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Conversion of Plutonium-Containing Materials Into Borosilicate Glass Using The Glass Material Oxidation And Dissolution System

C. W. Forsberg, E. C. Beahm, G. W. Parker, and K. R. Elam
Oak Ridge National Laboratory*
P.O. Box 2008, 105MIT
Oak Ridge, Tennessee 37830-6495
Tel: (423) 574-6783
Fax: (423) 574-3431
Email: forsbergcw@ornl.gov

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Conversion of Plutonium-Containing Materials into Borosilicate Glass Using The Glass Material Oxidation and Dissolution System

C. W. Forsberg, E. C. Beahm, G. W. Parker, and K. R. Elam
Oak Ridge National Laboratory, P.O. Box 2008
Oak Ridge, Tennessee 37831-6595

ABSTRACT

The end of the cold war has resulted in excess plutonium-containing materials (PCMs) in multiple chemical forms. Major problems are associated with the long-term management of these materials: safeguards and nonproliferation issues; health, environment, and safety concerns; waste management requirements; and high storage costs. These issues can be addressed by conversion of the PCMs to glass: however, conventional glass processes require oxide-like feed materials. Conversion of PCMs to oxide-like materials followed by vitrification is a complex and expensive process.

A new vitrification process has been invented, the Glass Material Oxidation and Dissolution System (GMODS) to allow direct conversion of PCMs to glass. GMODS directly converts metals, ceramics, and amorphous solids to glass; oxidizes organics with the residue converted to glass; and converts chlorides to borosilicate glass and a secondary sodium chloride stream. Laboratory work has demonstrated the conversion of cerium (a plutonium surrogate), uranium (a plutonium surrogate), Zircaloy, stainless steel, multiple oxides, and other materials to glass. Equipment options have been identified for processing rates between 1 and 100,000 t/y. Significant work, including a pilot plant, is required to develop GMODS for applications at an industrial scale.

DISCLAIMER

1. INTRODUCTION

The management of plutonium containing materials (PCMs) is a major problem for the United States. The problems include (1) environmental, health and safety [ES&H] issues, (2) safeguards and national security, (3) waste disposal, and (4) economic storage. With the end of the cold war, there is now excess plutonium, but new policies for managing PCMs have not been fully defined.

Three major classes of PCMs can be identified: transuranic (TRU) waste, scrap and residue, and weapons materials. TRU waste is primarily waste that is contaminated with plutonium. Scrap and residue are secondary process streams typically containing a few weight percent plutonium. Earlier, it was expected that these materials would be processed to recover the plutonium for national defense. However, with the end of the cold war, there is excess plutonium, and no incentive to recover plutonium from these streams. Weapons materials include weapons components, clean plutonium usable for weapons, and other relatively pure plutonium materials. There are no clear dividing lines between the categories. Furthermore, the categorization in terms of one issue (example: waste management) is often different than for a second issue (example: safeguards). Inventories of weapons materials are measured in tens of tons, inventories of scrap and residue are measured in hundreds of tons, and inventories of TRU waste are measured in tens of thousands of tons. Most of the plutonium is associated with weapons materials.

Most of these issues can be addressed by converting the PCMs to glass: however, conventional glass processes require oxide-like feed materials. Conversion of PCMs to oxide-like materials followed by vitrification is a complex and an expensive process. The Glass Material Oxidation and Dissolution System (GMODS) is a recently invented vitrification process (Forsberg et al., October 24, 1995) which converts metals, ceramics, and amorphous solids directly to glass; oxidizes organics with the residue converted to glass; and converts chlorides to borosilicate glass and a secondary sodium chloride stream. GMODS was investigated for conversion of PCMs to glass (Forsberg et al., October 1995).

GMODS is a new glassmaking process to make glass from unusual material (metals, ceramics, organics, chlorides, etc.). It is not a glass formulation. Plutonium glass compositions are being developed by others (Ramsey et al., 1995; Bates et al., November 1995).

A description of the GMODS technology is provided herein. The description is followed by the results of initial laboratory experiments. While the technology is being considered for PCMs, it is also applicable as a general purpose waste management process.

2. NEED TO VITRIFY PCMs

There are four major issues associated with PCMs. Many of the issues can be eliminated by converting the materials to a plutonium glass.

2.1 ENVIRONMENT, SAFETY, AND HEALTH (ES&H)

There are major ES&H problems with much of the plutonium scrap and residue and some of the other categories of PCMs (DOE, November 1994). Significant quantities of PCMs are in chemically unstable forms unsuitable for long-term storage. Plutonium generates alpha particles that can react with many chemicals. For example, reactions with water and organics often generate hydrogen and oxygen, which have the potential for combustion or explosion. Conversion to inert glass eliminates these storage hazards.

2.2 WASTE MANAGEMENT

If PCMs are declared wastes, they must be disposed of in geological repositories deep underground. There are waste acceptance criteria (WACs) for each disposal site. As wastes become more hazardous, there is usually a requirement for better waste forms. Glass is considered worldwide as the preferred waste form for high level waste (HLW). As plutonium concentrations in wastes increase, glass becomes a preferred waste form because it is chemically inert and is resistant to leaching by groundwater.

2.3 NATIONAL SECURITY

Plutonium is used for construction of nuclear weapons. Plutonium wastes should be disposed of under controlled conditions to minimize the possibility that it would be recovered and used in nuclear weapons. The National Academy of Sciences (1994) recently recommended that excess plutonium be disposed of as part of an arms control agreement so that the excess plutonium is no more accessible for building weapons than is plutonium in spent nuclear fuel (SNF). This is called the "spent fuel standard." Weapons material, scrap and residue, and perhaps some TRU waste may contain plutonium sufficient such that it should be processed to meet the spent fuel standard.

Multiple options for disposal of PCMs while meeting this standard are being proposed. Two classes of options involve glass. The first is creating a plutonium glass and the mixing the glass with HLW glass to make the plutonium inaccessible because of the resultant high radiation field. The second option is to dilute the plutonium in TRU waste to very low concentrations so that it is not practical to recover the plutonium (DOE, April 1995; IAEA, 1994). This would involve simultaneous processing TRU waste with higher assay plutonium streams so that the two streams become one homogeneous steam.

2.4 STORAGE ECONOMICS

The creation of plutonium has cost many tens of billions of dollars and is considered by some as a valuable resource. The future is uncertain. The plutonium may be needed as an energy source or for national defense. The nation may decide to store the plutonium for decades and make no decision on its disposition until it is better known if there is a future need. Glass has several advantages as a long-term storage form: (1) the glass becomes the first barrier against release of plutonium to the environment in an accident, (2) glass greatly reduces nuclear criticality storage concerns because of neutron absorbers in the glass, and (3) nuclear safeguards complexities are minimized when the plutonium is in a homogeneous chemical form in a standard geometry. These characteristics minimize the requirements necessary for the storage vaults and, hence, minimize storage costs (Forsberg, June 1995).

Decisions concerning what options to implement have not been made but it is likely that one or more or the options will require vitrification.

3. THE PROCESS: GMODS

3.1 CONVERSION OF METALS, CERAMICS, AMORPHOUS SOLIDS, AND ORGANICS TO GLASS

GMODS converts plutonium and other elements within the scrap and residue directly to borosilicate glass. GMODS may be operated as a batch (Fig. 1), semibatch, or continuous process. The process described herein is a batch process during which sequential process steps convert feeds to glass. The initial condition for the process is a melter filled with a molten oxidation–dissolution (lead borate) glass, which has a composition of two or more moles of lead oxide (PbO) per mole of boron oxide (B_2O_3). The PbO is a component of the glass and a sacrificial oxide. The process consists of the following steps:

3.1.1 Addition of feed material to the molten dissolution glass (Fig. 1b)

The ceramic (plutonium oxide (PuO_2), etc.) and amorphous components in the feed dissolve into the glass. While metals and organics do not dissolve into conventional molten glasses, the GMODS dissolution glass has special properties to process these materials *in situ*. The inclusion of the sacrificial oxide—PbO—in the molten glass provides a method to oxidize *in situ* (a) metals to metal oxides and (b) organics to carbon dioxide (CO_2) gas and steam. When plutonium or another metal is fed to the melter, it is converted to a metal oxide. These metal oxides dissolve into the glass; carbon oxides (in gaseous form) and steam exit the melter. The reaction product, molten lead, separates from the glass and sinks to the bottom of the melter to form a separate layer,

$$Pu + 2PbO \rightarrow PuO_2 + 2Pb \downarrow$$

$$C + 2PbO \rightarrow CO_2 \uparrow + 2Pb \downarrow$$

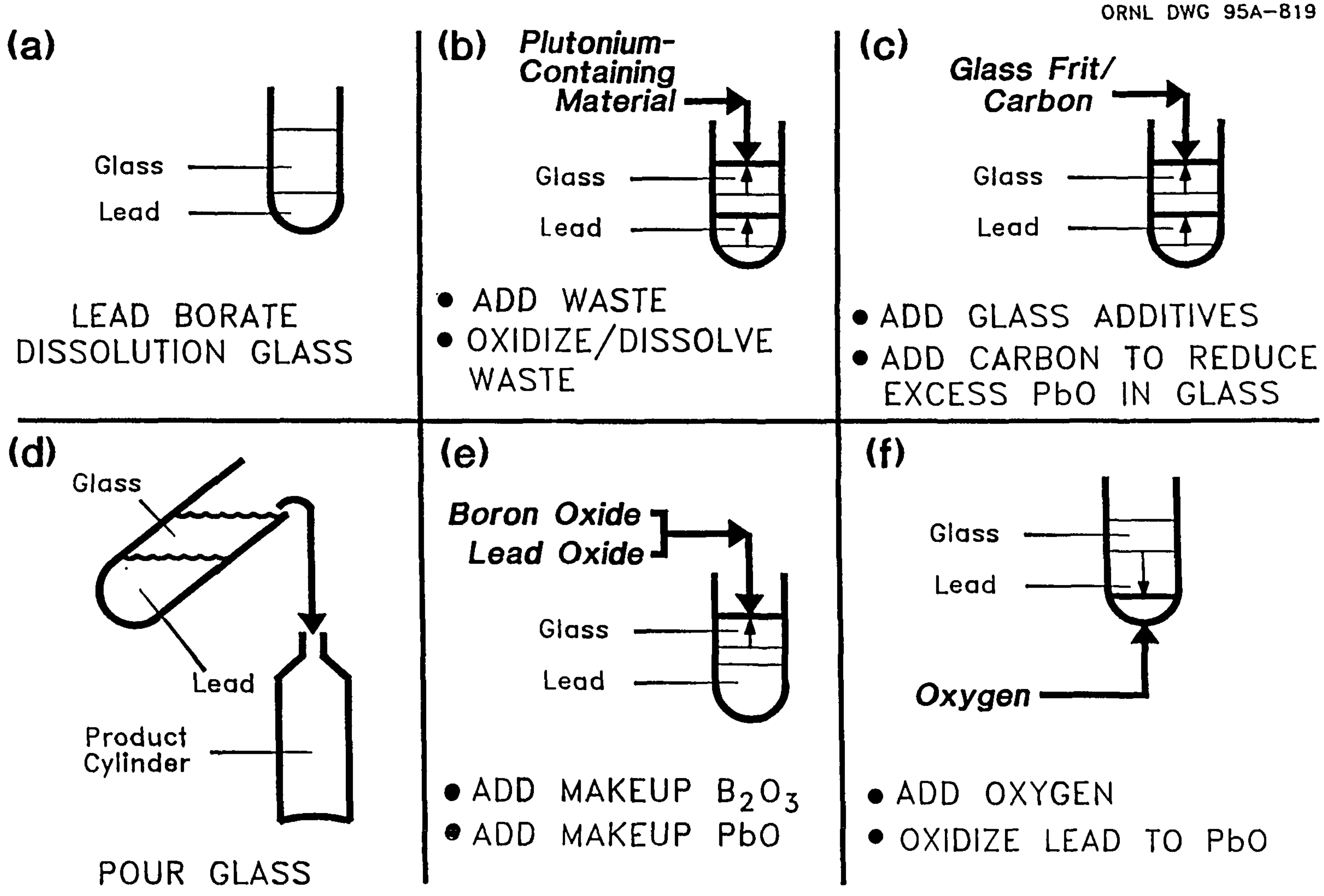

FIGURE 1. GMODS batch processing of plutonium-containing material to borosilicate glass.

3.1.2 Addition of glass additives [silicon oxide (SiO_2) etc.] to improve product quality (Fig. 1c)

The optimum compositions of glasses for rapid oxidation-dissolution of materials in molten glass are different in composition from those for long-term durability. Consequently, additives that create a more durable glass are introduced after feed oxidation-dissolution takes place.

3.1.3 Addition of carbon to remove excess PbO (Fig. 1c)

Carbon reduces the PbO to lead metal while producing gaseous CO_2. Excess PbO is removed from the dissolution glass for multiple reasons: (1) more durable glass, (2) reduction of the volume of glass, and (3) avoidance of the costs to provide added sacrificial PbO. The final glass may contain some or no lead, depending on the final desired glass composition.

3.1.4 Pouring glass from the furnace followed by solidification (Fig. 1d)

The product glass is poured into the waste canister.

3.1.5 Addition of B_2O_3 and PbO, as needed, to the melter for processing the next batch of materials (Fig. 1e)

Boron oxide and PbO that left with the product glass are replaced with new feed materials. Note that lead oxide is only added if the product glass contains lead oxide.

3.1.6 Reoxidation of the lead at the bottom of the melter to PbO by addition of oxygen (Fig. 1f)

Oxygen is injected into the molten lead. This oxidation step creates the new dissolution glass for the next batch of feed to be processed. Lead is an oxygen carrier that does not leave the system. The oxidation reaction is

$$2Pb + O_2 \rightarrow 2PbO$$

3.2 CONVERSION OF CHLORIDES TO GLASS AND A SECONDARY CLEAN SODIUM CHLORIDE STREAM

GMODS is designed to convert chloride-containing plutonium residues to glass and create a separate nonradioactive NaCl waste stream. Halogens, such as chloride, make poor-quality storage forms; hence, they must be separated from other components in plutonium residues. The analogy used in waste management is that good storage forms (silica, titanates, etc.) for radioactive materials can be found at any ocean beach. Materials that dissolve in seawater (chlorides, etc.) make poor storage forms.

The separation process for chlorides is shown in Fig. 2. In the dissolution glass, chlorides in the feed form lead chloride ($PbCl_2$), which is volatile at glass melter temperatures and exits to the aqueous sodium hydroxide (NaOH) scrubber. In the scrubber, the $PbCl_2$ reacts with the NaOH to yield insoluble lead hydroxide [$Pb(OH)_2$] and soluble NaCl salt. The insoluble $Pb(OH)_2$ is recycled back to the melter where it decomposes to PbO and steam, while the aqueous NaCl stream is cleaned and discharged as a chemical waste.

4. CONTINUOUS PROCESSING OPTIONS

The GMODS process can be configured as a batch, semibatch, or continuous process depending upon the quantities and characteristics of the feed. Figure 3 shows an alternative flowsheet configuration in which the lead metal is oxidized in an external loop. Such configurations may be preferred in the processing of feeds with high carbon contents which require large quantities of PbO as an oxidizer.

For large-scale operations (>1000 t/year), continuous processing is an option. In this context, it is recognized the GMODS has similarities to several state-of-the-art lead smelter processes such as the Queneau-Schuhmann-Lurgi (QSL) continuous lead-smelting process (Queneau, December 1989; Queneau and Schuhmann, August 1974: Deininger et al., 1995). An understanding of the QSL process and its industrial operations provides some perspectives on how a continuous GMODS process could operate.

Figure 4a shows the QSL process. The lead ore is fed continuously into the right side of the reactor. The feed includes lead sulfides and may include carbon. The carbon is an auxiliary fuel needed for some feeds. The reactor has a layer of molten slag floating on a layer of molten lead. Oxygen is injected into the molten lead to burn out the sulfides. Some of the key reactions are:

$$2\,Pb + O_2 = 2\,PbO$$

$$PbS + O_2 = Pb + SO_2$$

$$PbS + 2\,PbO = 3\,Pb + SO_2$$

The net result of these chemical reactions is oxidation of the lead sulfide with the generation of lead metal and a slag rich in lead oxide. The slag flows through a submerged weir to a second zone operated under chemically reducing conditions. Coal-oxygen submerged combustors produce a reducing gas that in turn reduces the lead oxide to lead metal that sinks into the lead pool. The slag exits as waste. The submerged combustors also provide added energy.

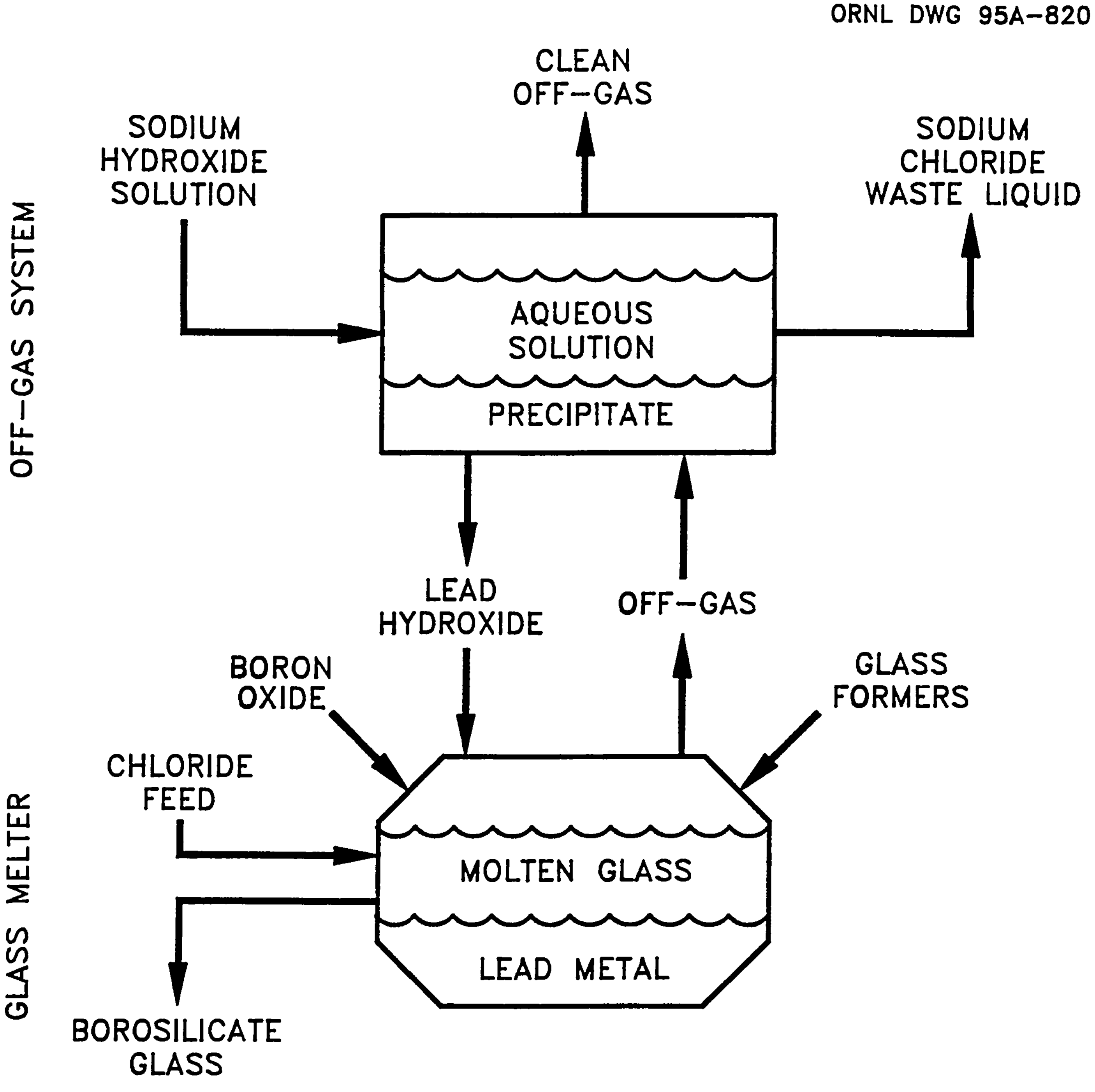

FIGURE 2. GMODS processing of chloride-containing materials.

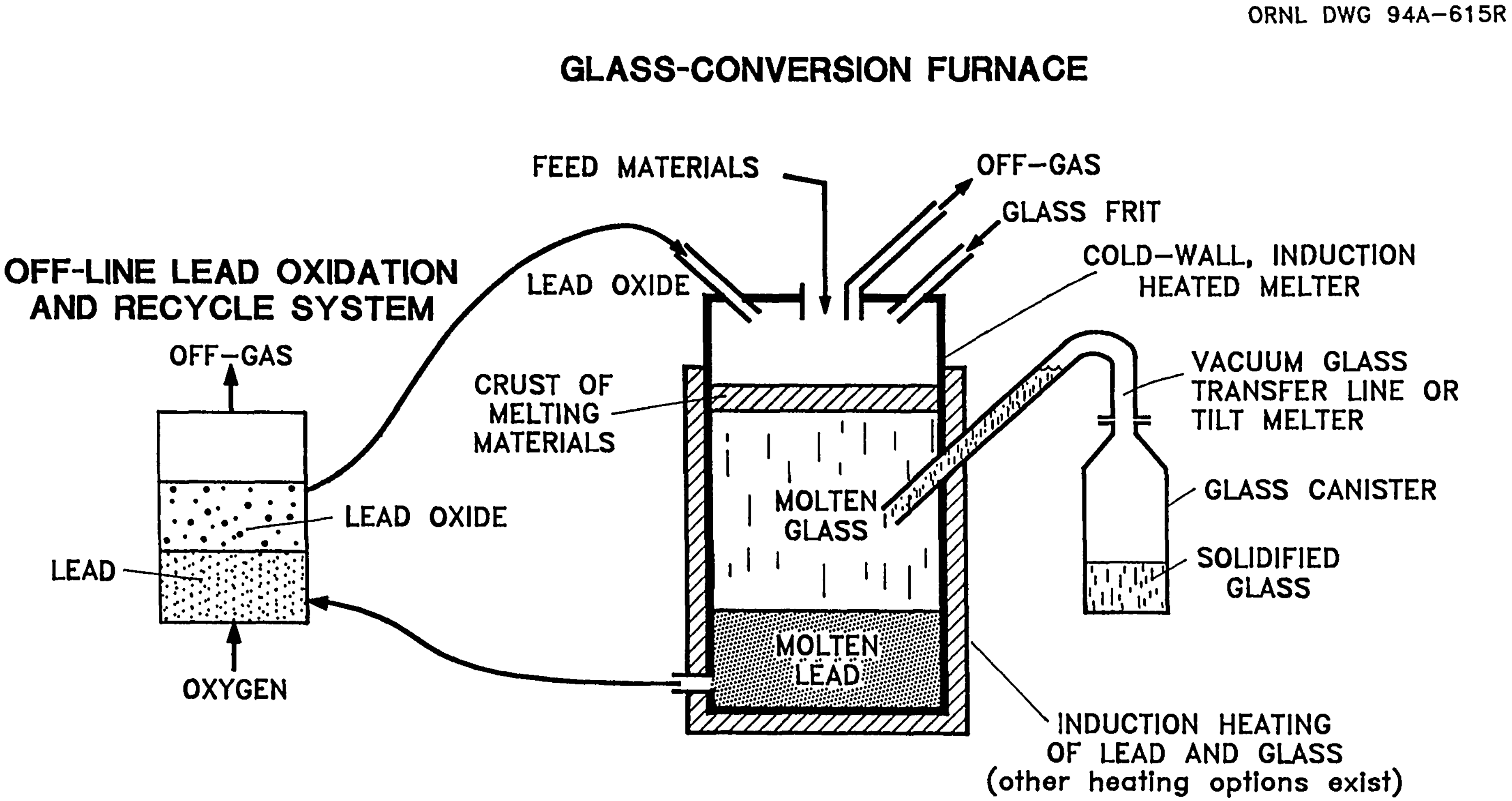

FIGURE 3. GMODS batch flowsheet with external lead recycle.

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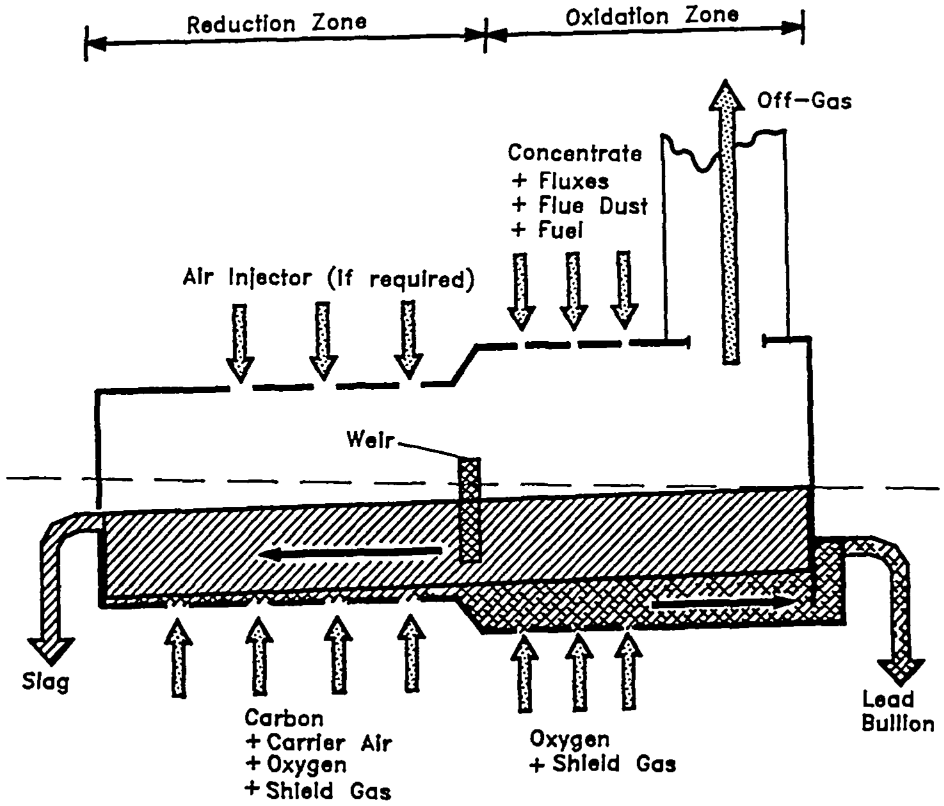
QSL Process For Lead Smelting



GMODS For Waste Treatment

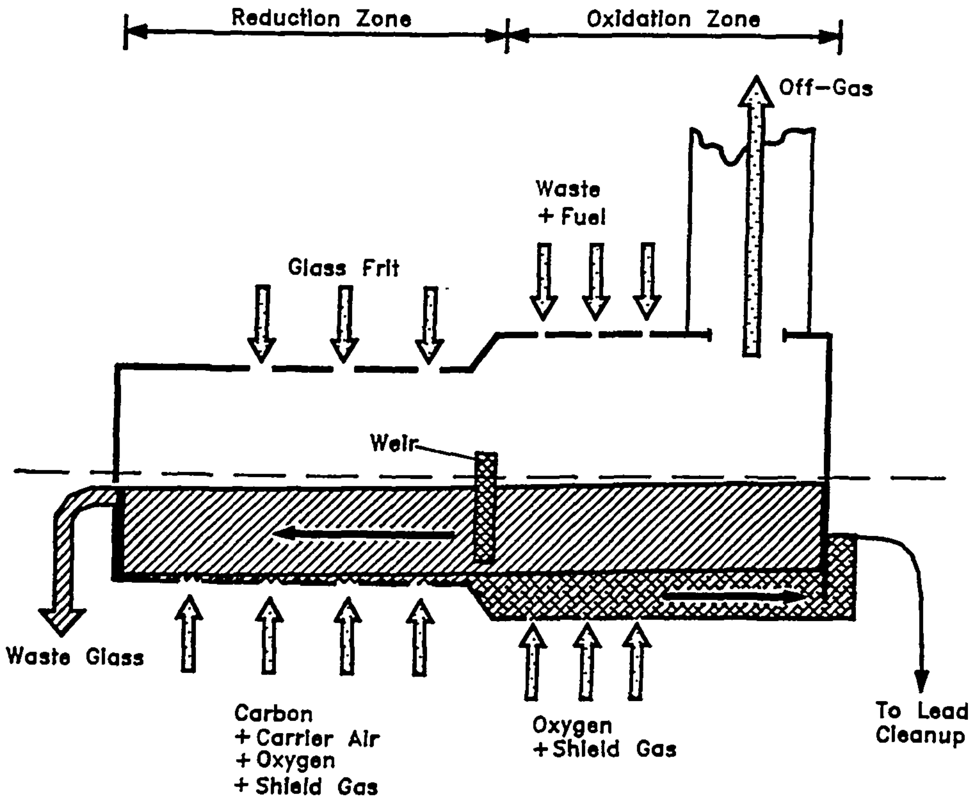


FIGURE 4. QSL and GMODS continuous processes.

The oxygen injectors and coal-oxygen combustors serve several other functions. They provide rapid mixing. They create sequential mixing zones across the length of the reactor, thus creating a countercurrent chemical reactor. This in turn maximizes the production of lead and minimizes the lead content in the slag steam.

The QSL process is similar to GMODS. If GMODS is used to process large quantities of material, a similar chemical reactor design may be appropriate (Figure 4b). The main differences between the two processes are:

Feed. The GMODS feed is waste, not lead ore or lead-battery recycle materials.

Product The GMODS product is glass, not lead. This requires high oxygen injection rates into the oxidizing part of the lead bath to fully convert lead metal to lead oxide. The lead oxide then reenters the slag.

Dissolution glass composition. The slag contains carefully controlled quantities of boron oxide to assist dissolution of metal oxides - particularly protective metal oxides that form on some metals.

Product composition The final slag composition is adjusted to produce a high quality glass.

5. EQUIPMENT

The GMODS equipment configuration depends upon the scale of operation. For throughputs up to several thousand tons per year, the primary GMODS equipment is an induction-heated, cold-wall melter (Fig. 5 shows a small commercial type), which is required because of the corrosive characteristics of the initial dissolution glass. Cold-wall melters have cooling jackets in the wall to produce a "skull" of solidified material that protects the wall from the melter contents. They are used to melt high-temperature materials (e.g., titanium and superalloys) and to produce ultrapure materials (e.g., glass for fiber optics). Russia, France, and the United States are modifying such equipment for processing various radioactive wastes. Batch size may be as large as hundreds of kilograms for PCMs with low plutonium concentrations. In Europe, cold-wall melters are currently being developed for throughputs of up to 800 kg/h.

For large scale processing (>10,000 t/year), large-scale chemical reactors similar to the QSL reactor (Figure 6) are a potential option. QSL lead smelters have typical capacities of 60,000 to 75,000 t/y. There are differences between waste processing and lead smelting. Chemical reactor throughput is dependent primarily upon the feed throughput measured in moles. Lead concentrates have a higher average molecular weight compared to typical elements in waste streams and thus throughput of waste measured in mass would be less than lead concentrates for the same size of chemical reactor. The cumulative contact-handled TRU waste inventory in the United States through 2022 is estimated to be about than 140,000 m^3 with a mass (before

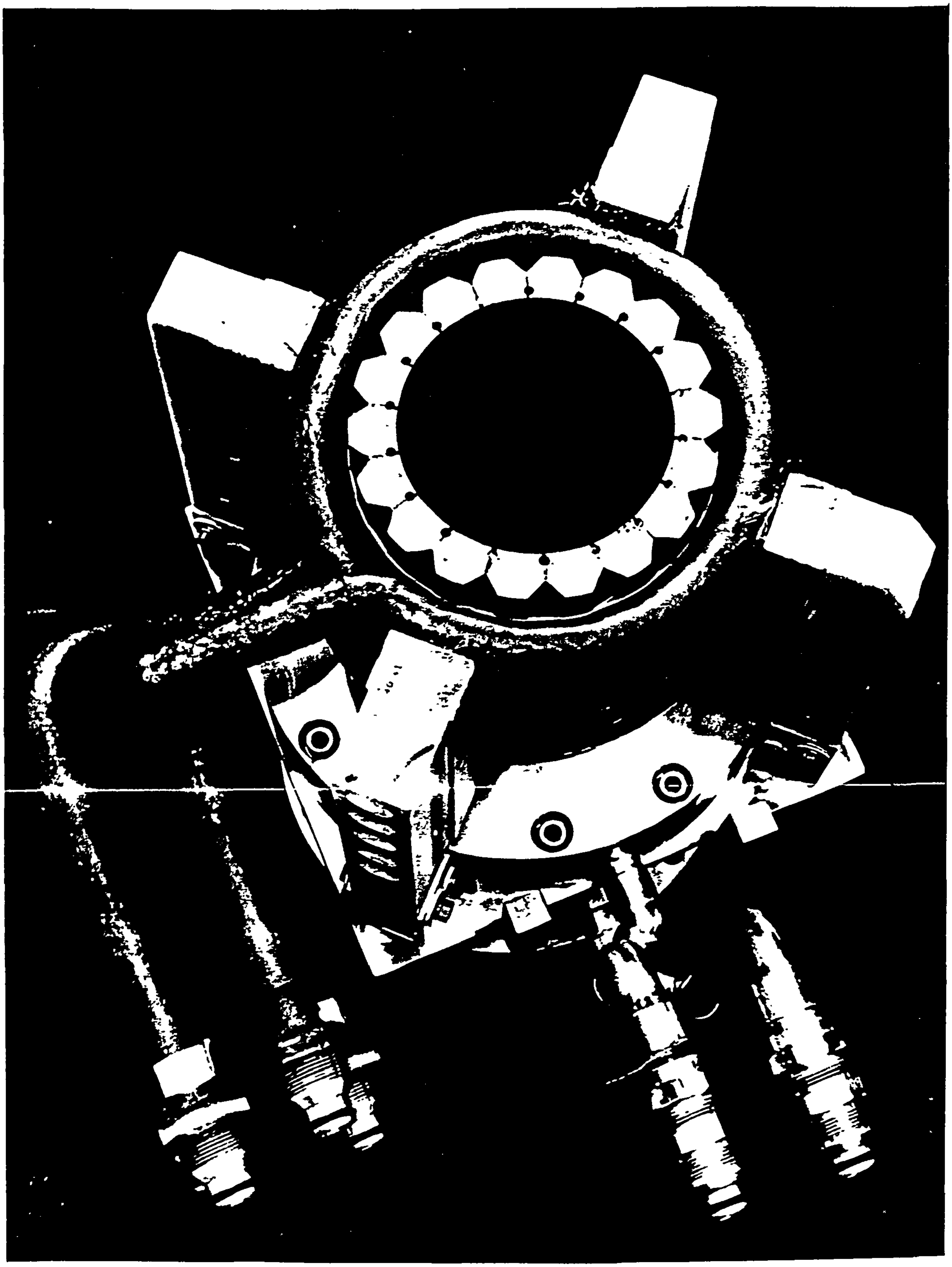
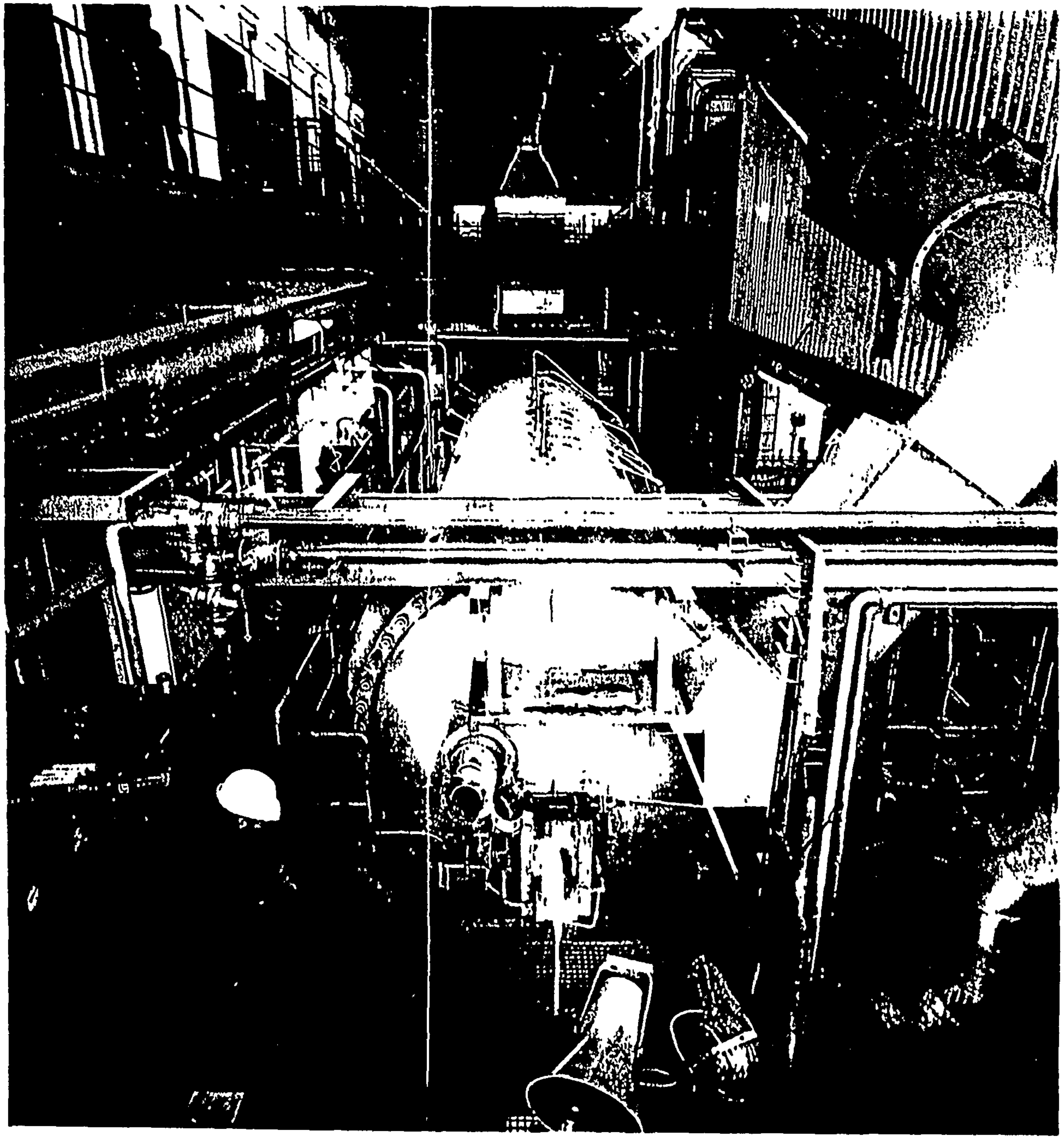


FIGURE 5. Small commercial, cold-wall induction-heated melter (courtesy of Consarc).



Interior of QSL plant producing lead (Courtesy of Lurgi Corp.)

treatment) of about 300,000 t (DOE, September 1995). A chemical reactor to process the inventory would be similar in size to a QSL lead-smelter chemical reactor. For comparison, the total quantities of radioactive low-level waste (LLW) generated in the United States annually is about 80,000 m^3.(160,000 t). Probably two units would be required to process the annual production of LLW in the United States into glass.

There are a variety of other metal and glass industrial processes (Olabin, 1995; Abbasi, 1996) that use submerged combustion systems, submerged gas injection systems, and/or cold-wall melters. Some industrial systems use cold-wall melters that include a ceramic liner between the metal and frozen process fluid. For silica based systems (Olabin 1995), typical heat fluxes through the wall are 20 to 70 kw/m^2. For such systems, larger scale operations minimize energy consumption by reduction of the chemical reactor vessel surface to volume ratio.

6. STATUS OF DEVELOPMENT

6.1 THERMODYNAMICS

A preliminary thermodynamic study of the GMODS process has been completed (Forsberg October 1995). The thermochemical properties of the PbO-B_2O_3 system are the basis of GMODS. The capabilities to oxidize metals and to dissolve metal oxides are directly related to the thermochemical activity of PbO and B_2O_3. This system was assessed by Slough and Jones (1974). These authors used the Gibbs energy values reported by Kapoor and Frohberg (1973). Herein, we also have used the data of the latter.

The processing of metals in GMODS involves oxidation and dissolution in a PbO-B_2O_3 glass. The overall free-energy change for the process includes the free-energy change for the oxidation and the free-energy change for the dissolution. The final dissolution product will be at least a ternary system involving PbO-B_2O_3-metal oxide. No data are available about such systems on which to base a calculation on the distribution of species for the entire process. It may be possible to perform calculations on ternary and higher systems using thermodynamic solution models. Until that work is done, the best guide to treatability of material by GMODS is the oxidation of the metal using PbO.

The best way to compare the relative ease of oxidizing a given metal is to use oxygen potentials which are described in units of energy and are defined as $RT \ln P_{O2}$. Figure 7 shows plots of oxygen potentials for forming a number of metal oxides. This figure shows the important feature that any metal oxide that is higher than another can oxidize the metal in the lower position. Here, we are concerned about the ability of PbO to oxidize metals. Figure 7 shows that any metal (Sn, Fe, Zn, Cr, U, Pu, Al, etc.) that lies below the PbO:aPbO = 0.1 line will be oxidized when the activity of PbO is 0.1 where a is the activity coefficient. In this figure, only Cu_2O lies above the PbO lines. However, Zhou et al. (1993) have shown that copper in the +2 oxidation state, as in

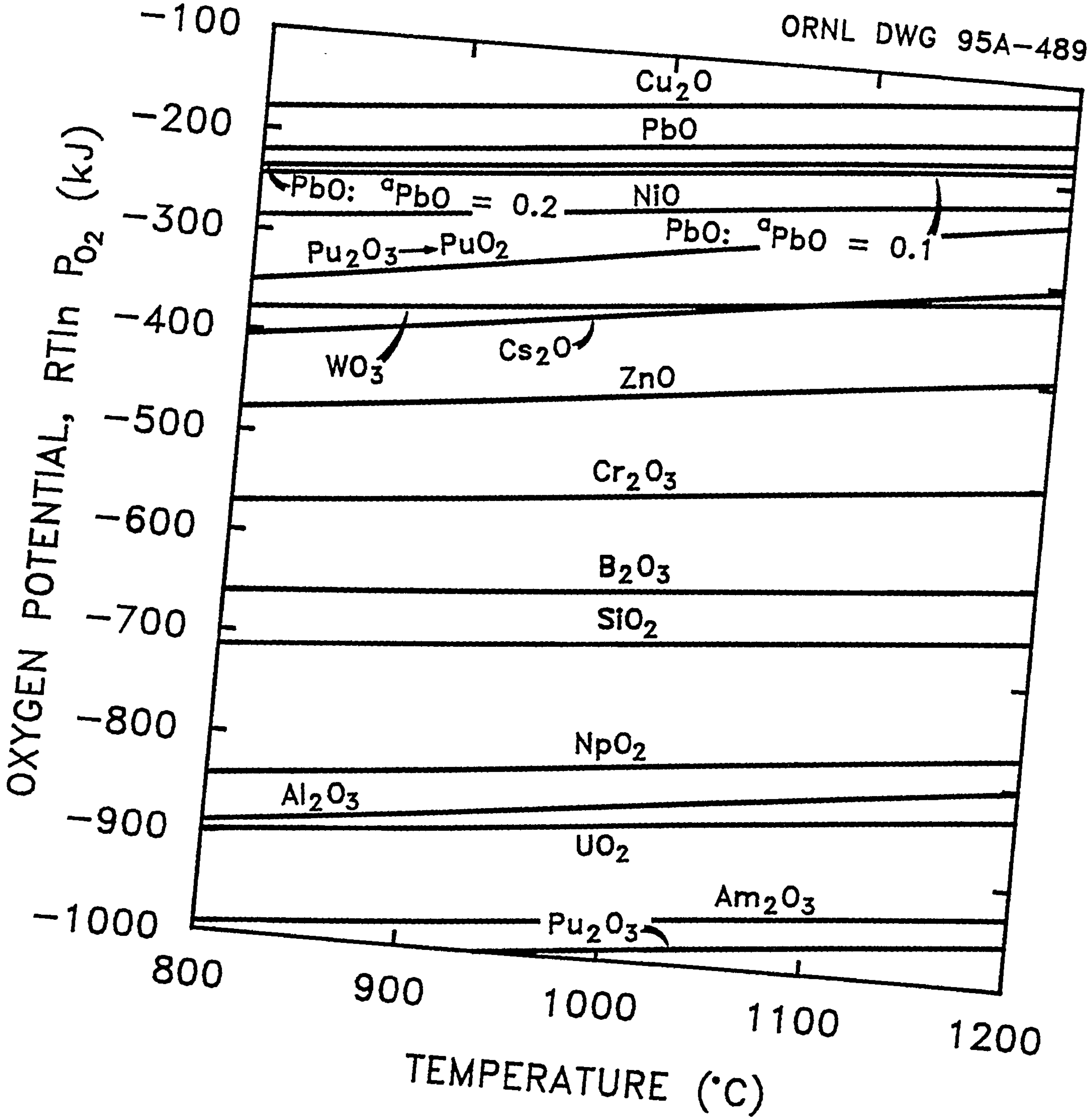


FIGURE 7. Oxygen potential in the lead-borate glass system.

CuO, is stable in $2PbO\text{-}B_2O_3$ glass. The stability of oxidized copper in this glass must result from the combination of oxidation and dissolution and not oxidation alone. Other metals (Ag, Au, Pt, and Pd) do not form oxides that are stable at high temperatures; therefore, they are not included here. These noble metals dissolve into the lead at the bottom of the melter. The oxygen potentials for the formation of ZrO_2 are similar to those of Al_2O_3.

Some metals, such as uranium (U) and plutonium (Pu), can form more than one oxide. The highest oxides are thermodynamically stable as far as oxidation is concerned. However, the overall oxidation and dissolution may result in a lower oxide in the borate glass. Tests of uranium oxide oxidation and dissolution resulted in a black product that is most likely to contain triuranium octoxide (U_3O_8).

Carbon may be introduced into GMODS either as waste to be treated or to reduce PbO to Pb with the production of CO_2. The equilibrium constant for this reaction is about 3×10^8 at 1000° C; therefore, even when the PbO activity is low, carbon will be oxidized.

The vapor pressures of the major glass components were estimated as a function of temperature. In many glass systems, the maximum glass temperature is limited by volatilization of components from the glass. As shown in Table 1, over the expected range of activity coefficients (and corresponding ratios of PbO to B_2O_3 in the glass), volatilization of lead oxide is not a concern. The partial pressures of B_2O_3 will be several orders of magnitude lower than those of PbO. For some feed materials, there may be other components that limit operating temperatures.

TABLE 1. Vapor pressure of PbO in the $PbO\text{-}B_2O_3$ system

Temperature °C	**P_{PbO} (atm)** At $a_{PbO} = 0.1$	**P_{PbO} (atm)** At $a_{PbO} = 0.2$
800	2.9×10^{-7}	5.9×10^{-7}
900	3.9×10^{-6}	7.8×10^{-6}
1000	2.8×10^{-5}	5.6×10^{-5}
1100	1.5×10^{-4}	3.0×10^{-4}
1200	6.3×10^{-4}	1.3×10^{-3}

6.2 INVESTIGATION OF PROCESS STEPS

Some steps of the GMODS process are new, while others are parts of standard industrial processes. Experiments were performed to understand and prove the unique features of GMODS. Literature searches have been conducted to understand those parts of the process that are used in other industrial processes. Each step has also been accomplished in our laboratory.

Laboratory experiments were conducted in platinum and high-fired aluminum oxide crucibles within vertical tube furnaces. Platinum was used for experiments that did not involve lead (lead dissolves into platinum at high temperatures). Various ceramic crucible materials were investigated for use in oxidation process experiments. While the dissolution glass dissolves oxides, the rate of dissolution with Coors™ high-fired aluminum oxide crucible is sufficiently low for short-time experiments.

A typical experiment involved several hundred grams of material, with uranium and cerium being used as plutonium surrogates. Plutonium tests have been proposed. The plutonium content of most PCMs is, at most, a few weight percent; hence, in terms of chemical processing, plutonium is a minor component.

6.2.1 Addition of feed material to the molten dissolution glass (Fig. 1.b)

The addition of feed materials involves oxidation, dissolution, and mixing of feeds with the molten dissolution glass. Each of these steps has been investigated.

Tests demonstrated the dissolution of UO_2, ZrO_2, Al_2O_3, Ce_2O_3, MgO, and other oxides. The glasses were examined by a variety of methods to ensure complete dissolution. As expected, the glass melt with high concentrations of boron oxide had good dissolution capabilities for oxides. In analytical chemistry, B_2O_3 is the standard chemical reagent for fusion dissolution of unknown oxides because of its capability to dissolve such materials. Boron oxide is also the key component in many welding fluxes, which are used to dissolve iron oxides into a glassy slag during the welding process so that they are not incorporated into the weld.

Oxidation-dissolution tests demonstrated the oxidation of the following metals and alloys (followed by the dissolution of their oxides into the melt): U, Ce, Zircaloy-2, Al, stainless steel, and other metals. Figure 8 shows cerium glass and lead by-product from a test of oxidation of cerium metal (plutonium surrogate).

Oxidation-dissolution tests also demonstrated the oxidation of carbon and graphite, with production of CO_2. For centuries, PbO has been used to oxidize organics (Ercker, 1500). It is the basis for the fire assay method for recovering noble metals (primarily gold) from silicate rock. Lead oxide, various organics, and silicate rocks are mixed together and heated. As the mixture melts, the PbO is reduced to metal by the organic. The noble metals in the molten mass then dissolve into the lead, which forms a separate layer that sinks to the bottom. This layer is then processed to separate the noble metal from the lead.

Limited chloride dissolution tests with NaCl demonstrated that lead exits the dissolution glass as $PbCl_2$, thus providing a separation of the chloride from other materials. This is a major

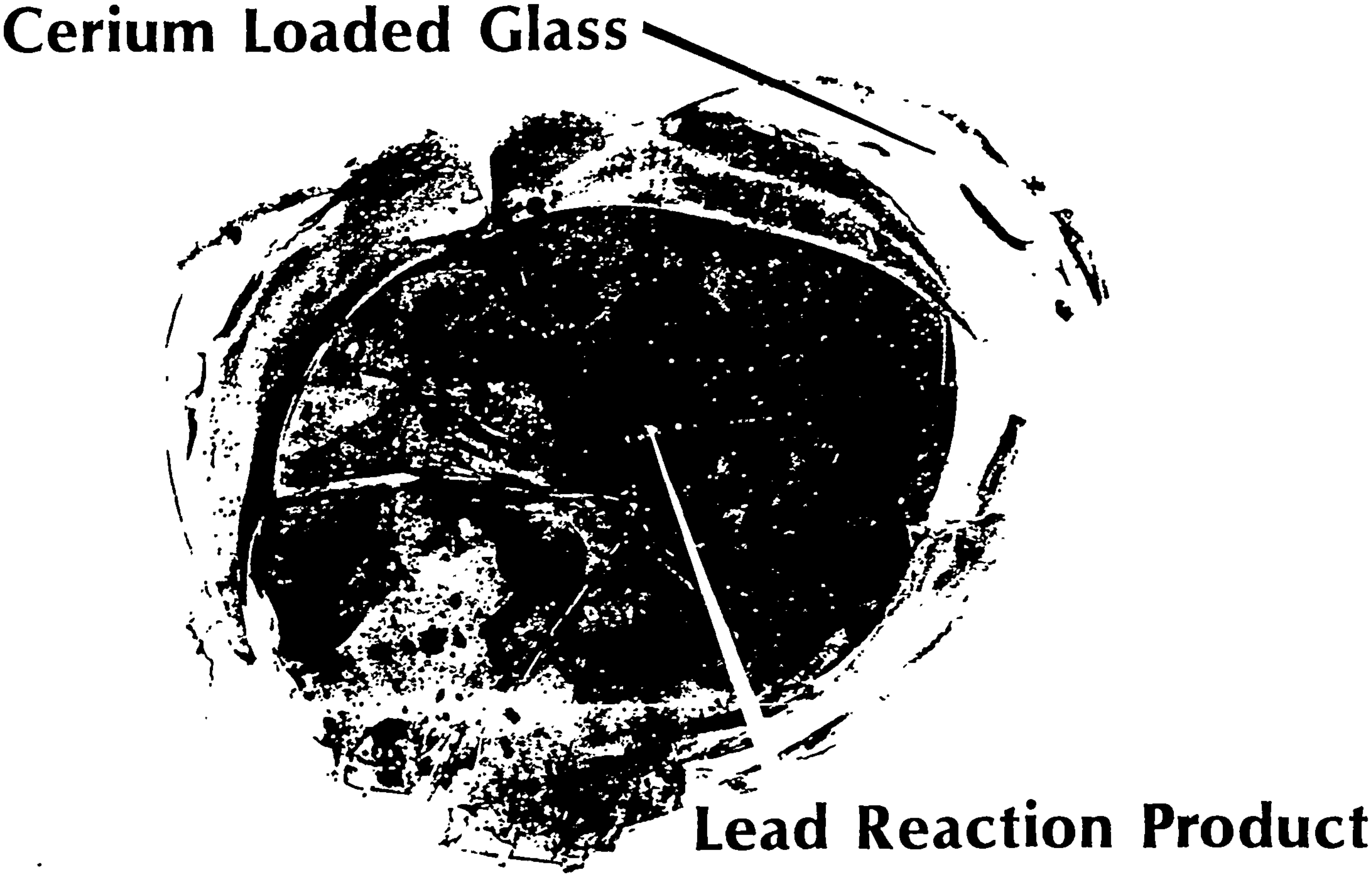


FIGURE 8. Cerium glass and lead metal from completed oxidation-dissolution tests with cerium metal.

mechanism for lead to escape from processes where lead and chlorides coexist at high temperatures (Linak and Wendt, 1993). The basic chemistry is understood.

Experimental measurements were made of the viscosity of the dissolution glass with various added materials (Table 2). Experience in the glass industry indicates that molten glass viscosities should be below 100 centipoise (about the viscosity of olive oil) for good mixing and creation of homogeneous glasses. Based on our experimental data, the GMODS dissolution glass temperature will need to be between 800 and 1000° C. The final processing temperature after addition of the silica will be above 1000° C because this addition increases glass viscosity.

6.2.2 Addition of glass additives [silicon oxide (SiO_2) etc.] to improve the product quality (Fig. 1c)

This process step is essentially identical to that used for producing many specialty glasses (McKinnis et al., 1959).

6.2.3 Addition of carbon to remove excess PbO (Fig. 1c)

This process step is used in several lead-smelting processes, such as the QSL process, to recover lead metal from PbO in molten slag (King, 1995). This step has also been demonstrated with high level waste (HLW) glass in hot cells for recovery of fission product noble metals at Pacific Northwest Laboratory (Jensen et al., 1984). These scientists used a modification of the fire-assay method described previously. Because some proposed plutonium glasses are variants of HLW glasses, this experience is particularly relevant.

6.2.4 Pouring glass from the furnace followed by solidification (Fig. 1.d)

Pouring glass from a furnace and solidifying the glass is a standard operation in the glass industry.

6.2.5 Addition of B_2O_3 and PbO, as needed, to the melter for processing the next batch of materials (Fig. 1e)

The addition of B_2O_3 and PbO is a standard operation used by the glass industry for producing lead borosilicate glass (fine crystal).

6.2.6 Reoxidation of the lead at the bottom of the melter to PbO by addition of oxygen (Fig. 1f)

This oxidation step is one of several processes used for producing PbO for batteries and other uses (Carr et al., 1995).

6.3 FLOWSHEET ANALYSIS

An analysis of GMODS was performed using the process simulator FLOW (Ferrada, 1995; Ferrada, 1996). The simulator includes a set of rules to choose glass compositions that meet process (viscosity, etc.) and performance requirements, using Savannah River HLW glass as a basis. The analysis identified critical process parameters when processing plutonium scrap and

Summary of viscosity measurements (in cP) vs. temperature for several GMODS glasses

Temperature °C	**600**	**650**	**700**	**750**	**800**	**850**	**900**	**950**	**1000**
PbO:B_2O_3 ratio									
1:1			260	100	55				
2:1	200		45		30				
3:1	105	65	45		30				
4:1	80		60		25				
2:1 w/20% U_3O_8		2000*		125			22		
2:1 w/10% ZrO_2					560*				390*
2:1 w/10% ZrO_2 and 10% U_3O_8						2000*		1150*	
2:1 w/6.7% ZrO_2 and 13.3% U_3O_8					710*		300*		

* Glasses at these conditions behaved as Bingham fluids. Common in fluids with suspended solids.

TABLE 2. Measured viscosities of lead borate glasses

residue to a borosilicate glass, which is designed to be equivalent in performance to HLW glass. The two key observations were as follows:

Higher temperature operation minimizes glass volumes. Incentives exist to maximize the GMODS operating temperature. For example, processing 1 kg of plutonium-containing chloride salt residues at 1103° C yields 6.5 kg of glass under standard conditions. Allowing the processing temperature to increase to 1167° C reduces the final glass quantities to about 3 kg. In this case, the waste loading in the glass is limited by the need to minimize molten glass viscosity during process operations to ensure good glass mixing. Increasing the processing temperature decreases the glass viscosity, minimizes the need to add NaO to lower glass viscosity by changing the chemical composition, and allows a higher waste loading in the product glass. With the use of cold-wall, induction-heated melters that are not temperature-limited, the limitation on the maximum process temperature is volatilization of selected glass components.

Feed blending reduces glass volumes. Incentives also exist to blend different feeds to minimize glass volumes. For example, blending plutonium salt and ash residue streams and converting them to glass reduces the final volume of glass by about 50% as compared with separate conversion of the two materials to glass. Final glass volumes in this case are minimized by coprocessing because the ash stream provides necessary silica and aluminum to the final product glass, while the chloride stream provides necessary sodium to the final product glass.

The flowsheet simulator also afforded a bounding estimate of glass quantities if scrap and residue at Rocky Flats were converted to glass by GMODS. Most of the plutonium scrap and residue in the United States is at this one site. For "lean" scrap, 232 m^3 of glass would be produced with an average plutonium content of 0.06 wt%. For "rich" scrap, 34 m^3 of glass would be produced with an average plutonium content of 2.4 wt%. The actual quantities of glass may be significantly less when higher process temperatures are used.

The quantities of glass produced from processing plutonium scrap and residue or TRU waste are not determined by the plutonium (because of its low concentration), but rather by other components in the scrap or residue. The set of constraints includes glass processing temperatures, solubility limits of specific elements in the product glass, and glass durability under repository conditions. If the goal is to minimize glass volumes in order to minimize storage or disposal volumes, selected preprocessing of some residues can be undertaken to minimize specific elements that most impact glass volumes. This choice involves a series of trade-offs between multiple processes. (Note that organics and chlorides in feeds have little impact on final glass volumes because GMODS is a separations as well as a glassmaking process.)

6.4 DEVELOPMENTAL PERSPECTIVES

The analytical evaluations and laboratory development work have demonstrated each step required for GMODS and identified equipment, instrumentation, and other components required for GMODS. A significant effort, however, will be required to convert GMODS into an industrial technology. This effort will include a better understanding of the process, integration of process steps into a system, and development of equipment. A pilot plant will be required to demonstrate the process.

7. SUMMARY

GMODS is a new process for the direct conversion of a wide range of PCMs to glass. It is designed to (1) convert metals, ceramics, and amorphous solids to glass; (2) oxidize organics with conversion of residues to glass; and (3) convert chlorides into a chloride-free borosilicate glass and a secondary clean NaCl stream. GMODS is an enabling technology since it creates new options for management of PCMs. The technology is applicable to other radioactive and hazardous chemical wastes. As a new technology, however, GMODS has significant technical uncertainties that must be resolved in additional studies.

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