Preparation

Each of the chemicals used in the crucible study was dried in a 101° C to 103° C oven for more than 24 hours prior to the crucible study. After they were removed from the oven, they were stored in a desiccator until used in the experiments.

Experimental Procedure

High purity alumina crucibles were filled with identical amounts of glass forming chemicals. Each crucible contained approximately 20 grams of frit, 2.5 grams of anhydrous borax, 2.5 grams of ferric oxide (Fe_2O_3), and 2.5 grams of sodium carbonate (Na_2CO_3). The type and amount of organic material, the presence of water, and the inclusion of a sealed lid were altered for each crucible. The parameters used for each crucible set are defined in Chapter 5. Cesium carbonate was added to those samples using elemental carbon as the carbonaceous material to provide cesium for the cesium retention study. Water was added to some of the crucibles to examine it's effect on the final redox state of the glass. All samples were ground and stirred using a mortar and pestle to assure uniform blending of the components. Crucibles were sealed, as required, with a commercial ceramic sealant.

A furnace capable of maintaining 1100° C was preheated to 600° C. After the samples were placed in the furnace at 600° C, the temperature was increased to 1100° C. The samples were maintained at 1100° C for three hours. The crucibles were then removed from the furnace and air quenched. The sealed samples remained sealed during quenching.

Table I

Approximate Composition of the Slurry Components Used in Phases II, III, and IV

Oxide	Sludge (weight percent)	PHA (weight percent)	Frit 202 (weight percent)
Al	16.86	1.20	
Ba	0.24	0.81	
B		29.30	8.00
Ca	4.39	0.08	
Cr	0.36	0.02	
Cs	0.01	1.00	
Cu	0.18	3.80	
Fe	44.12	0.81	
K	0.39	36.92	
Li			7.00
Mg	0.35	0.01	2.00
Mn	8.91	0.16	
Na	12.77	18.46	6.00
Ni	2.65	0.05	
Pb	0.41	0.01	
Si	4.18	0.07	77.00
Ti		7.22	
Zr	1.41	0.02	

Phase I: Analytical Methods

Recovery of Glass Samples

The glass from each crucible was removed by breaking the crucible with a hammer over a stainless steel tray. Prior to analysis, it was powdered to approximately 100 mesh using an agate ball mill. The powdered glasses were stored in labelled plastic vials.

Redox Ratio Analysis

The redox analysis for Fe(II)/Fe(total) ratio in waste glass followed the same procedure as that developed at Savannah River Site (Baumann, 1987). This method involved placing pulverized glass in a sulfuric/hydrofluoric acid mixture in the presence of ammonium vanadate. As the Fe(II) ions entered solution, they reacted with the VO_2^+ ion to produce Fe(III). After the glass dissolved, boric acid was added to complex the fluoride. A buffered Ferrozine solution was used to raise the pH and "regenerate" the original Fe(II). The solution turned a magenta color due to the formation of a ferrous-Ferrozine complex. The absorbance of this solution was determined colorimetrically at 562 nm. Ascorbic acid was then added to reduce all Fe to Fe(II). The resulting Fe(II) formed more of the ferrous-Ferrozine complex. A new absorbance was read and the Fe(II)/Fe(total) ratio was determined with the aid of calibration curves. A sample of this calibration curve is shown in Appendix A.

Cesium Content of Glass

The glass samples were analyzed by SRS for cesium content. The glasses were digested using nitric acid, hydrofluoric acid, boric acid, and hydrochloric acid with microwave dissolution and the resulting digestate was analyzed using atomic adsorption. A Varian Spectra400 Atomic Adsorption spectrophotometer was used.

The analysis was by flame emission at a wavelength of 852.1 nm, with a slit width of 0.1 nm, and using an air-acetylene flame

Phase II: Operational Parameters

A matrix of 12 trials for operating the melter was created allowing for different combinations of impeller height, impeller speed, melter temperature, slurry feed rate, and air feed rate. For each parameter, a high, middle, and low value were selected for testing. Following these initial 12 trials, 4 more trials were performed to refine the ranges. The parameters for the first 12 trials and the following 4 trials are shown in Table II. Trials were generally carried out for at least two hours except in cases where it was apparent after several minutes that the combination of parameter values for that trial would be unsuccessful such as those using high slurry feed rates. Qualitative observations were made during each trial.

Phase III: Oxygen Transfer Tests

Experimental Procedure

Two of the oxygen transfer tests performed were batch type experiments using no feed slurry. The melter was first filled with a known amount of glass from the Phase II tests. The impeller agitated the molten glass for several hours to assure that the molten glass was at equilibrium with the atmosphere. Next, a measured quantity of elemental carbon was added to the melt to increase the Fe(II)/Fe(total) ratio. When it was felt that the carbon had been fully reacted with the melt as evidenced by the absence of flares, sparks, or the evolution of gases, samples were taken from the surface of the melt. Operational conditions for the test were then initiated. The operating conditions are shown in Table III for batch tests 1 and 2. Samples were then taken periodically for the next several hours. The operational values for the melter parameters such as melter temperature and impeller speed were based on results from Phase II observations.

Table II

Phase II Operational Parameters Matrix

Trial	Melter T (deg C)	Imp Spd (rpm)	Imp Ht (inches)	Slurry (mL/min)	Air Feed (mL/min)
1	1050	202	4	66	200
2	1050	202	4	88	500
3	1050	302	4	114	800
4	1050	302	5	66	200
5	1060	420	5	88	200
6	1060	420	5	114	500
7	1060	202	6	66	500
8	1060	202	6	88	800
9	1070	302	6	114	800
10	1070	302	4	66	200
11	1070	420	5	88	500
12	1070	420	6	114	800
13	1060	302	4	54	600
14	1060	588	3.5	54	600
15	1070	370	4	54	800
16	1070	420	4	50	800

The second type of oxygen transfer test was conducted using continuous slurry flow. The melter was first allowed to approach equilibrium as in the batch style test. Next, the slurry feed containing approximately 35 to 40 percent solids described earlier made up of frit, sludge, and PHA material was started at a rate of 50 mL/min and an exit glass stream was established. Other operational values based on Phase II results for the continuous feed test are shown in Table III. When the melter was operating successfully under the slurry feed conditions, resin which had not been loaded with cesium, was batch fed in 30 to 100 gram portions to the melt to increase the Fe(II)/Fe(total) ratio. A total of 300 grams of resin were added in this manner. During the melter run, the redox state of the glass was monitored by two methods. First, samples of molten glass were taken periodically from the molten surface and of the exit glass. These samples were analyzed for the Fe(II)/Fe(total) ratio as an indication of the redox state of the glass. Second, the on-line redox analyzer utilizing a zirconium oxide probe was used which continuously monitored the redox state of the glass. A rough correlation was made between Fe(II)/Fe(total) ratio and EMF readings generated by the probe.

Table III

Operating Conditions for Phase III Oxygen Transfer Tests

Parameter	Batch Test 1	Batch Test 2	Continuous Feed
Melter Temperature	1070 degrees Celsius	1070 degrees Celsius	1070 degrees Celsius
Auxiliary Temperature	1055 degrees Celsius	1055 degrees Celsius	1055 degrees Celsius
Impeller Height	3.25 inches	2.75 inches	4 inches
Impeller Speed	405 rpm	405 rpm	405 rpm
Oxygen Flow	0 mL/min	0 mL/min	1000 mL/min
Water Feed Rate	0 mL/min	35-40 mL/min	0 mL/min
Slurry Feed Rate	0 mL/min	0 mL/min	50 mL/min

Glass Sampling Procedure

Glass was sampled from the surface of the melt during the batch type oxygen transfer tests. Inconel™ welding rod was inserted approximately 1.5 inches beneath the surface of the melt and removed. The glass was allowed to air quench on the rod. It was removed from the rod by covering the glass with a paper towel and lightly tapping with a hammer. The glass samples were stored in a labelled plastic vials.

Glass was sampled both from the surface of the melt and from the exit glass stream during the continuous type testing. Melt surface sampling was performed in the same way as the batch type testing. Pull samples were taken by allowing the exit stream to fall on a stainless steel plate. This glass was allowed to air quench and then stored in labelled plastic vials.

Fe(II)/Fe(total) Ratio Determination

Redox determination of all glass samples was performed using the colorimetric analysis developed at SRS described earlier in Phase I.

Phase IV: Vitrification of Ion Exchange Resin

Experimental Procedure

The glass was filled to approximately 6 inches with nominal 8.6% iron glass made from Phase III tests. The melter and auxiliary temperature controllers were set to setpoints of 1070° C and 1045° C, respectively. The oxygen sparger was then turned on at a rate of 1200 mL/min at STP. The scrubber was filled with a known amount of tap water and turned on. The bubbler was allowed to fill with tap water to the level control tube. After the scrubber water was allowed to circulate through the packed column for approximately thirty minutes, three scrubber solution sample blanks were taken. Three bubbler tank solution sample blanks were also taken from the exit tube of the level controller. The bucket which held the slurry and resin mixture was then filled with 11.312 L of the slurry previously described as approximately 35 to 40 weight percent solids and 295 grams of the wet resin loaded with nonradioactive cesium. A small mixer kept the resin and other solids in suspension. Three feed samples were taken from this initial slurry mixture. When the glass melt had reached the setpoint temperatures, the slurry feed was added to the melter at a rate of 51 mL/min. During the course of the run, samples from the packed column scrubber and the bubbler solution were taken approximately every hour. Samples of exit glass were taken approximately every thirty minutes. Readings from the redox probe were recorded manually in a log book every few minutes during the course of the entire run. A data acquisition system recorded all other important data every one to five minutes. The bucket level was maintained by adding resin and slurry to the bucket in the same ratio as the initial amount during the run. When the melter had processed approximately 3 tank volumes of glass, samples of the off gas were taken using both the EPA Modified Method 5 Sampling Train (OSWER, 1986) and the EPA Multiple Metals Sampling Train (USEPA, 1990). After the off gas sampling was completed, final samples of the scrubber solution, bubbler solution, glass, and feed were taken.

Sampling Procedure

Glass Sampling

Glass was sampled from the exit stream in an identical manner as in the Phase III continuous type test.

Bubbler Solution Sampling

Samples of the bubbler solution were taken from the solution pumped from the bubbler tank through the level controller. Since the tank was required to be airtight at all times, no sample was taken directly from the tank. It was felt that enough bubbling and mixing was going on in the tank that the sample from the level controller was representative of the concentration in the tank.

Scrubber Column Sampling

Samples from the scrubber column were taken from the stream being pumped back into the scrubber solution reservoir immediately after leaving the scrubber column.

Off Gas Multiple Metals Sampling Train

Sampling for metals in the off gas was performed using a modified version of the EPA Method 29 Sampling Train (USEPA, 1990). Since mercury was not present in the feed, the permanganate impingers normally used for sampling mercury were eliminated from the train. These impingers were replaced with additional HNO_3/H_2O_2 impingers. The reason for this is that several of the metals of interest such as Cs were not on the list of metals for which Method 29 was designed. Thus, these additional impingers were analyzed separately to determine if the first impingers had caught all the additional metals. For example, if each impinger solution contained the same amount of a certain metal, it could be determined that the results for that metal were inconclusive since all the metal had apparently not been captured with the impingers. However, if the final impingers had much lower concentrations of a certain metal than the first impingers, it could be concluded with reasonable certainty that the majority of that metal was captured.

Off Gas Modified Method 5 Sampling Train

The procedure used was as per EPA Modified Method 5 (OSWER, 1986).

Phase IV Analytical Methods

Feed and Glass Analysis

Glass and feed samples were analyzed by Corning Engineering Laboratory Services (CELS) in Corning, NY for the following elements: Fe, Na, Ca, Mg, Cr, Ni, Cs, B, Si, Li, K, Mn, and Al.

Glass samples were also analyzed by SRS for cesium. The procedure used was summarized earlier in the Phase I analytical methods section.

Off Gas Analysis

Multiple Metals Sampling Train

The components of the Multiple Metals Sampling Train were analyzed by Oxford Laboratories in Wilmington, NC for the following elements: Cs, Ni, Si, Pb, Ba, Fe, Mn, Mg, Cr, Na, Ca, Al, Li, K, and B.

Modified Method 5 Sampling Train

The XAD-2 resin module of the Modified Method 5 Sampling Train was analyzed by Triangle Laboratories in Raleigh, NC for semi-volatile organic compounds listed in the Clean Air Act and on Table 2 in SW-846 based on the guidelines of Method 8270. The column for the gas chromatography analysis was a J&W DB5-625, 30 m x 0.32 mm x 1µm. The carrier gas for the analysis was helium. The instruments used for performing the mass spectrophotometry were a Hewlett-Packard MSD, Chemsystem and Target data system. The parameters of the scan were 35-550 amu at 1.67 s/scan.

Bubbler and Scrubber Solution Analysis

Bubbler and scrubber solution samples were analyzed by SRS for total Cs content by SRS using a Varian Spectra400 Atomic Adsorption spectrophotometer. The analysis was by flame emission at a wavelength of 852.1 nm, with a slit width of 0.1 nm, and using an air-acetylene flame.

CHAPTER 5

RESULTS AND DISCUSSION

Phase I: Crucible Studies

The basis for the design of the Phase I crucible test matrix was to vary the type of organic material and also to test what effects the addition of water and a sealed environment had on the resulting glass product. Seven combinations of these test conditions were explored. The basic matrix showing the different combinations is shown in Table IV. Within each combination, the amount of the respective reducing agent was varied. It was not felt that the addition of water would have an effect on an open crucible so that combination was not pursued.

Table IV

Basic Matrix for Phase I Crucible Study Experiments

Set	Reducing Agent	Reducing Agent (g)	Water	Type of Environment
A	Carbon	0.125, 0.25, 0.29, 0.34, 0.375	No	Sealed
B	Carbon	0.125, 0.25, 0.375	Yes	Sealed
C	Resin	0.25, 0.50, 0.75	No	Sealed
D	Resin	0.25, 0.39, 0.50, 0.75, 0.81	Yes	Sealed
E	Carbon	0.125, 0.25, 0.375	No	Unsealed
F	Resin	0.25, 0.50, 0.75	No	Unsealed
G	None	None	No	Sealed

Table V shows the chemical contents of each crucible prior to melting and the type of environment (sealed vs. unsealed). As mentioned before, each crucible had the same base of glass forming materials. The glass frit was the primary glass forming material. It supplied the SiO_2 for the final glass sample. The borax was added mainly because the actual glass frit used for the vitrification of HLW is a borosilicate glass. The Fe_2O_3 was added to serve as a redox determinant and to provide additional oxygen for the oxidation of carbon or resin. The Fe(II)/Fe(total) or ferrous to total iron ratio is a common indicator of the redox state of a glass. Ferric oxide can serve as a redox buffer by being reduced prior to other glass forming elements and thus providing oxygen for oxidation reactions. The soda ash was used as a fluxing agent so that the final glasses would become more homogeneous. Cesium carbonate was added to spike those crucibles containing carbon as the reducing agent. The masses listed in Table V for each chemical were taken after the chemicals had been dried in a 101°C to 103°C oven for over 24 hours and then cooled in a desiccator.

Visual Observations

The crucibles were identified by a three section identification code. The first section is the page number of the log book issued to Dennis Bickford of SRS where they were first listed (Bickford, 1994). The second section is the letter from Table IV which describes the combination of elements in the crucible. The third section is a number which distinguishes the crucibles with identical page numbers and combinations of elements from each other based on their different organic compound loading. For example, the crucible sample identified with 17-A-3 means that this sample is described on page 17 of the log book, has carbon as the reducing agent, does not have water added, and is in a sealed environment.

Two of the crucible mixtures, 17- A-3 and 13-D-2, described in Table V did not form a homogeneous glass. These samples were discarded and underwent no further tests. Sample 17-A-3 contained 0.3749 grams of carbon. Two additional tests using set A conditions were performed with slightly lower carbon loadings. These samples were 21-A-1 and 21-A-2 and had 0.2922 and 0.3383 grams of carbon respectively.

Table V

Crucible Contents for Phase I Crucible Study Experiments

Crucible ID	Frit (g) (grams)	Borax(g) (grams)	Fe2O3 (g) (grams)	Carbon (g) (grams)	Cs2CO3 (g) (grams)	Resin (g) (grams)	Na2CO3(g) (grams)	Water (mL) (mL)	Lid? (Y/N)
17-A-1	20.0117	2.5005	2.5015	0.2489	0.0581		2.5046		Y
17-A-2	20.0063	2.5000	2.5076	0.1278	0.0628		2.5028		Y
21-A-1	19.9970	2.4994	2.5078	0.2922	0.0696		2.5094		Y
21-A-2	20.0040	2.5028	2.5033	0.3383	0.0735		2.5100		Y
17-B-1	20.0211	2.5059	2.4998	0.1261	0.0763		2.5013	2.00	Y
17-B-2	20.0004	2.5285	2.5078	0.2506	0.0543		2.5303	2.00	Y
17-B-3	20.0033	2.5160	2.5174	0.3801	0.0582		2.5050	2.00	Y
17-C-1	20.0002	2.5023	2.4986			0.2529	2.5095		Y
17-C-2	20.0000	2.5042	2.5178			0.5013	2.4968		Y
17-C-3	20.0051	2.5260	2.5155			0.7535	2.5424		Y
13-D-1	19.9700	2.4900	2.5200			0.2526	2.5228	2.00	Y
13-D-3	19.9500	2.5300	2.5000			0.7484	2.5700	2.00	Y
21-D-1	20.0128	2.5050	2.5157			0.2496	2.5181	2.00	Y
21-D-2	20.0060	2.5197	2.5018			0.3936	2.5032	2.00	Y
21-D-3	20.0014	2.5113	2.5006			0.8127	2.5055	2.00	Y
17-E-1	20.0000	2.5566	2.5162	0.1242	0.0743		2.5477		N
17-E-2	19.9814	2.5236	2.5021	0.2500	0.0625		2.4940		N
17-E-3	20.0250	2.5024	2.4934	0.3772	0.0543		2.5050		N
13-F-1	20.0400	2.5100	2.5200			0.2502	2.5369		N
13-F-2	20.0200	2.5100	2.5000			0.5029	2.5651		N
13-F-3	20.0000	2.5400	2.5100			0.7541	2.5806		N
13-G	20.0000	2.5200	2.5100				2.5000		Y

Both of these samples formed a homogeneous glass. Sample 13-D-2 contained 0.5039 grams of resin. This was anomalous because sample 13-D-3 which had a higher resin loading was processed at the same time and formed a homogeneous glass. Three additional tests were performed using both higher and lower resin loadings. Two of the samples, 21-D-1 and 21-D-2, had lower resin loadings and one sample, 21-D-3, had a higher loading. All three of these samples formed homogeneous glasses. It was not immediately clear why these two crucible mixtures failed to form a glass.

After powdering the glasses to approximately 100 mesh in an agate ball mill, the glass samples exhibited colors dependent on their final redox state. Glasses which had low Fe(II)/Fe(total) ratios or were less reduced were yellow in color. Glasses which had higher ratios or were more reduced were green in color. For example, crucible 13-G which had no reducing agent addition was bright yellow. Crucibles such as 21-D-3 which had high reducing agent loadings were medium to dark green.

Redox Ratio

The final average redox values for each crucible as indicated by the Fe(II)/Fe(total) ratio are listed in Table VI. The values shown represent the average of at least two analyses performed at Clemson University and one analysis performed at SRS. The analysis provided by SRS served to check the Clemson values for accuracy. They were not used in the following correlations. Seven crucibles warranted an additional analysis because the first two analyses did not provide similar results. In these cases, all four values were averaged for the final result. In all cases, the SRS experimental values correlated well with the average Clemson University experimental values.

Equations were developed to correlate the redox results from the crucible study with the parameters which could affect the final redox state of the glass. These

Table VI

Final Fe(II)/Fe(total) Values for Phase I Crucible Tests

Crucible	Clemson University Fe(II)/Fe(total)	SRS Analysis Fe(II)/Fe(total)
17-A-1	0.675	0.722
17-A-2	0.427	0.436
17-A-3	Did not form glass	Did not form glass
17-B-1	0.377	0.380
17-B-2	0.603	0.599
17-B-3	0.775	0.833
17-C-1	0.244	0.250
17-C-2	0.382	0.391
17-C-3	0.427	0.502
13-D-1	0.279	0.276
13-D-2	Did not form glass	Did not form glass
13-D-3	0.549	0.558
17-E-1	0.044	0.022
17-E-2	0.050	0.051
17-E-3	0.374	0.378
13-F-1	0.088	0.073
13-F-2	0.206	0.180
13-F-3	0.273	0.293
13-G	0.055	0.022
21-A-1	0.686	0.658
21-A-2	0.682	0.722
21-D-1	0.202	0.204
21-D-2	0.262	0.326
21-D-3	0.515	0.574

parameters included the type and amount of resin, the presence of water, and the presence of a lid.

The correlation based on the entire set of crucibles ($R^2 = 0.92$) was determined to be,

$$\mathrm{Fe(II)/Fe(total)} = (1.28 * C) + (0.343 * R) + (0.0292 * W) + (0.159 * L)$$

and for only the sealed crucibles ($R^2 = 0.96$)

$$Fe(II)/Fe(total) = (2.10 * C) + (0.530 * R) + (0.0255 * W)$$

where C is the grams of carbon, R is the grams of resin, W is the mL of water, and L is the type of environment. A value of 1 was given to L if a lid was used and 0 if there was no lid. The data for the set of unsealed crucibles were limited and did not generate an accurate correlation when analyzed separately.

The relative reducing ability of the two type of reducing agents can be calculated from the two correlations based on the ratio of their coefficients. In the correlation relating the entire set of crucibles the ratio of the carbon coefficient to the resin coefficient is approximately 3.7. This indicates that 1 gram of carbon and 3.7 grams of resin have the same capability as reducing agents under similar circumstances. For the correlation limited to the sealed crucibles, the ratio of the coefficients is closer to 4.0.

Since there was not a quantitative value that could be placed on whether the crucible environment was sealed or open, a value of 1 was used in determining the correlation if the environment was sealed and a value of 0 was used if the environment was open. This value system basically turns the variable on and off. The magnitude of this coefficient indicates that a difference of approximately 0.159 in the respective Fe(II)/Fe(total) ratios should be seen between two glass samples processed under otherwise identical conditions. This difference becomes significant when the Fe(II)/Fe(total) ratio of 0.33 which SRS uses to define an acceptable glass is considered (Ramsey, 1991).

Since varying amounts of water were not used, the correlation is not meant to predict the result either qualitatively or quantitatively if more or less than 2 mL of water are used. Thus, the only comparisons that can be made involving water are those which compare 0 mL of water with 2 mL of water. Although there are not enough data to support any quantitative conclusions involving water, it seems that since the coefficient for water is positive, the presence of water hinders the reoxidation of the glass rather than assisting as an oxygen donor. This hindrance is only minor, however, since the magnitude of the coefficient for water is so small in relation to the other coefficients and the SRS guidelines for an acceptable glass.

A graphical comparison of the predicted Fe(II)/Fe(total) redox ratios and the observed experimental values based on these correlations for the entire set of crucible data and the set of sealed crucibles are shown in Figures 5 and 6 respectively. An additional 45° line has been added which represents a 100 percent correlation between the predicted redox ratios and the observed experimental results.

Figure 7 shows the effect of reducing agent loading on the final redox state of the glass as indicated by the Fe(II)/Fe(total) ratio. Since the same mass of resin and carbon behave differently and a slightly different amount of glass resulted in each crucible, the ratio of the coefficients in the correlation relating the entire set of crucibles was used to "normalize" the masses of reducing agents. The ratio used was 3.7. The normalization was performed by multiplying the masses of carbon in those crucibles with carbon as the reducing agent by the coefficient ratio. This normalized value is essentially the mass of reducing agent as resin. This value was then divided by the predicted mass of glass based on the crucible materials to get the mass of reducing agent as resin per gram of glass. It is apparent that the sealed crucibles follow a somewhat linear trend. The open crucible, on the other hand, do not follow any sort of trend and are therefore difficult to correlate.

Based on weight percentages given by Bibler (1991), the empirical formula for the organic portion of the resin is $C_{2.96}H_{5.80}O_{2.84}$. Using this formula and assuming that the carbon combustion reaction proceeds 100 percent towards carbon dioxide (CO_2) and that the hydrogen combustion proceeds 100 percent towards water (H_2O), the theoretical chemical oxygen demand can be calculated as

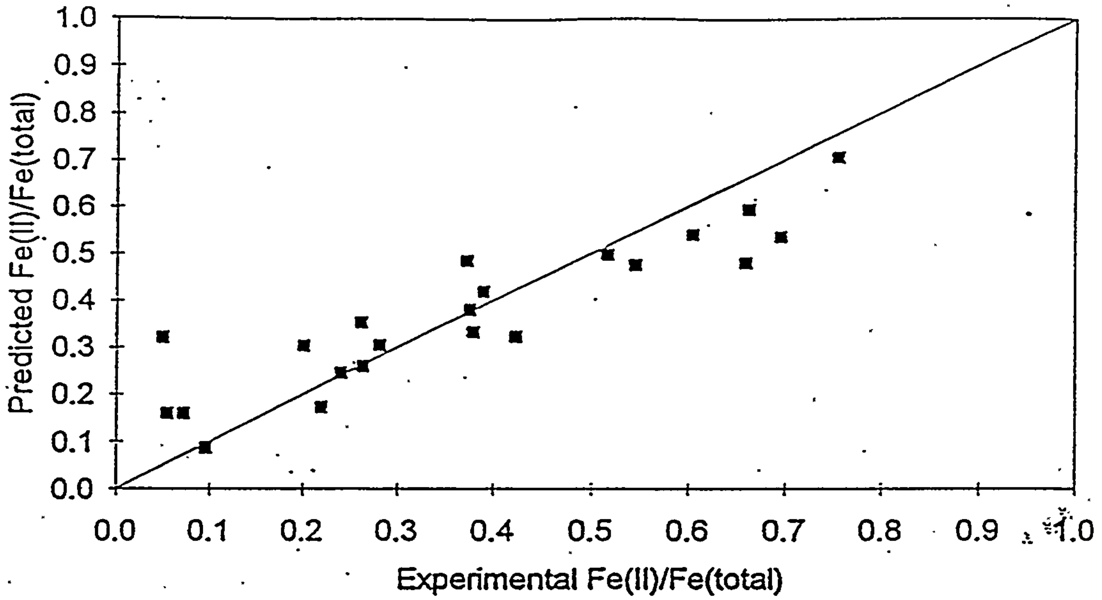

Figure 5. Comparison of Experimental Values with Predicted Values for the Entire Set of Crucibles in Phase I. Note: The solid line indicates perfect correlation.

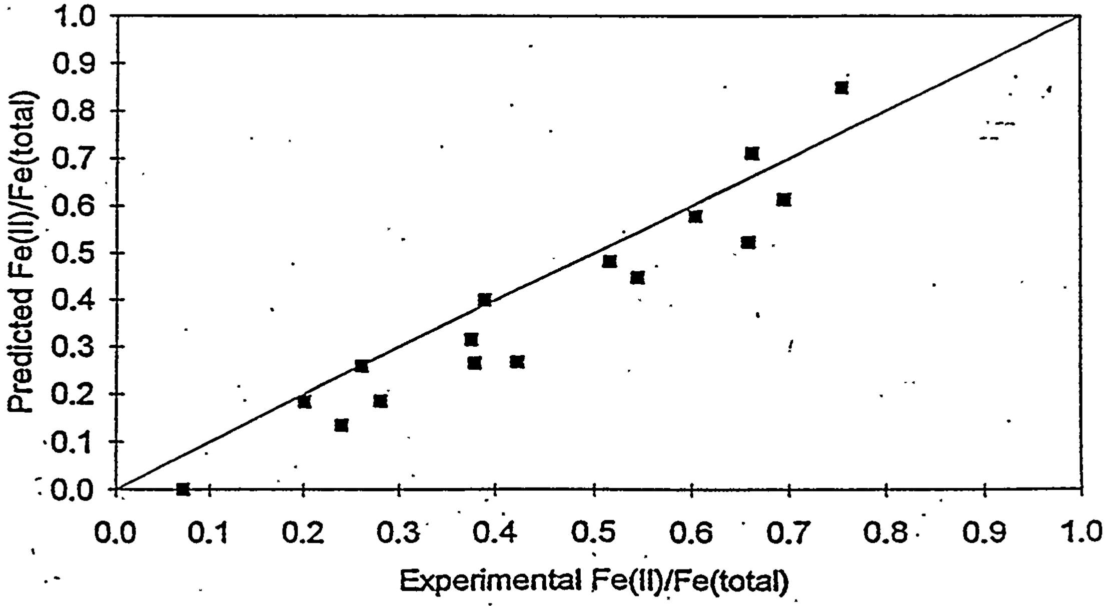

Figure 6. Comparison of Experimental Values with Predicted Values for the Sealed Set of Crucibles in Phase I. Note: The solid line indicates perfect correlation.

2.99 moles O_2 / 100 grams resin. This value takes into account the existing oxygen in the resin molecule and ignores any oxygen demand attributed to the potassium, cesium, or sodium present as exchangeable elemental cations in the resin. If 100grams of carbon are combusted and the same assumptions apply, the chemical oxygen demand is 8.33 moles O_2 / 100 grams carbon. Thus, the theoretical ratio of reducing effectiveness of carbon to resin can be calculated as 8.33 divided by 2.99, or 2.79. This ratio is very similar to the experimental values of approximately 3.7 and 4.0 calculated earlier based on the crucible study correlations. If the combustion reactions of the resin were more correctly assumed to proceed 100 percent towards CO, the theoretical chemical oxygen demand decreases to 1.51 moles O_2 / 100 grams of resin. In this case, the theoretical ratio of reducing effectiveness of carbon to resin can be calculated as 8.33 divided by 1.51, or 5.52. It is probable that during these crucible tests, the combustion of carbon did not proceed 100 percent towards either CO_2 or CO indicating the theoretical ratios compare well with the experimental values.

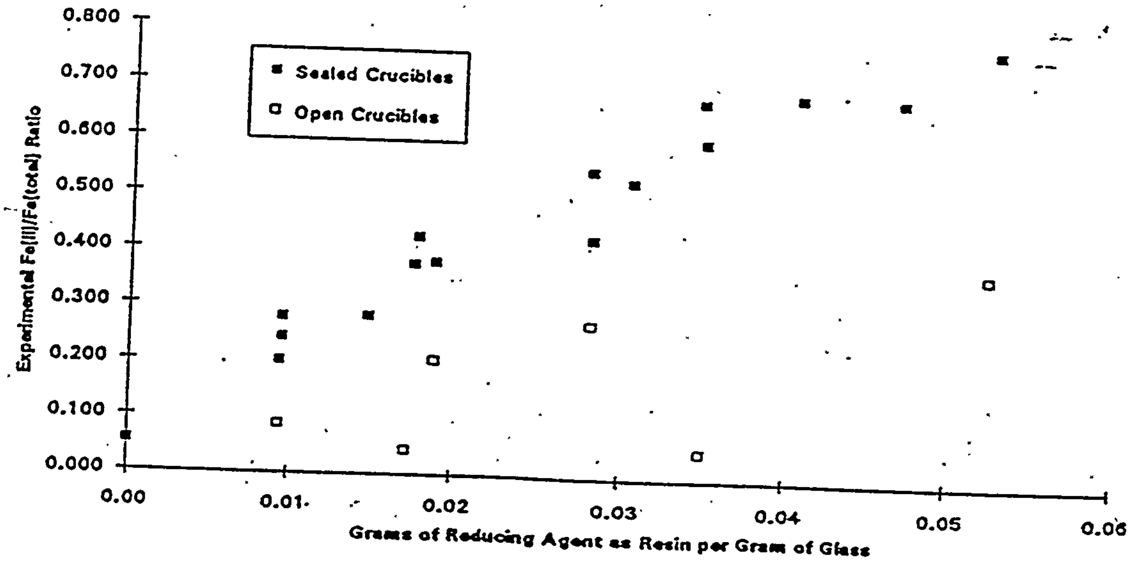

Figure 7. Correlation Between Grams of Reducing Agent as Resin and Final Fe(II)/Fe(total) Ratio in Glass for Entire Set of Crucibles

The crucible data can also give an early indication for the maximum level of resin loading in the glass that is operationally feasible. Preliminary assessments by SRS indicate a Fe(II)/Fe(total) of 0.33 in a glass as a maximum value to prevent nickel sulfide precipitation in the melter (Ramsey, 1991). These crucible studies indicate the organic loading giving this ratio is approximately 0.32 grams of reducing agent as carbon or 1.26 grams of reducing agent as resin per 100 grams of glass in a sealed environment. For the unsealed set of crucibles, the ratio increases to approximately 4.91 grams of reducing agent as resin or 1.23 grams of reducing agent as carbon per 100 grams of glass.

Cesium Content

Each crucible glass was intentionally loaded with one of two forms of nonradioactive cesium based on the type of organic material. The resin was preloaded with resin by SRS at a mass ratio of 0.16 grams of cesium per gram of dry resin. Those crucibles which used carbon as their reducing agent were spiked with cesium carbonate. The predicted cesium oxide weight percent was calculated based on the initial composition of raw chemicals. This value was compared to the experimental value to determine the retention of cesium in the crucible glass.

Table VII lists the final Cs_2O weight percent in each crucible along with the predicted weight percent based on the initial composition of raw chemicals and the calculated cesium retention in the glass. The average cesium retention for the crucibles utilizing carbon as the reducing agent was 66.8 percent with a standard deviation of 4.9 percent. The average cesium retention for the crucibles utilizing resin as the reducing agent was 88.6 percent with a standard deviation of 6.6 percent. Thus, cesium retention was favored with the resin over that of the cesium carbonate, i.e., the intimate mixing of the cesium with the organic resin did not increase cesium volatility.

Final redox ratio and mass of reducing agent did not seem to influence cesium retention.

Table VII

Cesium Retention in Phase I Crucible Study

Crucible ID	Type of Reducing Agent	Predicted (wt% Cs2O)	Experimental (wt% Cs2O)	Cs Retention	Final Fe(II)/Fe(total)	Reducing Agent (grams)
17-C-2	Resin	0.32%	0.31%	97.57%	0.382	0.5013
13-D-3	Resin	0.48%	0.46%	97.13%	0.549	0.7484
13-D-1	Resin	0.16%	0.15%	95.11%	0.279	0.2526
17-C-3	Resin	0.48%	0.45%	93.74%	0.427	0.7535
17-C-1	Resin	0.16%	0.15%	90.54%	0.244	0.2529
13-F-1	Resin	0.16%	0.14%	87.90%	0.088	0.2502
13-F-3	Resin	0.48%	0.41%	85.25%	0.273	0.7541
13-F-2	Resin	0.32%	0.27%	84.87%	0.206	0.5029
21-D-1	Resin	0.16%	0.13%	81.95%	0.202	0.2496
21-D-2	Resin	0.25%	0.20%	81.31%	0.262	0.3936
21-D-3	Resin	0.52%	0.41%	79.31%	0.515	0.8127
17-E-3	Carbon	0.18%	0.13%	72.60%	0.374	0.3772
17-B-3	Carbon	0.19%	0.14%	72.59%	0.775	0.3801
17-E-1	Carbon	0.24%	0.17%	70.26%	0.044	0.1242
17-E-2	Carbon	0.20%	0.14%	69.37%	0.050	0.2500
21-A-1	Carbon	0.23%	0.16%	69.02%	0.686	0.2922
21-A-2	Carbon	0.24%	0.16%	68.07%	0.682	0.3383
17-B-2	Carbon	0.18%	0.11%	63.35%	0.603	0.2506
17-A-2	Carbon	0.20%	0.13%	61.60%	0.427	0.1278
17-B-1	Carbon	0.25%	0.15%	61.51%	0.377	0.1261
17-A-1	Carbon	0.19%	0.11%	59.38%	0.675	0.2489
13-G	None	0.00%	< 0.0040%	Not Calc.	0.055	0.0000

Phase II : Establishing Operational Parameters

The operating parameters chosen for the operational matrix in Phase II are critical in determining the success of a melter operation based on trials performed before this research. The melter temperature can establish the melt rate which in turn can determine the maximum feed rate. The impeller speed combined with the impeller height can influence the oxygen transfer rate as well as how rapidly the feed components are incorporated into the melt. The maximum slurry feed rate is a result of the chosen operating parameters. It is generally wise to set the operating parameters in order to maximize this rate. The air feed rate can influence the oxygen transfer rate but may hinder the success of a melter operation by lowering the melter temperature or increasing the volatilization of metals or entrainment of particulate matter.

Operational Parameters

Some of the operating parameters such as air sparger flowrate and auxiliary temperature varied during the Phase II work did not significantly influence the success of the melter operation. Some of the parameters, however, such as slurry feed rate and melter temperature were important in determining the operational stability of the melter. The final melter operational settings chosen based on the 16 trials are listed in Table VIII.

Table VIII

Phase II Final Operating Conditions

Parameter	Value
Melter Temperature	1070 degrees Celsius
Slurry Feed Rate	50 mL/min
Impeller Height	4 inches
Impeller Speed	405 rpm
Auxiliary Temperature	1055 degrees Celsius
Air Sparger Flowrate	> 800 mL/min @ STP

Melter Temperature

The operating temperatures of the melter were limited by the limits on the materials of construction. The upper limit of the Inconel 601 was approximately 1070° C (Bickford, 1994). Based on previous melter operation, the lowest melter temperature which allowed acceptable melter operations was 1050° C. This range was not large enough to provide a great deal of operational differences between the low and the high temperatures. The higher operational temperatures did, however, show some noticeable improvements in prevention of the formation of a cold cap.

Impeller Speed and Height

The impeller speed was measured in Hertz (Hz) and converted to revolutions per minute (rpm) based on a correlation provided by the melter manufacturer. The impeller height was measured from the bottom of the vessel to the lower edge of the impeller blades. One restriction on the height of the impeller was that the blades must remain completely submerged in the molten glass in order to maintain the lowest current density across the impeller blades. If the blades are only partially submerged, the full amount of current is passed through a smaller area (the submerged area) and can increase the deterioration of the impeller. Therefore, in order to maintain an impeller height at 6 inches, for example, the additional glass height due to foaming would need to be the same height as the impeller blades, or approximately 2.25 inches. In a condition where the glass height was 6 inches (no foaming, full tank), the maximum impeller height would be approximately 3.75 inches measured from the bottom of the impeller to the bottom of the tank.

The impeller speed and height were important in determining the effectiveness of the vortex action in drawing the feed down into the melt. The relationship between the speed and height is an inverse relationship. If the impeller speed is increased, the impeller height must be decreased to prevent the exposure of the impeller within the vortex. If the impeller speed is decreased, the impeller height must be increased to create an effective vortex at the melt surface. During these trials, it was not possible to set the impeller at heights above 4 inches measured from the bottom of the blades to the bottom of the vessel for extended periods of time because the molten level including glass and foam was not consistently over 6.25 inches. Since the impeller blades have a height of approximately 2.25 inches, it was necessary to maintain a molten level including glass and foam of at least 6.25 inches in order to completely cover the impeller blades. The final set of operational values set the impeller height at approximately 4 inches and the impeller speed at 25 Hz or 405 rpm.

Air Sparger Feed Rate

Nitrogen was used during Phase II testing of the air sparger to test the influence of a separate gas stream on the operational feasibility of the melter system. There were no noticeable differences in melter operations at different gas flow settings. Under normal operating conditions, either oxygen or compressed air would be used as the sparging gas to assist in the combustion of the organic materials. The same results were expected for oxygen or compressed air that were found for nitrogen. The highest flow rate tested in Phase II was 800 mL/minute.

Slurry Feed Rate

The slurry feed rate was the most important of the five operating parameters in determining the melter operating stability. The three flowrates chosen in the initial matrix were too high for successful operation of the melter. Either the melt rate of the feed or the rate which feed was drawn down into the glass melt was too small to allow for successful operation of the melter. During the final refining trials, the feed rate was set at 50 mL slurry/minute or the equivalent of 1.36 kg/hour of glass. This flowrate could be maintained continuously without operator assistance. In addition to problems associated with the melt rate and the incorporation of the feed into the melt, higher flowrates seemed to lead to periodic extreme foaming. Lower flowrates did not produce these foaming instances.

Observation Categories

The qualitative observations recorded during Phase II trials primarily fell into three categories. These categories were the formation of a cold cap, melter output, and foaming. Each of these categories was directly related to the successful operation of the melter.

Formation of a Cold Cap

The prevention of the formation of a cold cap was the most important category of observations. The melter occasionally developed a layer of unmelted feed on the surface. This occurred if the vortex action of the impeller was not sufficient to draw the feed contents under the melt surface or the melt rate was inadequate. Occasionally a cold cap would begin to form and then disperse without operator assistance. These instances were usually attributed to insufficient vortex action. If the cause of the cold cap formation was more severe such as grossly insufficient vortex action or a too high slurry feeding rate, a very sturdy cold cap layer was created. This layer was able to support the incoming slurry and would eventually cover the entire molten surface. Since one of the primary reasons for testing the stirred tank melter was to prevent the resin from forming a crust, it was necessary to change the operating conditions to prevent the slurry from forming a cold cap.

Foaming

Foaming is generally caused by the release of water vapor and other gases such as carbon dioxide from the melt. During these trials, the foaming was attributed primarily to the steam released from within the melt as water was pulled below the surface and also from combustion gases formed due to the addition of the small amounts of organic compounds in the feed. During Phase II operation, the melter exhibited periodic instances of extreme foaming. These instances generally occurred if the melter temperature dropped well below the setpoint and the joule heating circuit was forced on at high amperage. The foaming would quickly subside if the power to the joule heating circuit was turned off. It was unclear as to the exact cause of these instances. Lower feed rates generally resulted in fewer occasions of extreme foaming.

Melter Output

The overflow spout drain in the WV-0.25 was designed to allow for a steady output of glass as long as the molten glass level was above 15.24 cm (6 in). However, since the operating temperature is limited in the WV-0.25 melter and the drain diameter is so small, it was easy for the glass to cool as it traveled downward through the exit pipe of the melter. This sometimes caused a "nesting" effect, small strands of glass collecting on top of each other within the drainpipe, which led to clogging of the drain hole. It was therefore necessary from an operational standpoint to be able to operate the melter so that a steady stream exited the melter. In order to maintain a steady pull from the overflow drain, it was necessary to heat the lower two inches of the drain tube with a propane burner. The drain tube heating system effectively heated the entire drain tube except for these bottom few inches. There were no problems with maintaining a steady output from the melter when the propane burner was used as long as the feed system was operating properly as well. In cases of high slurry feed rates, the melter was unable to provide enough power to sufficiently melt all of the incoming slurry and therefore the melter pull or output rate was less than the expected based on the feed rate.

Phase III: Oxygen Transfer Tests

There were two types of oxygen transfer tests performed during the Phase III research. The first type was a batch type test. This type of test involved filling the melter with a known amount of glass containing a known amount of iron and then reducing the glass by adding a reducing agent such as carbon. Samples were then taken over the next several hours and analyzed for the Fe(II)/Fe(total) ratio. Two of these tests were performed with different operational conditions. Both tests used impeller agitation to assist in oxygen transfer. During one of the tests, water was fed to the melter during the course of the run. The second type of test was a continuous feed test. This test closely resembled operational conditions. Slurry was fed to the melter at approximately 50 mL/min and reducing agent was added to the melt in order to increase the Fe(II)/Fe(total) ratio. Samples were taken over the next several hours and analyzed for the Fe(II)/Fe(total) ratio. A zirconium oxide redox probe was also used during this test to continuously measure the redox state of the glass.

It is assumed that the oxygen transfer rate can be approximated by the rate of oxidation of FeO. This means that oxygen transfer rates can be estimated by observing the change in the Fe(II)/Fe(total) ratio and knowing the total amount of iron in the melt. In other words, the change from FeO to Fe_2O_3 uses the following stoichiometry:

$$4\,FeO + O_2 \rightarrow 2\,Fe_2O_3\,.$$

Thus, the number of moles of oxygen entering the melt can be approximated by multiplying the moles of iron in the melt that change from Fe(II) to Fe(III) by the stoichiometric ratio of Fe(II) to O_2 equal to 0.25.

Recovery Curve During Batch Test

Data from the first batch type test that used only impeller agitation to assist in oxygen transfer is illustrated in Figure 8. A relatively weak ($R^2 = 0.76$) equation describes this curve linearly. This equation is

$$y = 0.00230 * t + 1.400$$

where y is the moles of oxygen in the melt existing as Fe_2O_3 and t is the elapsed time in minutes.

This equation gives an approximation of the oxygen transfer rate as 0.00230 moles O_2 per minute with the impeller running at approximately 405 rpm and at a height of 2.25 inches from the bottom of the vessel.

In order to calculate the feed rate of resin which this oxygen transfer rate could accommodate, it is simpler to first look at carbon. The combustion of carbon follows the stoichiometry

$$C + O_2 \rightarrow CO_2.$$

Thus, an oxygen transfer rate of 0.0023 moles O_2/min could accommodate 0.0023 moles C/min or 0.0276 grams C/min. Since it was concluded from Phase I research that approximately 4 grams of resin behaved the same as 1 gram of carbon, a resin flow rate of 0.1104 grams resin/min could be accommodated under these test conditions.

Data from the second batch test that used a combination of impeller agitation and water feed is illustrated in Figure 9. A stronger linear fit ($R^2 = 0.97$) describes this curve. The linear equation is

$$y = 0.00153 * t + 2.04$$

where y is the moles of oxygen in the melt existing as Fe_2O_3 and t is the elapsed time in minutes. This equation gives an approximation of the oxygen transfer rate as 0.00153 moles O_2/minute. Using the same procedure as above, the equivalent flow rate of resin is 0.0734 grams resin/min under otherwise similar test conditions.

The oxygen transfer rate was lower in the second batch test. The only difference between the two tests was the addition of the water stream. As seen in the crucible studies, the presence of water seemed to hinder the reoxidation of the melt. As mentioned earlier, it is not possible to make any definite conclusions concerning the effect of water on the redox state of a glass melt based on the amount of relevant data.

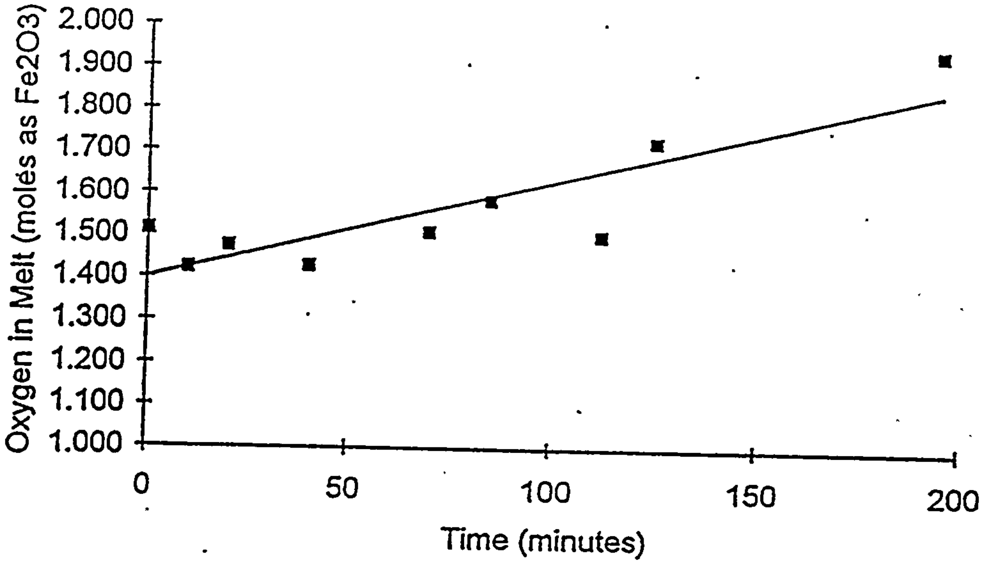

Figure 8. Recovery Curve for Phase III Batch Test One

Recovery Curve During Continuous Slurry Feed Test

The continuous feed test was performed in order to evaluate the oxygen transfer when slurry was being continuously fed to the melter which more closely resembled normal operating conditions. In addition to sampling exit glass for Fe(II)/Fe(total) to evaluate the oxidation of FeO, a zirconium oxide redox probe was used to continuously monitor the redox state of the glass.

After the full 300 grams of resin had been added batch style to the melt to reduce the Fe_2O_3 to FeO, the melt was allowed to reoxidize. During the last 55 minutes of recovery, it was found that the Fe(II)/Fe(total) ratio increased linearly. A linear equation ($R^2 = 0.98$) can be used to describe the final 55 minutes of data shown in Figure 10. This equation is

$$y = 0.00956 * t + 2.54$$

where y is the moles of oxygen in melt existing as Fe_2O_3 and t is the elapsed time in minutes. The approximate oxygen transfer rate under these test conditions was 0.00956 moles O_2/min. This oxygen transfer rate would accommodate a resin feed rate of 0.459 grams of resin/minute..

Phase IV: Vitrification of Ion Exchange Resin

A mixture of nonradioactive cesium-contaminated resin and the slurry described earlier in Chapter 4 composed of frit 202, metal oxide sludge, and PHA material was fed to the melter for 20 hours or the equivalent of roughly 3.1 tank volumes throughput. During the course of the run, samples of feed, exit glass, bubbler tank solution, and scrubber solution were taken in order to approximate a cesium mass balance on the melter and to determine the effect of the resin feed on the redox state of the glass. Samples of the off gas were also taken using a modified method 5 train and a multiple metals sampling train in order to characterize the off gas with respect to any semi-volatile organic compounds present as products of incomplete combustion, volatile metals, and particulate matter.

Overall Cesium Mass Balance

A mass balance on cesium was performed around the melter system. This balance involved the feed stream, the exit glass, and the off gas. It covered the entire 20 hours (1385 minutes) of run time.

The following sections explain how each stream was analyzed for the total cesium content.

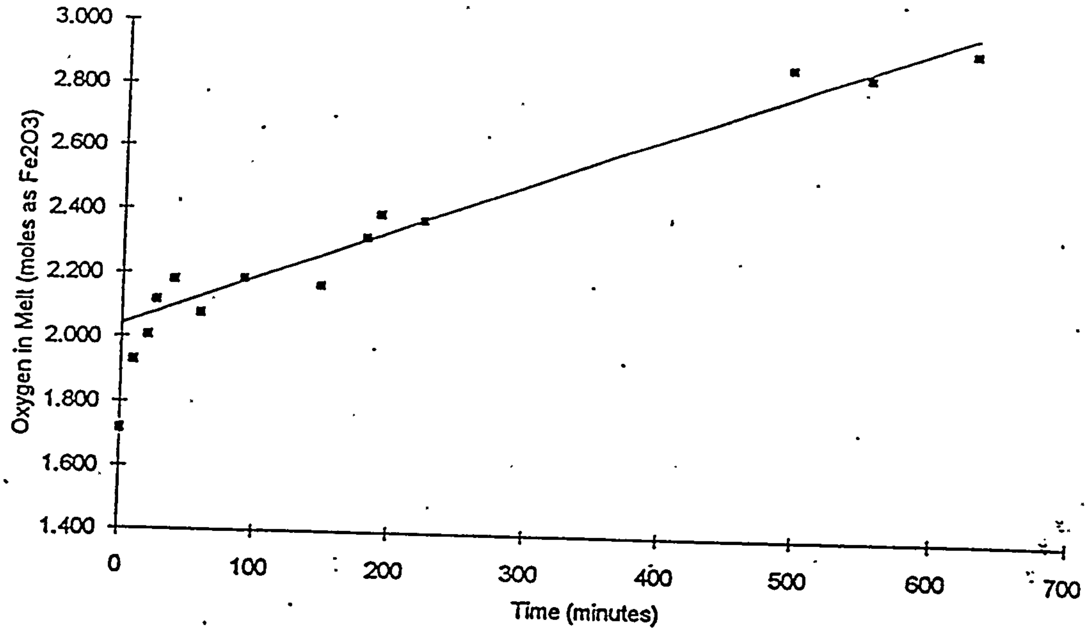

Figure 9. Recovery Curve for Phase III Batch Test Two

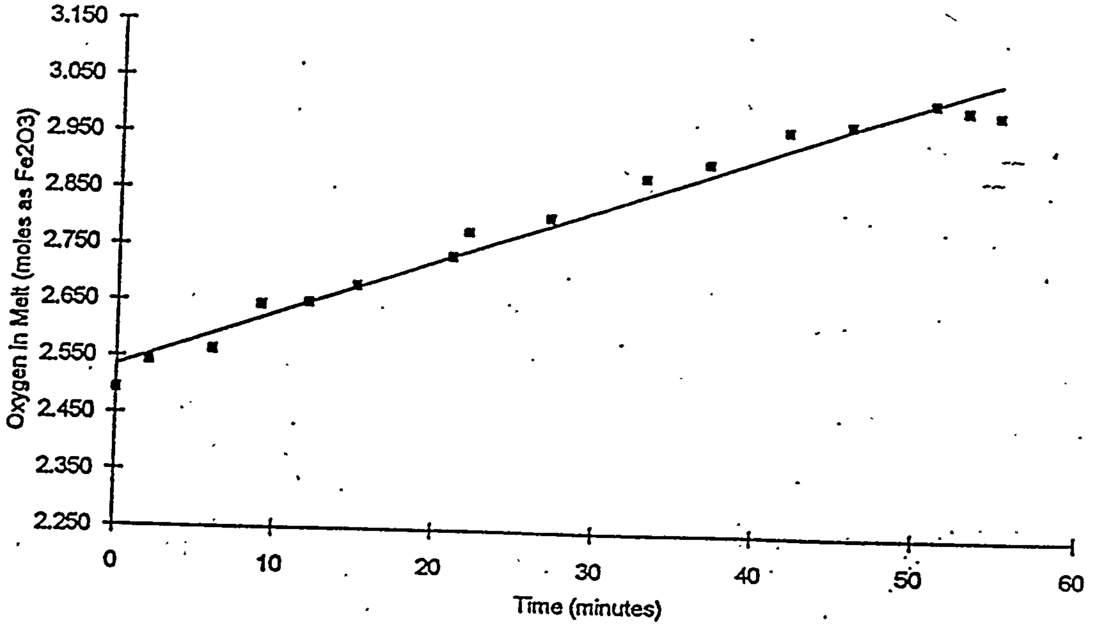

Figure 10. Recovery Curve for Phase III Continuous Feed Test

Feed Stream

The feed slurry mixture was prepared in a 5 gallon bucket during the course of the run. When the slurry level dropped in the bucket, more of the resin and slurry mixture was added in the same ratio as existed in the initial batch. This ratio was approximately 1.302 grams of wet resin per 50 mL of slurry. Duplicate samples were taken from the initial batch and the final batch mixtures. The samples were taken as the slurry was pumped from the slurry feed nozzle so they would be an accurate representation of what was actually being fed to the melter.

The samples taken at the beginning and at the end of the test were analyzed by CELS for certain oxides and loss on ignition (LOI) at 850°C. The results of these analyses are shown in Table IX. It is apparent from the results that the composition of the slurry being fed to the melter changed over the course of the run. Based on the predicted composition of the mixture, the weight percent of Cs_2O in the dry slurry solids should be approximately 0.396 wt%. Neither of the sample analyses reflect this predicted amount. One possible reason why the initial results are much lower than the predicted results could reflect the method of analysis by CELS. Each sludge sample was dried at 850°C. The high volatility at this drying temperature could result in a lower measured weight percent. One possible reason why the measured weight percent of cesium in the final sample analysis is much higher than the predicted amount is inadequate mixing in the bucket. Each of the measured oxide weight percents in the final slurry increase from the initial sample analysis result except silicon, magnesium, lithium, and boron. These are 4 of the 5 oxides which constitute frit 202. Sodium is the other oxide in the frit but it is also present in large amounts in the PHA material and the oxide sludge so a decrease in frit 202 would not significantly affect the final weight percent of sodium. Since no evidence of settling was seen during the Phase IV operation by visual inspection or by probing the bottom of the bucket with a rod, no corrective action was taken during the test.

In addition to the oxide analysis and LOI test, a semi-quantitative inspection was done on the glass to determine why the oxide weight percentages did not equal 100 percent. This type of chemical analysis gives weight percentage ranges for each oxide. The results of this analysis are shown in Table X. It appears that the oxides of titanium, lead, copper, and zirconium which were not analyzed for by CELS probably make up the difference between the sum of the weight percentages and 100 percent.

In order to calculate the total amount of cesium fed to the melter, the total amount of cesium used in making up all of the slurry/resin batches for the full 20 hours and the amount of cesium remaining in the bucket after the test was complete must be known. The difference between these two values is the total amount of cesium fed to the melter. The total amount of wet resin used in making the slurry and resin mixture was 2036 grams. Based on the resin being 38.40% solids and loaded with cesium at a mass ratio of 0.16 to 1, the total amount of cesium used in making the entire amount of feed mixture was 125.09 grams. The full 125.09 grams of cesium was not fed to the melter, however, because there was 20.18 kg of feed mixture remaining in the bucket after the testing was complete. The amount of cesium remaining in the bucket after testing was completed is difficult to accurately define because the CELS oxide analysis results do not agree with what would be predicted based on the quantities of resin and slurry used in making the batch. Both the predicted value for the weight percent of Cs_2O in the final slurry and the final CELS analysis value were used in the cesium mass balance calculations to provide a cesium retention range. If the calculations are done based on the predicted 0.396 wt% Cs_2O in the residual feed mixture and an LOI of 64.75 percent, the total amount of cesium which remained in the bucket was 25.26 grams. Therefore, the total amount of cesium fed to the melter is calculated as 99.83 grams. If the CELS analysis value of 0.550 wt% Cs_2O is used in the same calculation, the total amount of cesium which remained in the bucket was 35.08 grams. This results in a total amount of cesium fed to the melter of 88.18 grams.

Table IX

Phase IV CELS Feed Analysis Results

Oxide	Analysis of Initial Sample (wt%)	Analysis of Final Sample (wt%)
Cs	0.26	0.55
K	2.39	2.90
Li	4.85	4.50
Na	6.46	6.54
Al	2.95	3.35
B	7.77	7.60
Ca	1.02	1.26
Cr	0.13	0.16
Fe	12.05	14.20
Mg	1.55	1.48
Mn	2.63	3.12
Ni	1.11	1.30
Si	54.35	50.75
TOTAL	97.51	97.68
Loss on Ignition	63.00%	66.50%

Table X

Phase IV Semi-Quantitative Analysis of Feed

Range (wt%)	Element
>30	
10-30	Fe, Si
3-10	Al, Na
1-3	B, K, Mg, Mn
.3-1	Ca, Cu, Ni, Zr
.1-.3	Pb, Ti
.03-.1	Ba, Cr
.01-.03	Sr
.003-.01	Mo
.001-.003	
<0.001	Ag

Glass Stream

The glass was collected in large graphite crucibles during the course of the run. Samples of the exit glass were collected on a stainless steel plate approximately every thirty minutes. Four of the glass samples were sent to CELS for oxide analysis. Table XI shows the final analysis results. As seen in Figure 11, the temporal changes in cesium concentration resemble what would be expected in a continuously stirred tank reactor (CSTR).

In order to calculate the total amount of cesium retained in the glass, it is necessary to know the average weight percent of Cs_2O in the glass collected in the crucibles and also the weight percent of Cs_2O in the glass remaining in the vessel after the run was completed. The sum of the cesium in the collected glass and the glass remaining in the crucible is the total cesium retained in the glass.

The total amount of cesium in the glass collected in the crucibles can be calculated by dividing the area of the curve in Figure 11 by the total run time to get an average concentration. A second order polynomial was used as a basis in order to calculate the area. This polynomial was

$$C = -1.427E\text{-}07\ t^2 + 4.47E\text{-}04\ t + 2.19E\text{-}04$$

where C is the concentration in the exit glass in wt% Cs_2O and t is the time in minutes. If this curve is integrated from t = 0 to t = 1385 minutes, the area under the curve is calculated as 302.65 wt% Cs_2O•min. If the area is divided by the total time, the result is the average concentration or 0.218 wt% Cs_2O. If the average concentration is multiplied by the total glass collected in the crucibles, the result is the total amount of Cs_2O collected in the exit glass. Since the total amount of glass collected in the crucibles was 25.87 kg, the total amount of cesium in the collected glass of 53.20 grams.

The cesium in the glass remaining in the vessel after the testing was completed can be calculated by multiplying the final weight percent of Cs_2O in the exit glass by the total amount of glass remaining in the vessel. Table XI shows the average last measured weight percentage of Cs_2O to be 0.347. The total amount of glass remaining in the vessel was 8.85 kg giving a total amount of cesium remaining in the vessel after the test was complete of 28.97 grams. The total amount of cesium retained in the glass is the sum of these two values or 82.17 grams. This is between 82.3 percent and 93.2 percent of the total cesium fed to the melter.

Off Gas Deposits

The off gas deposits were taken from the stainless steel piping immediately exiting the melter and the 2 inch riser. The deposits were dark brown to black in color and had the texture of fine soot. There were some very small yellow particles mixed in with the soot like material. A total of 12.70 grams of deposit were collected. The analysis of these solids provided by CELS is shown in Table XII. CELS also performed a semi-quantitative spectrographic analysis on the deposits. These results provided estimates of the oxide weight percent of all elements present in the sample. Five elements were not analyzed for in the quantitative analysis which showed up in significant amounts in the semi-quantitative analysis. These elements were copper, zirconium, titanium, barium, and lead. Estimated weight percentages provided by CELS for these five oxides are also shown in Table XII.

A loss on ignition test at 850 degrees Celsius was performed on the solids collected from the bubbler solution. These solids were similar to the solids collected as deposits on the off gas piping in appearance. The average loss on ignition of these solids was 8.96 weight percent.

The sum of the weight percentages based on the quantitative analysis, the semi-quantitative analysis and the loss on ignition using the bubbler solution solids was 98.0

Table XI

Phase IV CELS Analysis of Exit Glass Samples Taken at Different Times

wt% oxide	0 minutes	627 minutes	920 minutes	1385 minutes
Cs	0.00	0.24	0.30	0.35
K	2.43	2.70	2.76	2.76
Li	4.75	4.79	4.82	4.80
Na	6.69	6.69	6.73	6.76
Al	3.09	3.05	3.04	3.07
B	7.90	7.75	7.76	7.80
Ca	1.70	1.24	1.23	1.24
Cr	0.19	0.17	0.17	0.17
Fe	12.00	12.25	12.50	12.57
Mg	1.56	1.53	1.56	1.56
Mn	2.64	2.74	2.80	2.80
Ni	1.15	1.18	1.20	1.21
Si	54.10	52.70	53.55	53.67
Total	98.19	97.01	98.38	98.73

Note: The analysis results shown for 1385 minutes are the average of two analysis results.

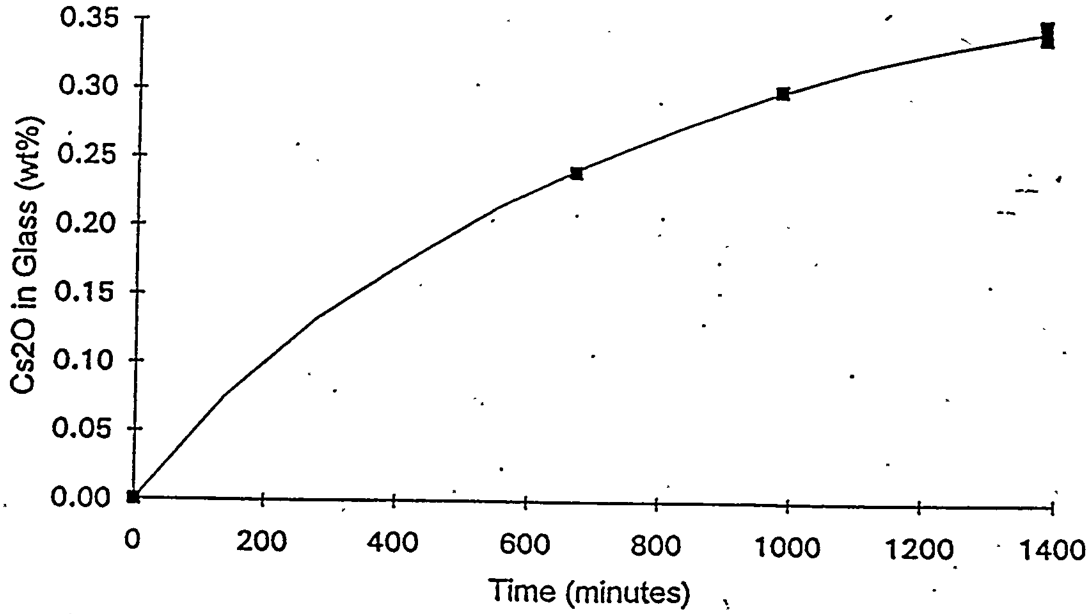

Figure 11. Phase IV CELS Analysis Results for Cs_2O in Glass

percent. Since estimates were used for copper, zirconium, titanium, barium, lead, and carbon, the 2.0 percent which is not accounted for based on these analyses is not significant.

Based on the CELS value for the weight percentage of Cs_2O and the total mass of solids collected, the total amount of cesium existing in the off gas deposit is 0.14 grams. This is between 0.14 and 0.16 percent of the total cesium fed to the melter.

Bubbler Solution

The purpose of the bubbler tank in combination with the venturi scrubber and spray quencher was to remove the larger particles from the off gas stream and also to cool the off gas stream enough to condense most of the volatile metals. Samples of the bubbler solution were taken from the liquid leaving the bubbler tank through the level controller. Four of these samples were filtered and sent to SRS for analysis. The results of the analyses are listed in Table XIII and shown graphically in Figure 12.

In order to calculate the amount of volatile cesium captured in the bubbler solution, it is necessary to know the total amount of cesium leaving the bubbler tank through the level controller and the total amount of cesium remaining in the bubbler tank after the testing was complete.

The total amount of cesium that was captured in the bubbler solution which exited the bubbler tank through the level controller can be calculated by multiplying the area of the curve in Figure 12 by the average flow rate. A second order polynomial was used as a basis in order to calculate the area. This polynomial was

$$C = -1.157E\text{-}06 \cdot t^2 + 3.192E\text{-}03\, t + 4.763$$

where C is the concentration in the exit bubbler solution in mg Cs/L and t is the time in minutes. If this curve is integrated from t = 0 to t = 1385 minutes, the area under the

Table XII

Phase IV CELS Oxide Analysis, Semi-Quantitative Analysis, and Loss on Ignition Results of Off Gas Deposits

Oxide	Final Analysis wt% as oxide
Cs	1.17
K	6.49
Li	0.77
Na	7.25
Al	6.53
B	7.67
Ca	3.00
Cr	0.61
Fe	32.10
Mg	0.50
Mn	6.82
Ni	2.89
Si	6.16
Cu	1.25 (a)
Zr	4.00 (a)
Ti	1.20 (a)
Ba	0.30(a)
Pb	0.30 (a)
C	8.96 (b)

(a) - These results are estimated based on the semi-quantitative spectographic analysis provided by CELS

(b) - The result is based on a loss on ignition at 850 degrees Celsius of the solids collected in the bubbler solution.

Table XIII

Phase IV SRS Results of Bubbler and Scrubber Solution Analyses for Cesium

Time (minutes)	Bubbler Solution (mg Cs/L)	Scrubber Solution (mg Cs/L)
0	0.0046	Not Detected
670	2.6942	0.2271
1075	2.1131	0.4518
1281	2.1617	0.5491
1385	2.2278	0.6615

curve is calculated as 2043.727 mg Cs•min/L. Since the average flowrate of bubbler solution exiting the bubbler solution tank was approximately 0.916 L/min, the total amount of cesium in the exiting bubbler solution was 1.87 grams.

The cesium in the glass remaining in the vessel after the testing was completed can be calculated by multiplying the final concentration of cesium in the bubbler solution by the total amount of bubbler solution remaining in the tank. The final concentration of cesium in the bubbler solution was 2.23 mg Cs/L. The total amount of solution remaining in the tank was 91.77 liters giving a total amount of cesium remaining in the tank after the test was complete of 0.205 grams. The total amount of cesium captured in the bubbler solution is the sum of these two values or 2.07 grams. This is between 2.1 and 2.4 percent of the total cesium fed to the melter.

The particulate form of cesium captured in the off gas treatment system was not quantified. When the samples were being pulled from the level controller tube, there were small quantities of solids present in the solution. The total particulate cesium in the off gas was hard to accurately quantify for two primary reasons. First, the solids captured in the bubbler solution were not analyzed. Since there was a significant amount of solids present in the bubbler tank at the beginning of the run, it was felt that an analysis of these solids would not be valuable. Most of the solids were removed from the tank prior to the run but some residual solids remained. Second, the samples were not filtered immediately. The solids were allowed to settle in the sample container and cesium attached to the particulate could have desorbed into solution.

Scrubber Column Solution

Scrubber solution samples were taken from the solution immediately after it left the scrubber column. These samples had no visually detectable solids present. Four of these samples were sent to SRS for analysis. The results of these analyses are listed in Table XIII and showed graphically in Figure 13. The total amount of cesium captured by the scrubber column solution can be calculated by multiplying the total volume of solution in the scrubber tank by the concentration of the solution after the run was completed. Based on a final scrubber solution volume of 325.4 liters and a final concentration of 0.662 mg/L, the total cesium captured in the scrubber solution was 0.215 grams. This represents between 0.22 and 0.24 percent of the total cesium fed to the melter.

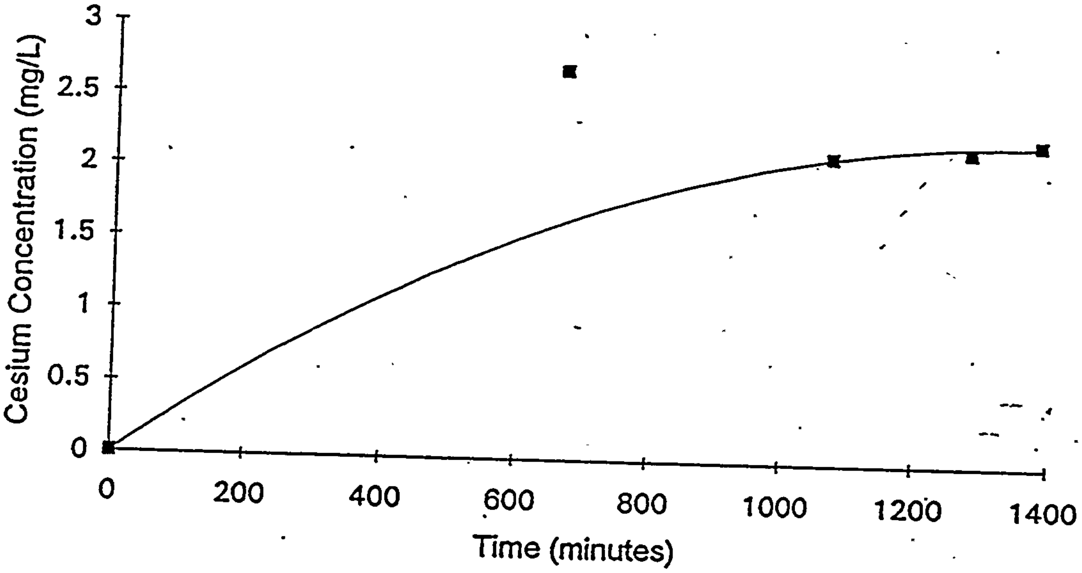

Figure 12. Phase IV Results from Bubbler Solution Analysis

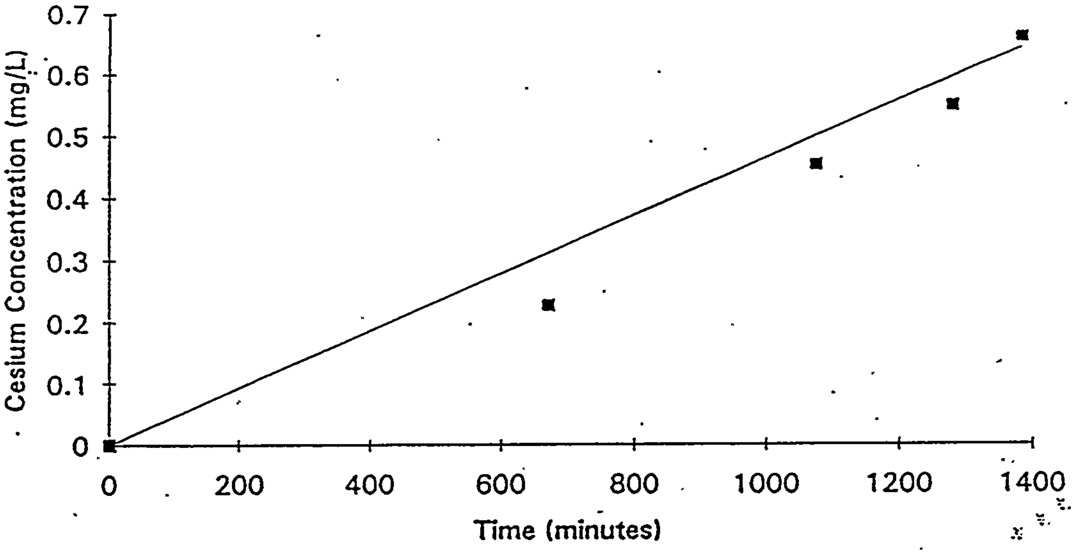

Figure 13. Phase IV Results from Scrubber Solution Analysis

Summary of Results from the Mass Balance

A summary of the results from the cesium mass balance is shown in Table XIV. Between 84.7 and 96 percent of the cesium that entered the melter system was accounted for in the exit glass stream and the off gas treatment system. A cesium retention efficiency in the glass was calculated as between 82.3 and 93.2 percent. Between 2.4 and 2.8 percent of the cesium was found in the off gas treatment system.

There are several reasons for having a fraction of cesium unaccounted for in the mass balance. First, it was already mentioned that the calculations for the total amount of cesium fed to the melter were probably inaccurate because it was unclear on the total amount of cesium remaining in the bucket after the test was complete. Second, cesium present in the particulate form captured in the bubbler solution was not included. If the tank had been cleaned thoroughly before the test and samples could be filtered quickly, the results from this sampling could be valuable. Third, the underlying assumption that all of the cesium was captured in the off gas system has not been confirmed. It is possible that some of the cesium could have passed through the scrubber column and therefore not been included in the mass balance. Chapter 6 lists some of the recommendations which could possibly improve the accuracy of this type of analysis.

Analysis of Off-Gas

The off gas stream was sampled for metals and semi-volatile organic compounds using a multiple metals sampling train and a modified method 5 sampling train, respectively. The field data sheet for each of these sampling runs is presented in Appendix B.

Table XIV

Phase IV Cesium Mass Balance Summary

Location	Grams of Cesium	Percent of Total Cesium
Feed Stream	88.18 - 99.83	
Exit Glass	82.17	82.3 - 93.2
Off Gas Deposits	0.14	0.14 - 0.16
Bubbler Solution (Particulate)	Not Calculated	Not Calculated
Bubbler Solution (Volatile)	2.07	2.1 - 2.4
Scrubber Solution	0.22	0.22 - 0.24
Unaccounted Cesium	15.23 - 3.58	4.00 - 15.24

Multiple Metals Sampling Train

The multiple metals sampling train was operated for one hour. It was run in accordance with the proposed method 29 with some minor additions. The two impingers normally containing a permanganate solution contained additional nitric acid and hydrogen peroxide. This was done since some of the metals which were sampled for were not on the list of metals for which the sampling train was designed. By adding the additional impingers at the end, the efficiency of removing the metals from the off gas was increased. The final two impingers were also analyzed separately from the first three impingers so the metals removed across the train of impingers could be seen by examining the concentration gradient.

During the multiple metals sampling run the feed stopped for approximately 10 minutes due to a blockage in the feed nozzle. This problem was corrected as quickly as possible but still significantly affected the results.

The total particulate loading was not performed on this sampling run because the samples of filter and front end washes were sent to the outside laboratory. The concentration of water vapor in the off gas stream was 71.0 grams per cubic meter at an average stack temperature of 636°C. The sampling rate was approximately 130 percent of isokinetic. This means that the average velocity pulled through the sample nozzle was 1.3 times the velocity of the off gas in the pipe.

The results from the analysis of the multiple metals sampling train components are shown in Table XV. These results are in total micrograms of a specific metal found in each component of the sampling train. It was practically impossible to make any quantitative conclusions based on this data because of the feeding problem. The analyses were divided into two main parts, the front end and the back end. The front end analysis involves a combined sample of the quartz filter, the acetone wash of the probe liner, nozzle, and filter bell inlet, and the nitric acid wash of the same three components. The back end analyses include the five impingers. The first impinger is a knock out impinger and serves to remove water from the sampled gas stream. The following four impingers contain a nitric acid/hydrogen peroxide mixture which serves to remove volatile metals from the sampled gas. The first, second, and third impingers were analyzed together. The fourth impinger and fifth impinger were each analyzed separately.

The front end and the last two impingers were not analyzed for silicon and boron. According to the laboratory which performed the analyses, conclusions concerning particulate silicon are almost impossible because of the silicon present in the quartz filter. Boron analyses are also difficult because much of the boron is lost through volatilization during the filter digestion step. The final two impingers were not analyzed for silicon and boron due to an irreversible mistake by the lab.

Some important qualitative observations can be made from the multiple metals sampling train analysis. First, the partitioning of the cesium shows that less than half of the cesium present in the off gas exists in the volatile form. Any quantitative observations drawn from the results of this analysis are inconclusive due to the feed system malfunction. Approximately 34 percent of the total cesium which was captured in the multiple metals sampling train was found in the impingers (volatile) rather than on the filter (particulate). Second, there were several other metals which partitioned significantly into the volatile form. Other elements which partitioned more than 10 percent in the volatile form include lead (15.2%), chromium (25.4%), sodium (14.5%), calcium (10.7%), lithium (15.0%), and potassium (18.5%).

The amount of volatile cesium collected in the volatile form in the bubbler and scrubber solutions can be roughly checked by the amount of volatile cesium collected in the Multiple Metals Sampling Train. The total amount of volatile cesium collected in one hour using the Multiple Metals Sampling Train was 2362 micrograms through a 0.375 inch diameter orifice. If this value is corrected to what passed through the 2 inch pipe, the approximate cesium flowrate is 0.0672 grams Cs per hour. Thus, during a trial lasting 1385 minutes, the total amount of volatile cesium that would be expected is 1.55 grams. The total amount of cesium in the bubbler and scrubber solution from Table XIV was 2.29 grams. Although these values are not identical and the amount captured is more than the amount predicted through a rough estimation, this comparison shows that the values calculated for the amount of volatile cesium in the bubbler and scrubber solutions is at least reasonable.

Modified Method 5 Sampling Train

Table XVI lists the six predominant semi-volatile organic compounds found in the off gas based on results from the modified method 5 sampling train analysis. They were benzoic acid ($C_6H_5CO_2H$), naphthalene ($C_{10}H_8$), phenanthrene ($C_{14}H_{10}$), fluorene ($C_{13}H_{10}$), fluoranthrene ($C_{16}H_{10}$), and pyrene ($C_{16}H_{10}$). Each of these are feasible since they are all based on an aromatic or ring structure. Since the resin is a polymer based on resorcinol which is also an aromatic, it makes sense that the major products of incomplete combustion would also be aromatics.

The modified method 5 sampling train also provided results for particulate loading calculations. The particulate loading was 433 mg per cubic meter of off gas at an average temperature of 664°C. The major components of these solids based on the analysis of the multiple metals sampling train solids and the off gas deposits were boron, iron, sodium, manganese, potassium, calcium, aluminum, and carbon.

The total mass of particulate captured in one hour of sampling through a 0.375 inch orifice was 0.5059 grams. If this value is corrected to what passed though the 2 inch pipe, the estimated total particulate emissions is 14.39 grams of particulate per hour. The slurry feed rate used during the trial was approximately 50 mL/min. Assuming a specific gravity of 1.2 and an LOI of 64.75 percent, the solids feed rate into the melter was approximately 1215 grams per hour. Thus, the amount of particulate captured in the off gas accounts for approximately one percent of the total solids fed to the melter.

Table XV

Phase IV Multiple Metals Sampling Train Results

Element*	Front End Wash Blank (micrograms)	Back End Wash Blank (micrograms)	Front End Analysis (micrograms)	Impingers 1,2, and 3 (micrograms)	Impinger 4 (micrograms)	Impinger 5 (micrograms)
Cesium	<1.00	<1.00	4510	2020	174	167
Nickel	1.79	2.11	7880	530	2.75	2.82
Silicon	NA	NA	NA	548	NA	NA
Lead	1.49	<1.00	1130	174	14.5	13.8
Barium	4.86	<1.00	601	57.5	<1.00	<1.00
Iron	32.5	6.01	72200	4750	31.2	14.8
Manganese	1.38	<1.00	15000	1080	2.41	2.15
Magnesium	10.3	<6.25	788	62	<6.25	<6.25
Chromium	1.4	5.4	395	113	10.9	10.6
Sodium	128	18.7	22200	3280	283	223
Calcium	47	<12.5	3980	427	28.2	22[illegible]
Aluminum	100	6.21	8720	775	19	10
Lithium	<1.00	<1.00	2370	381	20.6	19.3
Potassium	32.5	16.5	23700	4700	342	332
Boron	NA	NA	NA	8320	NA	NA

Table XVI

Phase IV Modified Method 5 Sampling Train Results

Compound	Analysis One (micrograms)	Analysis Two (micrograms)	Blank (micrograms)
Benzoic Acid	348.87	304.73	17.36
Napthalene	297.44	495.30	5.14
Fluorene	11.65	9.50	(1.43)
Phenanthrene	113.82	130.11	(1.07)
Fluoranthene	52.50	71.87	(0.84)
Pyrene	83.21	81.55	(0.90)

Note: Numbers in Parenthesis Indicate Detection Limit

Redox Ratio

Samples of the glass were taken periodically from the exiting glass stream and analyzed for the Fe(II)/Fe(total) ratio. The results of this analysis are shown in Figure 14. Redox measurements using the zirconium oxide redox probe were also taken but did not correlate with the corresponding Fe(II)/Fe(total) ratio so these probe results were not used in the redox analysis. None of the samples analyzed exceeded 0.3 for the Fe(II)/Fe(total) ratio. The average Fe(II)/Fe(total) ratio after approximately one hour of operating time was 0.176.

At a feed rate of 0.50 grams of dry resin per minute, it appears that there would be no significant problems associated with an over reduced melt.

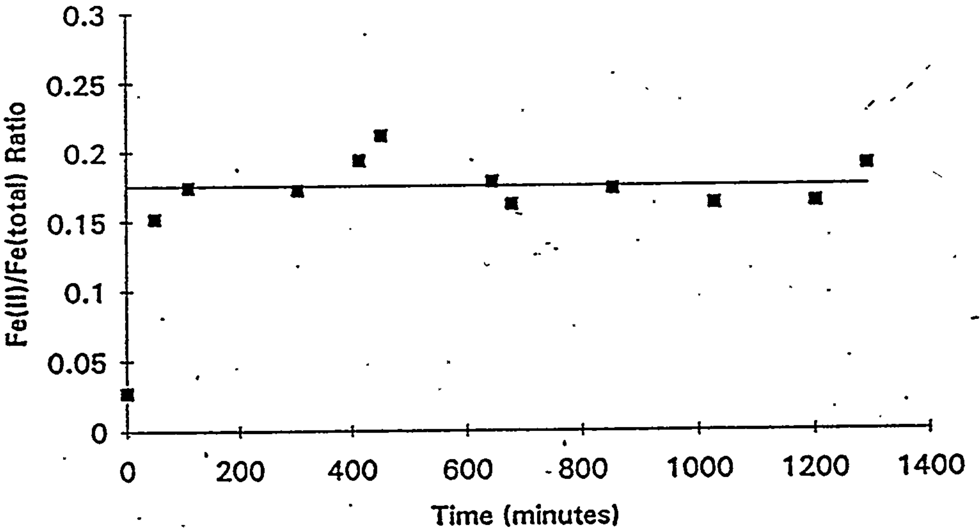

Figure 14. Phase IV Fe(II)/Fe(total) Ratio Results

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were reached after completing the four phases of research.

1. The reducing effectiveness of the organic resin used in this research is approximately four times less than elemental carbon on a mass basis.

2. During the crucible study, the average cesium retention for those glass samples which had resin as a reducing agent was 88.6 percent with a standard deviation of 6.6 percent. The average cesium retention for those glass samples which had elemental carbon as a reducing agent and cesium added as cesium carbonate was 66.8 percent with a standard deviation of 4.9 percent.

3. There was no apparent correlation between the final redox state of a glass and the cesium retention based on the crucible study data.

4. Based on the limited amount of data, the addition of water seemed to result in a more reduced final glass sample.

5. A set of operating conditions which allowed for successful operation of the melter were defined. Slurry feed rate and melter temperature were the two most important operational parameters in achieving successful melter operation.

6. The oxygen transfer rate under batch type conditions using only the impeller agitation was 0.0023 moles O_2/min for a 0.25 ft^2 melter. When water was fed to the melter under similar operating conditions, the oxygen transfer rate dropped to 0.00153 moles O_2/min for a 0.25 ft^2 melter.

7. The oxygen transfer rate with a slurry feed rate of 50 mL/min, an oxygen sparging rate of 1000 mL/min at STP, and using impeller agitation was 0.00956 moles O_2/min. This is the equivalent of approximately 0.50 grams of dry resin/min.

8. During Phase IV, the melter was successfully operated for 20 hours using a feed mixture of slurry and resin contaminated with nonradioactive cesium. There were no significant operational problems during the course of the run.

9. Between 82.3 and 93.2 percent of the cesium fed to the melter during Phase IV was retained in the glass. Between 4 and 15.5 percent of the cesium was unaccounted for in the mass balance.

10. There were six primary semi-volatile organic compounds found in the off gas sampling. They were benzoic acid, naphthalene, fluorene, phenanthrene, fluoranthene, and pyrene.

11. The multiple metals sampling train results were used as a qualitative check on the form, particulate or volatile, elements took in the off gas. Elements which were found to be at least 10 percent in the volatile form during the Phase IV experiment include lead (15.2%), chromium (25.4%), sodium (14.5%), calcium (10.7%), lithium (15.0%), and potassium (18.5%).

12. The particulate loading during the Phase IV experiment was approximately 433 mg per cubic meter of off gas at an average temperature of 664°C. The primary elements found in these solids were carbon, boron, iron, sodium, manganese, potassium, calcium, and aluminum.

The following recommendations should also be considered when additional work is performed dealing with the vitrification of ion exchange resin or other organic compounds in a stirred tank melter.

1. The dilution air pulled through the off gas treatment system should be minimized in order to allow for accurate calculations of off gas components. Accurate off gas sampling results can assist in performing a mass balance.

2. More oxygen transfer tests should be performed in order to define a set of parameters which maximize the rate of oxygen transfer into the glass melt so that the corresponding feed rate of resin can also be maximized.

3. Another test similar to the Phase IV study should be performed for a longer period of time in order to assure steady-state operation.

4. Methods and equipment should be developed so that reproducible results can be acquired without having to send samples to a third party for analysis. This would eliminate any financial boundaries on the number of samples that can be analyzed and greatly increase the amount of data.

5. Off gas sampling should be done at other locations along the off gas treatment system such as downstream from the scrubber and between the bubbler solution tank and the scrubber in order to calculate other values such as scrubber efficiencies.
6. Attempts should be made to incorporate a redox probe such as the one used in these experiments into all phases of research.
7. A better and more reliable feed system should be established which is able to feed the slurry and resin mixture homogeneously at metered rates.

APPENDICES

Appendix A

Sample Calibration Curve from Fe(II)/Fe(total)
Redox Analysis

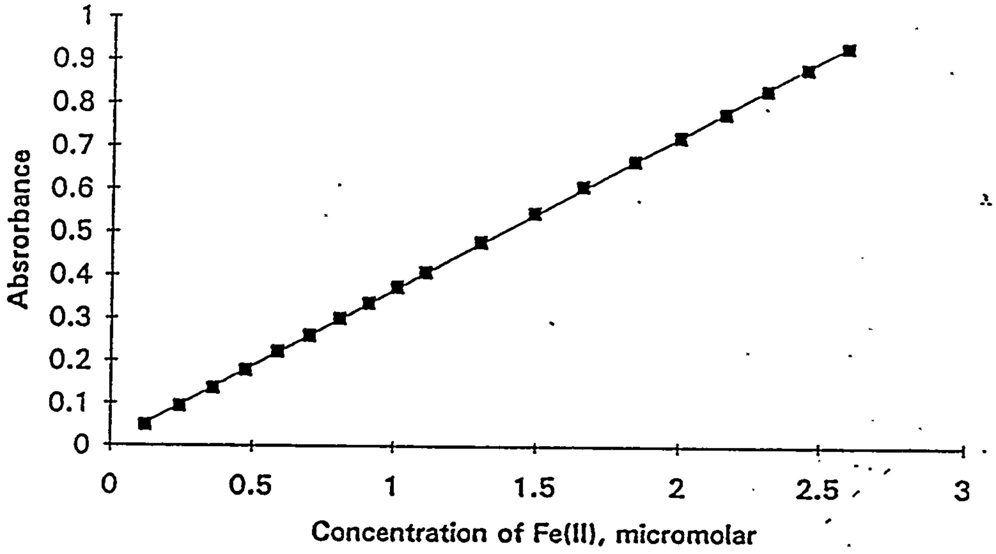

Figure A-1. Sample Calibration Curve from Fe(II)/Fe(total) Redox Analysis

Appendix B

Field Data Sheets from Off Gas Sampling

Table B-I

Field Data Sheet for Multiple Metals Sampling Train

Time (min)	Volume (cub ft)	Vacuum (in Hg)	Pitot del P (in H2O)	Orifice del P (in H2O)	Probe T (F)	Stack T (F)	Meter In (F)	Meter Out (F)	Filter T (F)	Exit T (F)
0	288.20	2.5	0.10	1.50	259	655	67	67	239	59
5	292.39	2.5	0.10	1.50	251	640	71	67	246	53
10	295.83	2.5	0.10	1.50	248	636	73	68	250	55
15	299.30	2.5	0.10	1.50	250	632	76	68	250	59
20	302.80	3.5	0.10	1.60	248	635	77	68	250	59
25	306.37	3.5	0.10	1.60	248	631	78	69	250	59
30	309.92	3.5	0.10	1.60	250	625	79	69	250	59
35	313.46	3.5	0.10	1.60	248	615	79	69	250	59
40	316.93	3.5	0.10	1.50	247	618	79	69	250	58
45	320.38	3.5	0.10	1.50	248	628	78	69	250	59
50	324.00	3.5	0.10	1.50	247	642	78	69	250	58
55	327.19	3.5	0.10	1.50	248	667	78	69	250	57
60	330.63	3.3	0.10	1.50	250	651	77	69	250	57

Table B-II

Field Data Sheet for Modified Method 5 Sampling Train

Time (min)	Volume (cub ft)	Vacuum (in Hg)	Pitot del P (in H2O)	Orifice del P (in H2O)	Probe T (F)	Stack T (F)	Meter In (F)	Meter Out (F)	Filter T (F)	Exit T (F)
0	246.85	6	0.10	1.50	266	675	67	66	247	42
5	250.00	7.5	0.10	1.50	267	671	69	67	242	41
10	253.35	7.5	0.10	1.50	266	667	73	67	242	42
15	256.61	7.5	0.10	1.50	266	664	75	68	243	42
20	259.98	7.5	0.10	1.50	266	664	76	69	242	42
25	263.31	7.5	0.10	1.50	265	665	78	69	242	43
30	266.68	7.5	0.10	1.50	266	663	79	70	247	43
35	270.17	8	0.10	1.50	265	670	80	70	248	43
40	273.50	8.5	0.12	1.75	265	664	80	71	248	43
45	277.15	8.5	0.12	1.70	264	658	81	72	248	44
50	280.80	8.5	0.12	1.75	266	656	82	72	248	45
55	284.32	8.5	0.12	1.75	265	656	82	72	249	45
60	288.07	8.5	0.12	1.75	265	654	82	72	247	45

REFERENCES

Arculos, R.J. and Delano, J.W. (1981) Geochemica et Cosmochemica Acto. 45, 899-913.

Armstrong, K.M. and Klingler, L.M. (1985) "Evaluation of a Unique System for the Thermal Processing of Radioactive and Mixed Wastes," MLM-3340, EG&G Mound Applied Technologies, Miamisburg, OH.

Asano, M. and Yasue, Y (1985) "Vapor Species over Na_2O-B_2O_3-SiO_2-Cs_2O Glass," *J. Nucl. Sci. Technol.*, 22, pp. 1029-1032.

Baumann, E., Coleman, C.J., Karraker, D.G., and Scott, W.H. (1987) "Colorimetric Determination of Fe(II)/Fe(III) Ratio in Glass," DP-MS-87-18, E.I. du Pont Nemours & Co., Aiken, SC.

Bibler, J.P. and Wallace, R.M. (1987) "Preparation and Properties of a Cesium Specific Resorcinol-Formaldehyde Ion Exchange Resin", DPST-87-647, E.I. du Pont Nemours & Co., Aiken, SC.

Bibler, N.E., Bibler, J.P., Andrews, M.K., and Jantzen, C.M. (1991) "Initial Demonstration of the Vitrification of Nuclear Waste Sludge Containing an Organic Cs-Loaded Ion Exchange Resin," WSRC-MS-91-465, Westinghouse Savannah River Co., Aiken, SC.

Bickford, D.F. and Choi, A.S. (1991), "Control of High Level Radioactive Waste-Glass Melters, Part 5: Modelling of Complex Redox Effects," Proceedings of the Fifth International Symposium on Ceramics in Nuclear and Hazardous Waste Management," Cincinnati, OH, pp. 267-280.

Bickford, D.F. (1994) Log Book Issued to Dennis Bickford by Westinghouse Savannah River Site.

Bickford, D.F. (1994) Westinghouse Savannah River Site, Personal Communication.

Bickford, D.F. and Diemer, R.B. (1986) "Redox Control of Electric Melters with Complex Feed Compositions: I. Analytical Methods and Models," *Journal of Non-Crystalline Solids*, 84, pp. 276-284.

Burns, G.W., Scroger, M.G., Strouse, G.F., Croarkin, M.C., and Guthrie, W.F. (1993) "Temperature-Electromotive Force Reference Functions and Tables for the Letter-Designated Thermocouple Types Based on the ITS-90," National Institute of Standards and Technology Monograph 175.

Federal Register (1990), 55 (106), p. 22627.

Kamizono, H., Kikkawa, S., Togashi, Y., and Tashiro, S. (1989) "Volatilization of Cs-137 and Ru-106 from Borosilicate Glass Containing Actual High-Level Waste," *J. Am. Ceram. Soc.*, 72 [8], pp. 1438-1440.

Klingler, L.M. and Abellera, P.L. (1989) "Joule-Heated Glass Furnace Processing of a Highly Aqueous Hazardous Waste Stream," MLM-3577, EG&G Mound Applied Technologies, Miamisburg, OH.

Odoi, R. (1979) "Volatility of Alkali Fission Products During Solidification Processes," IAEA-SM-236/23, International Atomic Energy Agency.

Office of Solid Waste and Emergency Response (1986), "Test Methods for Evaluating Solid Waste, Vol. II: Field Manual/Chemical Methods," SW-846.

Pearson, W.D. (1991) "Savannah River Site High Level Waste Program and the Defense Waste Processing Facility," Proceedings of the Fifth International Symposium on Ceramics in Nuclear and Hazardous Waste Management," Cincinnati, OH, pp. 3-10.

Ramsey, W.G., Jantzen, C.M., and Bickford, D.F. (1991), "Redox Analyses of SRS Melter Feed Slurry; Interactions Between Nitrate, Formate, and Phenol Based Dopants," Proceedings of the Fifth International Symposium on Ceramics in Nuclear and Hazardous Waste Management," Cincinnati, OH, pp. 259-266.

Richards, R.S. and Lacksonen, J.W., (1991) "Stir-Melter™ Vitrification of Simulated Radioactive Waste, Fiber Glass Scrap, and Municipal Waste Combustor Fly Ash," Proceedings of the Fifth International Symposium on Ceramics in Nuclear and Hazardous Waste Management," Cincinnati, OH, pp. 309-320.

Sanders, D.M. and Haller, W.K. (1977) "The Effect of Water Vapor on Sodium Volatilization in Two Silica Based Glasses," *Journal of the American Chemical Society.*

Schumacher, R.F. (1991) "DWPF Batch 1, Waste Glass Investigations," Proceedings of the Fifth International Symposium on Ceramics in Nuclear and Hazardous Waste Management," Cincinnati, OH, pp. 453-463.

Spalding, B.P. and Jacobs, G.K. (1989) "Evaluation of an In Situ Vitrification Field Demonstration of a Simulated Radioactive Liquid Waste Disposal Trench," ORNL/TM-10992, Oak Ridge National Laboratories, Oak Ridge, TN.

USATHMA, (1988), "Bench Scale Glassification Test on Rocky Mountain Arsenal Soil," AMXTH-TE-CR-88015, U.S. Army and Toxic and Hazardous Materials Agency.

USEPA (1990) *Methods Manual for Compliance with the BIF Regulations*," EPA/530-SW-91-010, PB-91-120-006, U.S. Environmental Protection Agency.

USEPA (1992) *Handbook: Vitrification Technologies for Treatment of Hazardous and Radioactive Waste*, EPA/625/R-92/002, U. S. Environmental Protection Agency.

Wallace, R.M. and Bibler, J.P. (1988) "An Improved Method for Decontaminating Soluble High-Level Waste Using Ion Exchange," DPST-88-789, E.I. du Pont Nemours & Co., Aiken, SC.

Wicks,G. and Bickford D. (1989) "Doing Something About HLW," *Technology Review*, 92 (6).