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Direct Vitrification of Plutonium- Containing Materials (PCMs) with the Glass Material Oxidation and Dissolution System (GMODS)

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MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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**DIRECT VITRIFICATION OF PLUTONIUM-CONTAINING MATERIALS (PCMs)
WITH THE GLASS MATERIAL OXIDATION AND DISSOLUTION SYSTEM (GMODS)**

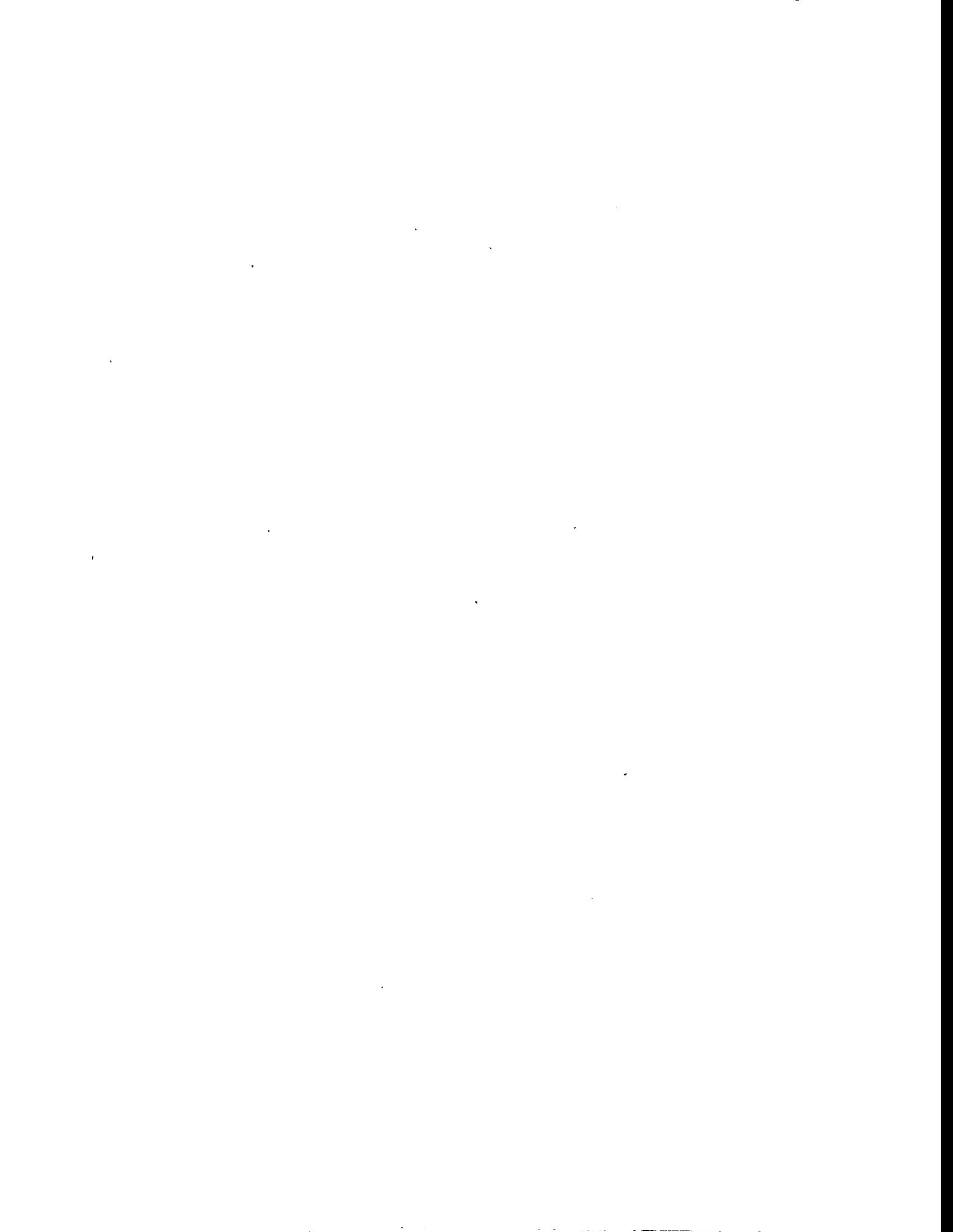
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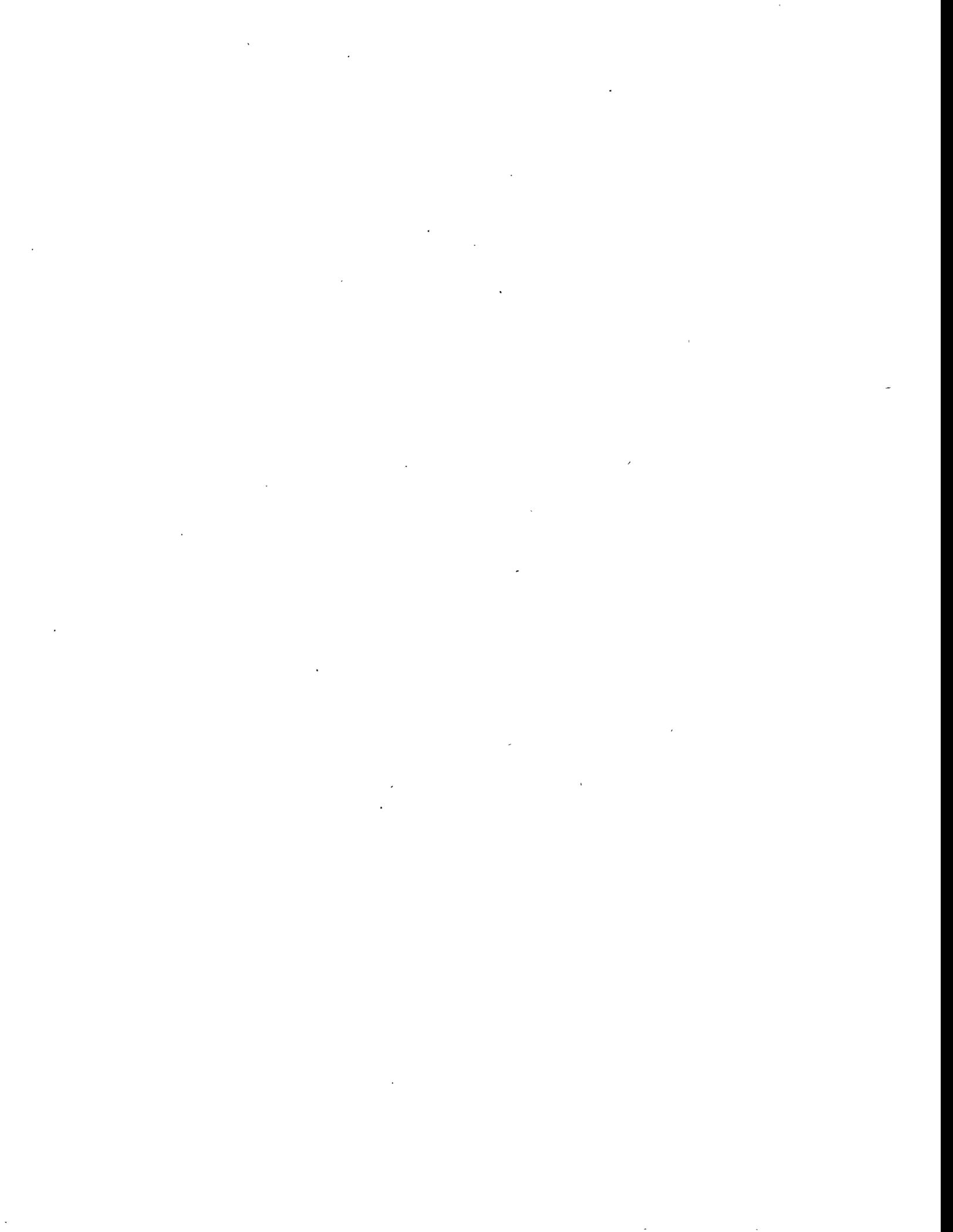
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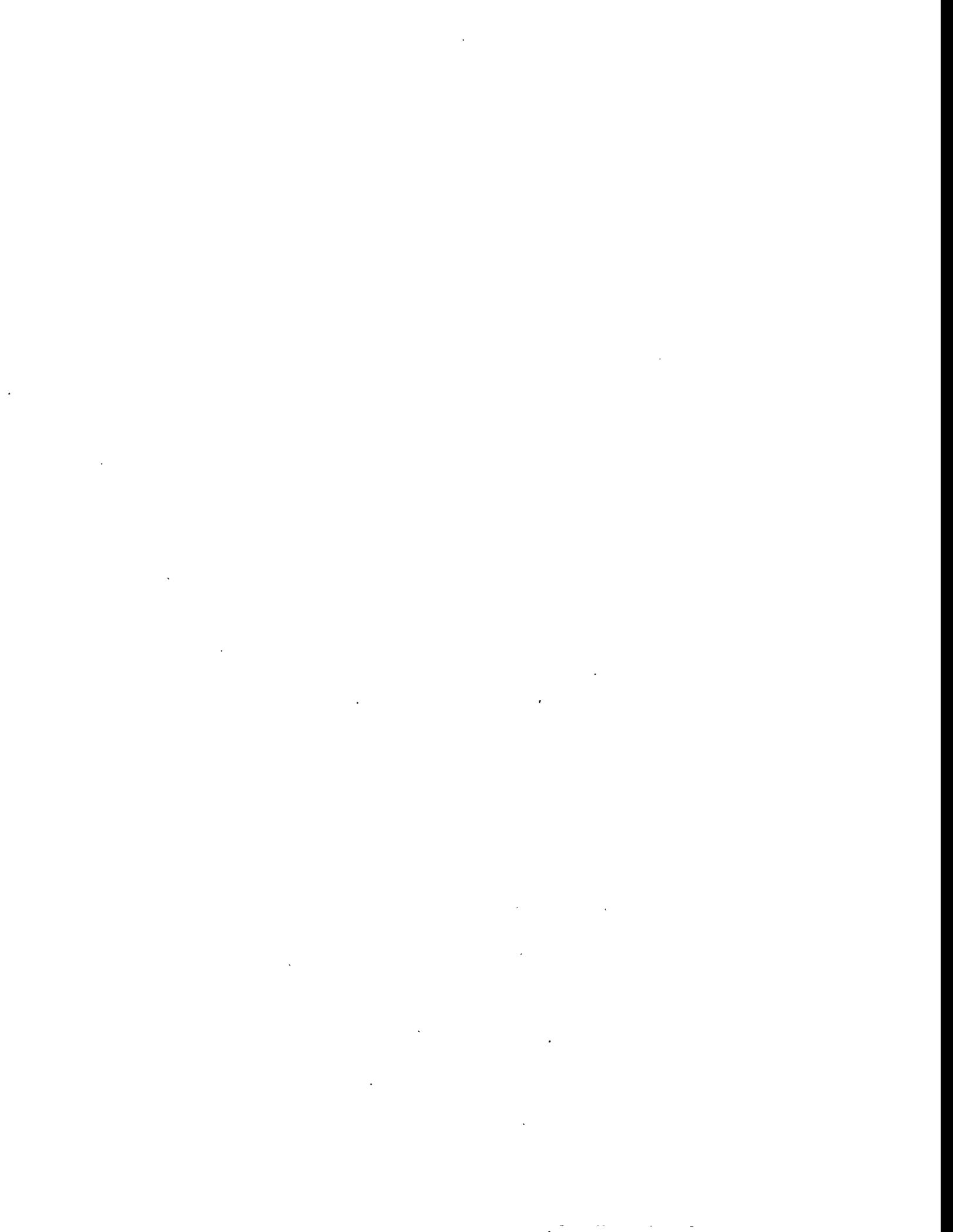
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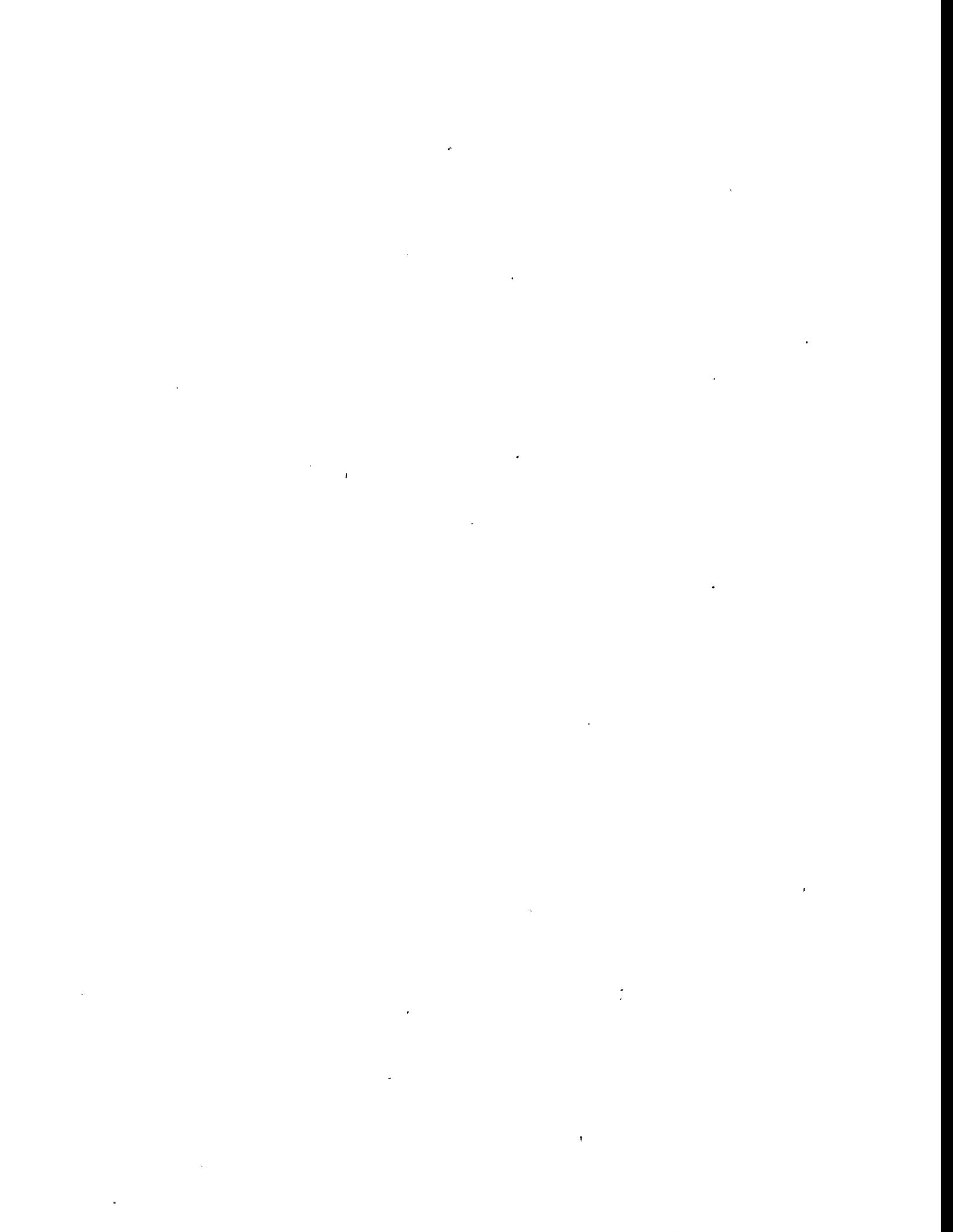
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ACRONYMS

CEA	Commissariat A L'Energie Atomique (French Atomic Energy Commission)
DOE	United States Department of Energy
GMODS	Glass Material Oxidation and Dissolution System
HEU	High-enriched uranium
HLW	High-level-waste
ISM	Induction skull melting
LEU	Low-enriched uranium
LLW	Low-level waste
LWR	Light-water-reactor
MP	Melting point
NAS	National Academy of Sciences
PCMs	Plutonium-containing materials
RPM	Revolutions per minute
SGN	Societe Generale Pour Les Techniques Nouvelles (France)
SNF	Spent nuclear fuel
SRS	Savannah River Site
TMI	Three Mile Island
U.S.	United States
VNIINM	All-Union Scientific Research Institute of Inorganic Materials (Russia)
WAC	Waste acceptance criteria



DIRECT VITRIFICATION OF PLUTONIUM-CONTAINING MATERIALS (PCMs) WITH THE GLASS MATERIAL OXIDATION AND DISSOLUTION SYSTEM (GMODS)

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EXECUTIVE SUMMARY

The end of the cold war has resulted in excess PCMs from nuclear weapons and associated production facilities. Consequently, the U.S. government has undertaken studies to determine how best to manage and dispose of this excess material. The issues include (a) ensurance of domestic health, environment, and safety in handling, storage, and disposition, (b) international arms control agreements with Russia and other countries, and (c) economics. One major set of options is to convert the PCMs into glass for storage or disposal. The chemically inert characteristics of glasses make them a desirable chemical form for storage or disposal of radioactive materials. A glass may contain only plutonium, or it may contain plutonium along with other radioactive materials and nonradioactive materials.

GMODS is a new process for the direct conversion of PCMs (i.e., plutonium metal, scrap, and residues) to glass. The plutonium content of these materials varies from a fraction of a percent to pure plutonium. GMODS has the capability to also convert other metals, ceramics, and amorphous solids to glass, destroy organics, and convert chloride-containing materials into a low-chloride glass and a secondary clean chloride salt stream.

This report is the initial study of GMODS for vitrification of PCMs as input to ongoing studies of plutonium management options. Several tasks were completed: initial analysis of process thermodynamics, initial flowsheet analysis, identification of equipment options, proof-of-principle experiments, and identification of uncertainties.

Incentives exist to develop GMODS if it is decided to immobilize PCMs in glass:

- GMODS is a single-step process for the conversion of PCMs to glass vs alternative multistep processes. Conventional glass-making processes require that potential feed materials be (a) converted to oxides or materials that decompose into oxides before being fed to a glass melter and (b) reduced in size. Pretreatment of metals (including plutonium metal), organics, chlorides, and other materials to convert them to oxides as a feed to a glass melter is a complex process.
- Direct conversion of plutonium scrap and residues to glass avoids the need to first separate the plutonium from such materials before conversion to glass. The large inventory of plutonium residues exists partly because existing separation processes have had difficulties in recovery of the plutonium

from these secondary process streams. This creates incentives to bypass the difficult plutonium separations problems if the final product is to be glass. Glass can accept many impurities within its structure. Direct conversion also converts heterogeneous solids (where nuclear materials accountability is difficult) into homogeneous glass with easier nuclear accountability and without concern about plutonium losses to other streams.

- The above characteristics of GMODS imply potential economic savings; easier nuclear materials accountability; reduced waste generation; and reduced health, environment, and safety concerns.

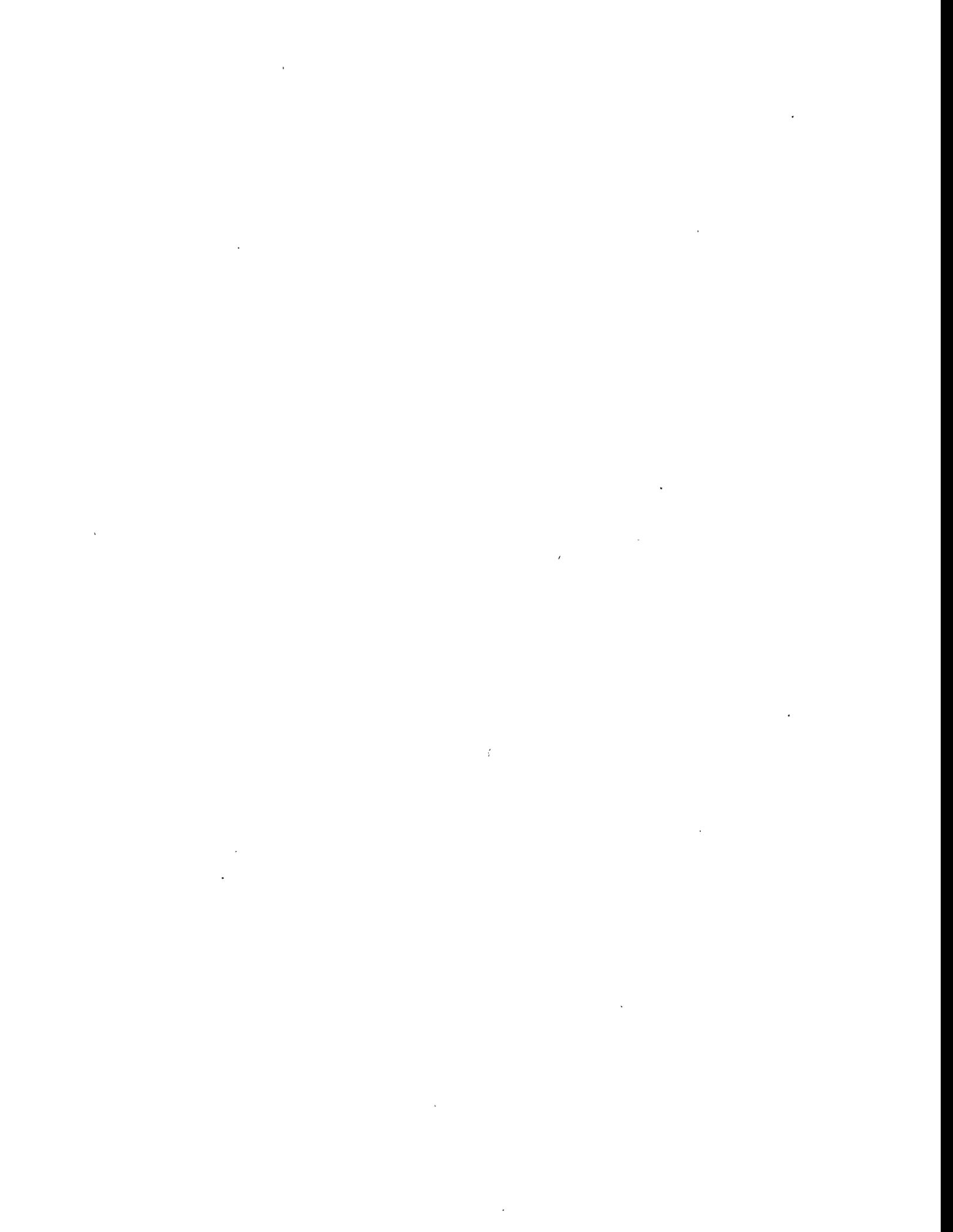
The basic concept of GMODS is to add unprocessed PCMs, glass frit, and a sacrificial oxide directly to a glass melter. A characteristic of molten glass systems is that they dissolve oxides—but not metals or organics. The addition of a sacrificial oxide to the molten glass provides a method to oxidize in situ (1) metals, such as plutonium, to metal oxides and (2) organics to carbon dioxide and steam. The metal oxides (such as plutonium oxide) dissolve in the glass, while carbon dioxide and steam exit the melter as gases. The feasibility of GMODS depends upon the selection of the sacrificial oxide and the glass formulation.

The preferred sacrificial oxide is lead oxide (PbO) in a lead-borate glass. Lead oxide, a component of many glasses, chemically reacts with metals such as plutonium metal in molten glass. The reaction products are metal oxides, such as plutonium oxide, that dissolve into the molten glass and lead metal. The lead metal separates from the glass, sinks to the bottom of the glass melter, and forms a separate molten-metal layer. The lead metal may be removed from the melter, oxidized separately to PbO, and recycled back to the melter to oxidize more plutonium. Lead is an oxygen carrier that does not leave the system.

After the PCMs are oxidized and dissolved into the glass, other additives (silica etc.) are introduced into the mixture to create a durable, long-term glass product. Any excess lead oxide is removed from the glass by the addition of carbon, which reacts with the lead oxide and creates (a) carbon dioxide gas, which exits the melter, and (b) lead metal, which separates from the glass. The product glass is poured from the melter and is solidified as glass logs or glass marbles. The lead metal is oxidized to lead oxide and recycled as the sacrificial oxide to convert the next batch of PCMs to glass.

The process thermodynamics of GMODS was evaluated, and the evaluation confirms thermodynamic process feasibility. Proof-of-principle experiments demonstrated the chemical feasibility of several critical chemical reactions. Cerium was used in these experiments as a substitute for plutonium. Proof-of-principle experiments showed that a variety of metals (cerium, uranium, aluminum, stainless steel, Zircalloy, etc.) were oxidized and converted to glass. Carbon was oxidized, and carbon oxides exited the molten glass. Chlorides were separated from the glass. Based on thermodynamic calculations and proof-of-principle experiments, flowsheets were developed, and key process equipment was identified.

The information and experiments to date suggests that GMODS has significant advantages for conversion of PCMs to glass. However, further significant development work would be required to make GMODS an industrial process.



1. INTRODUCTION

1.1 BACKGROUND

The end of the cold war has resulted in large inventories of excess plutonium-containing materials (PCMs) from weapons, weapons production, and weapons research. Methods to manage this plutonium are required. Several plutonium management options have been identified by the U.S. National Academy of Sciences (NAS) (NAS, 1994). NAS emphasized that the management of plutonium is an international security issue because plutonium is a key component of nuclear weapons. This creates unique issues compared to the disposition of other materials. The plutonium management options selected will depend upon decisions concerning plutonium management within the United States and international agreements between the United States and Russia.

One major subset of plutonium management options is to convert plutonium (in multiple chemical forms) to glass. A plutonium-containing glass may be produced for several different purposes:

Storage. Plutonium may be stored for long periods of time because no consensus can be reached as to how to dispose of plutonium or as to a policy to store it should it be needed for future national security or energy needs. There are storage concerns [U.S. Department of Energy (DOE), November 1994]. Plutonium in metal form is chemically reactive. Many other PCMs are chemically reactive. Plutonium must be stored in small quantities to avoid nuclear criticality. Nuclear materials accountability for plutonium scrap is difficult. Converting plutonium to an inert, homogeneous glass provides a safe, economic, long-term storage form which can be managed and accounted for more easily.

Direct disposal. Plutonium may be disposed of in a special disposal facilities such as deep boreholes. For plutonium to be disposed of, it must be in a form that meets both national security and waste management requirements. Plutonium glasses can meet waste management requirements for a waste form.

Conversion to high-level waste (HLW) glass. Plutonium may be mixed with other radioactive wastes to produce HLW glass suitable for disposal in conventional geological waste repositories. Both national security and waste management requirements must be met.

1.2 REPORT OBJECTIVE

The objective of this report is to describe the Glass Material Oxidation and Dissolution System (GMODS) for the direct conversion of PCMs to glass. This includes: (1) the technology (including flowsheets, mass balances, etc); and (2) the status of the technology. This report provides (1) a basis to evaluate GMODS, (2) an understanding of what future work is required, and (3) a single source document of what is known. This report, which is a baseline document, includes available information from multiple sources, including experimental data collected from other programs that are applicable to GMODS.

1.3 DESCRIPTION OF GMODS

GMODS is a recently invented chemical process (Forsberg, Beahm, and Parker, 1994*a*, 1994*b*) for the (1) direct conversion of metals, ceramics, and amorphous solids to glass, (2) oxidation of organics with residuals converted to glass, and (3) conversion of chlorides to a low-chloride glass and a secondary clean sodium chloride stream. GMODS is a unique glass-making process that eliminates the need for pretreatment before glass making. Conventional glass-making processes require that feed materials to glass furnaces first be converted to oxides or into compounds that decompose to oxides when heated. The processes to convert various materials to oxides before they are converted to glass are often complex and expensive. GMODS may accept feeds such as plutonium metal, scrap, residue, and other complex mixtures. GMODS is not a new glass. The final product is similar to plutonium glasses made by other processes.

1.4 CAVEATS

The following caveats apply to this report.

- The options for plutonium management are still being defined; thus, there are major uncertainties in both what PCMs are to be processed and what the product specifications will be. These uncertainties strongly impact what will be the preferred flowsheet options and choices of equipment for processing PCMs. To address this uncertainty, the main report describes the generic GMODS technology in its various forms with a series of appendixes that have specific flowsheets for specific applications.
- GMODS is a new technology. Patent applications were filed in 1994. There are significant uncertainties. This report is the first detailed report describing the technology.

1.5 ORGANIZATION OF REPORT

This report is organized so that the body of the report provides a brief description of GMODS for processing PCMs. Section 2 defines possible applications and their implications to the GMODS process in terms of feed materials, throughput, and product requirements. Section 3 describes the basic process; Sect. 4 describes the total system; Sect. 5 describes the process equipment; and Sect. 6 the glass product. Section 7 presents a sample flowsheet for a single application with defined feeds and products. The appendixes provide the detailed information about flowsheets, choice of options, and results of experiments.

2. GMODS APPLICATIONS FOR IMMOBILIZING PCMS

GMODS may be used for different plutonium-immobilization applications. An understanding of potential applications defines the potential requirements for the process. This section provides a description of possible applications and some of the constraints associated with each application. Figure 1 summarizes these options.

2.1 APPLICATIONS FOR CONVERSION OF PCMs TO GLASS

Three potential applications for conversion of PCMs to glass have been identified by the NAS and DOE. Each application may have different glass product requirements and, hence, different process requirements. The choice of products will depend upon national decisions.

2.1.1 Storage

Plutonium may be converted to glass for safe storage until (a) disposition options are selected or (b) as a strategy to maintain multiple future options for use or disposal of plutonium. Plutonium can be recovered from the glass if required. Alternatively, the plutonium glass can be used as an intermediate form for other applications. The stored glass would meet three criteria: (1) stable chemical form resistant to corrosion (including water), fire, and other mishandling; (2) nuclear criticality safety ensured by glass compositions containing neutron poisons (not criticality control by geometry); and (3) simple nuclear safeguards with plutonium in homogeneous glass in numbered product glass packages with known quantities of material in each package. These characteristics minimize storage costs.

Plutonium weapons components are designed for long-term storage; however, scrap and residue are not designed for storage. Much of the plutonium scrap and residue are in chemical and nuclear forms unsuitable for long-term storage (DOE, November 1994). There are major unresolved safety issues associated with current storage methods. Storage costs for these materials in current forms are high.

2.1.2 Disposition of Plutonium as an HLW Glass

NAS (1994) has stated that excess plutonium presents significant risks from theft, diversion, and reuse to build nuclear weapons. It recommends consideration of immobilization of excess plutonium in glass with other radioactive materials so that the plutonium can not be easily converted back to weapons. This recommendation was made in the context of possible international agreements with Russia for the disposal of excess plutonium as part of an international arms control agreement. NAS defined this recommendation as a

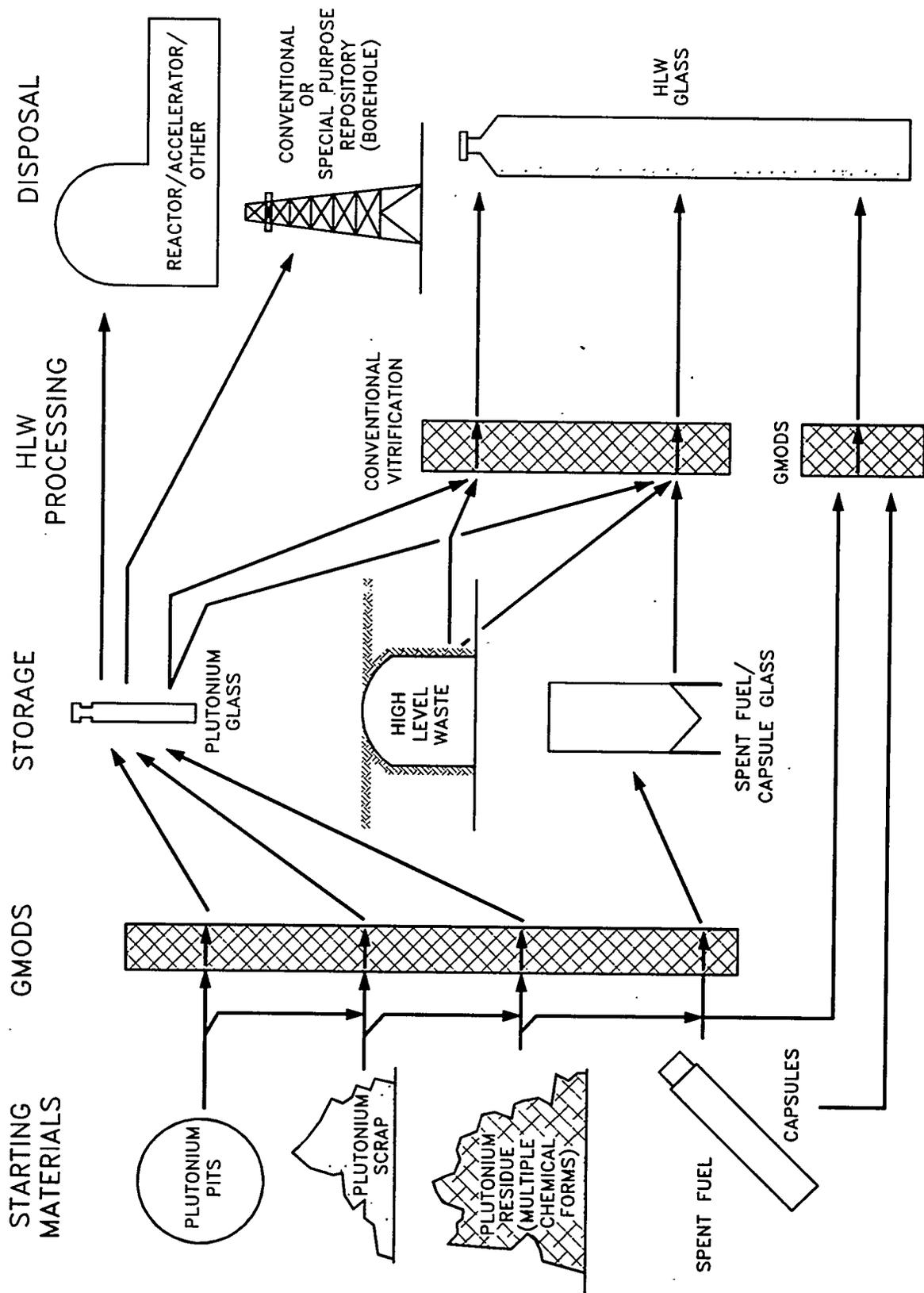


Fig. 1. GMODS processing options for PCMs.

“spent fuel standard.” Under this standard, excess plutonium is to be converted into a form that is no more accessible than is plutonium in commercial spent nuclear fuel (SNF). The rationale is: SNF containing plutonium is readily available worldwide to nation states; thus, there are no incentives to make excess plutonium less accessible. Plutonium in SNF is difficult to recover for weapons purposes because of three characteristics:

- High radiation levels.
- Reactor-grade plutonium contains higher concentrations of heavier isotopes of plutonium (^{240}Pu , ^{241}Pu , ^{242}Pu); thus, it is harder to use as weapons material compared to relatively pure ^{239}Pu in weapons-grade plutonium.
- The chemical form of the SNF makes plutonium chemical separation of plutonium difficult. Chemical separation is complicated because the plutonium is typically ~1% of the SNF and the SNF is difficult to dissolve into a chemical solution for separation.

The immobilization of PCMs into a HLW glass would be done as a two step process: (1) conversion of PCMs to an intermediate glass and (2) mixing the intermediate glass with radioactive materials to produce a HLW glass. The intermediate glass could have either the same characteristics as glass for long-term storage or could have different characteristics. The engineering incentives for an intermediate glass form include:

- **Flowsheet feasibility.** Most immobilization options require that final forms meet strict product specifications. Conversion of PCMs in multiple chemical forms into a single chemical form creates a consistent feed for the final process.
- **Process safety.** Plutonium metal has several undesirable process characteristics. Plutonium in small quantities can cause nuclear criticality events. Plutonium metal is pyrophoric and moderately chemically reactive. Therefore, conversion of plutonium early in its chemical processing to a stable chemical form with neutron poisons that eliminate criticality concern substantially reduces safety concerns in later process steps.
- **Process economics.** Process economics is strongly dependent upon scale of operation. When using pure plutonium, only small batches of plutonium may be handled to avoid nuclear criticality problems. After plutonium is converted to a chemical form with neutron poisons, such limits can be relaxed. Proposals to incorporate plutonium into HLW glass include intermediate plutonium glass forms so that the plutonium can be fed to the large HLW vitrification plants without concern about criticality limits.
- **Transportation.** PCMs are at many sites. Some PCMs may not meet transport requirements which may necessitate conversion of these PCMs to a stable, immobilized form for transport to a centralized treatment or storage facility.

Immobilizing plutonium in HLW glass requires large quantities of highly radioactive materials as feed input to the plutonium immobilization process. There are three sources: HLW in tanks, ^{137}Cs capsules, and

SNF. The preferred source of radioactivity will depend upon the definition of the spent fuel standard and the timing of any plutonium disposition campaign. The definition of the spent fuel standard determines (a) how much radioactivity is required to immobilize a given quantity of plutonium and (b) if the weapons-grade plutonium must be diluted with reactor-grade plutonium. There are physical constraints on various sources of materials:

- HLW in tanks is limited, and near-term plans are to convert much of this waste to glass to minimize risk of HLW tank storage. Cesium-137 capsules with added radioactivity are available. There is effectively an unlimited quantity of SNF.
- There are foreign sources of reactor-grade plutonium to isotopically dilute weapons-grade plutonium; but, in the United States, the only major source of reactor-grade plutonium is SNF. If isotopic dilution of plutonium is required, a method to obtain the plutonium from spent fuel would be required.

If SNF is used as a source of radioactivity to make HLW glass, it must also be converted to HLW glass. GMODS is a potential technology to convert SNF to glass.

2.1.3 Direct Disposal in Geological Repository, Borehole, or Equivalent

The plutonium may be disposed of as radioactive waste. This requires conversion of the PCMs into forms that meet repository waste acceptance criteria (WAC) (Appendix B). If the plutonium concentrations in the final glass form are sufficiently low, the final glass form can be treated as other wastes. If the plutonium concentrations are higher, special disposal sites (such as boreholes) are required to address safeguards issues. NAS has recommended possible disposal of excess plutonium in deep boreholes or their equivalents. The objective is to physically isolate PCMs so they are very difficult to retrieve.

2.2 TYPES OF PCMs

There are three major categories of excess PCMs: weapons components, scrap, and residues. Their characteristics are summarized in Table 1. Several of these characteristics are noteworthy:

- Most of the plutonium in weapons components is metal.
- Most of the volume and mass of PCMs are in the form of residues. Although typical plutonium concentrations in the residues are only a few percent, the total mass of material suggests that these materials will require most of the process capability.
- The chemical compositions of each plutonium class are very different. Plutonium residues do not have a single definable chemical composition because they are in many types of materials with different chemical compositions.

- The variable chemical composition of PCMs is such that no element (including plutonium) or compound dominates the composition of the feed.

Table 1. General characteristics of PCMs

Characteristics	Plutonium form	
	Weapons components	Residues
Plutonium quantity	Tens of tons	Few tons
Plutonium concentration	>95%	<5%
Total mass of PCM	Tens of tons	Hundreds of tons
Accountability	Excellent (number count)	Difficult
Characterized	Well defined	Partly characterized
Buildings with inventory	Few	Many

The scrap category may include such materials as unirradiated nuclear-fuel-containing plutonium, plutonium from experimental facilities, lightly irradiated plutonium targets, and other materials. Residues are secondary process streams from chemical conversions and purification of plutonium. Both the United States and Russia have relatively large quantities of plutonium scrap and residue. The relatively large quantities of scrap and residue are a result of several factors:

- It is difficult to recover plutonium from these materials. Operational problems delayed recycle of much of this material during the cold war.
- The production cost of new plutonium is high. Recovery cost of plutonium from these sources was expected to be less than the cost of new plutonium. As a consequence, the material was not treated as a waste, but stock piled for future processing.
- Much of the material is in chemical forms unsuitable for disposal. As a valuable resource during the cold war, no waste processing technologies to treat the material were developed.

2.3 ROLES FOR GMODS

The current multiple chemical and mechanical forms of plutonium, the multiple disposition options for plutonium in glass and the various process options indicate that GMODS may be used for multiple purposes in the management of excess PCMs. The potential roles are to:

- Convert plutonium in multiple mechanical and chemical forms into a plutonium glass for (a) feed to other vitrification facilities (intermediate process form), (b) long-term storage, or (c) waste disposal.
- Convert plutonium (multiple mechanical and chemical forms) and cesium capsules and/or SNF simultaneously into an HLW glass for disposal.

3. GMODS PROCESS DESCRIPTION

3.1 BASIC GMODS PROCESS DESCRIPTION

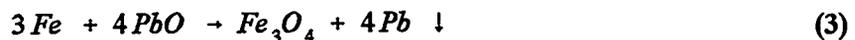
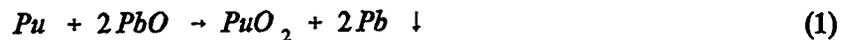
GMODS directly converts PCMs in metal, ceramic, organic, and amorphous solids to glass. It may be operated as a batch or continuous process. Figure 2 shows the process operated in the batch mode. Batches may be of any size—from kilograms to metric tons.

The initial condition for the process is a melter filled with molten oxidation-dissolution (lead borate) glass and lead metal. The lead borate glass has a composition of 2 mol of lead oxide (PbO) per mole of boron oxide (B₂O₃). The PbO is a component of the glass and a sacrificial oxide.

3.1.1 Waste Oxidation and Dissolution

In the first step, PCMs are added to the molten glass. The ceramic and amorphous solids in the PCMs dissolve into the glass. As a general rule, oxides dissolve into molten glasses. Metals and organics do not dissolve in molten glass. The inclusion of a sacrificial oxide in the molten glass provides a method to oxidize in situ (a) metals, such as plutonium, to metal oxides and (b) organics to carbon dioxide gas and steam. The resultant metal oxides, such as plutonium oxide, dissolve in the glass; carbon dioxide (in gaseous form) and steam exit the melter. The feasibility of GMODS depends upon the selection of the sacrificial oxide and the glass formulation.

The preferred sacrificial oxide is PbO. Lead oxide, which is a component in many glasses, reacts with metals in glass to yield metal oxides and metallic lead (Pb):



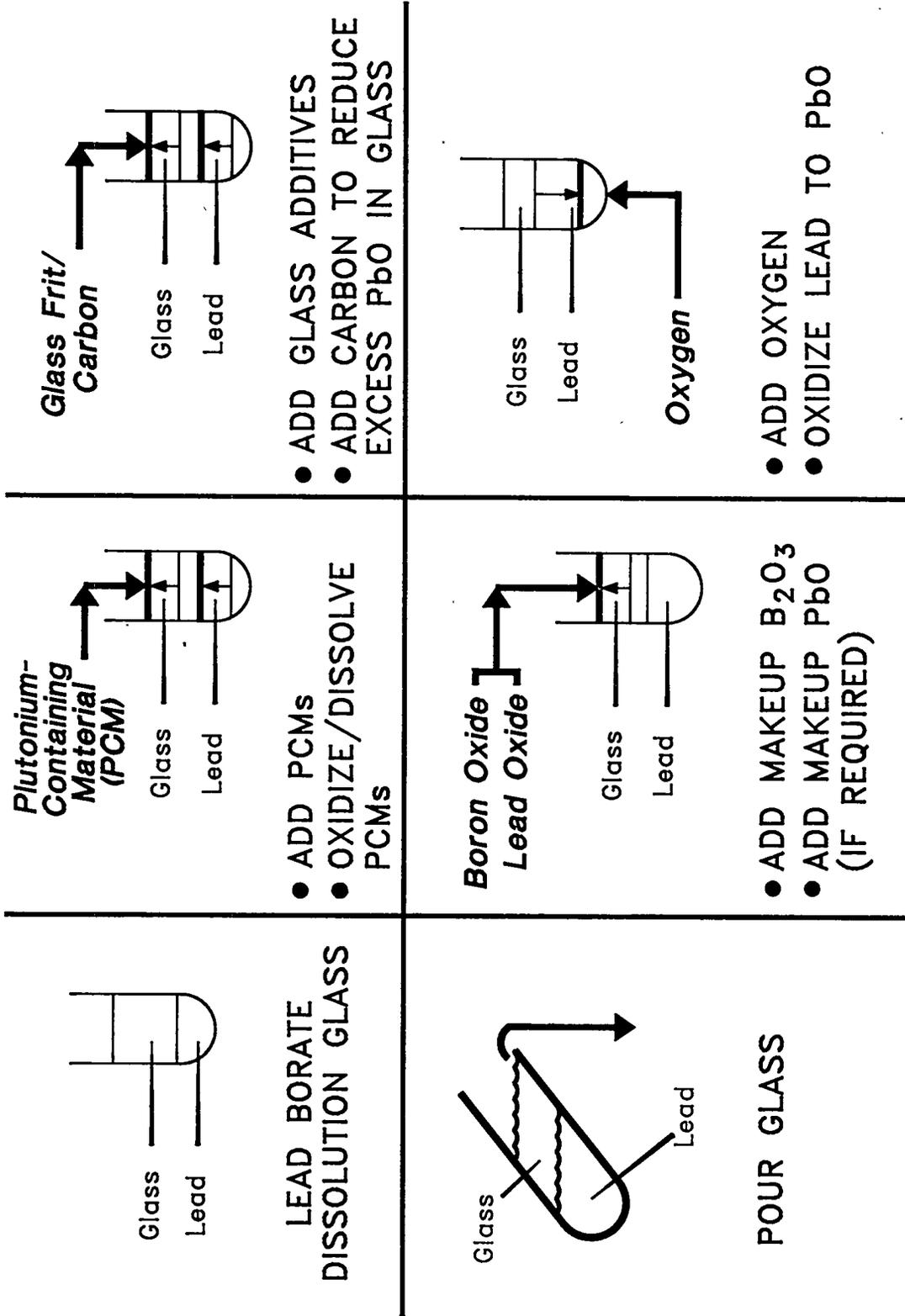


Fig. 2. GMODS batch processing of plutonium-containing wastes.

The reaction product, molten lead, separates from the glass and sinks to the bottom of the melter. Thermodynamic calculations (Appendix C) have determined the preferred oxide chemical forms for many elements after the PCMs have reacted with PbO in molten lead borate glass, and laboratory experiments (Appendix D) have confirmed that these reactions do occur (Table 2). Figure 3 shows the results of one proof-of-principle experiment.

The lead at the bottom of the melter forms a high-density liquid such that various PCMs will float at the lead-glass interface while reacting with the PbO and dissolving into the glass. This flotation process protects the bottom liner of the melter from both physical abrasion and chemical attack by unprocessed materials.

The properties of lead-borate glass allow rapid oxidation and dissolution of metal, ceramic, organic, and amorphous solids into glass. The PbO in this system is a powerful oxidant. Some metals will, however, form protective oxide coatings that slow chemical reactions. Boron oxide is a dissolution agent for metal oxides and rapidly solubilizes these metal oxides. It is the combination of both the PbO and B₂O₃ in appropriate ratios that makes GMODS feasible.

Dense, reactive metals, such as plutonium, when added to the glass, may sink through the glass into the molten lead. Some of the dense metal will react and dissolve into the glass during the descent. Plutonium has a low melting point (mp = 638° C); thus, it will melt at GMODS's operating temperatures (700–1000° C). When the plutonium metal enters the molten lead, it dissolves into the lead (Appendix A). Dissolved plutonium in the lead is then oxidized at the lead-glass interface and extracted back into the glass (Fig. 4). This oxidation and extraction process is a common phenomenon in many two-phase systems. We have experimentally confirmed this mechanism in GMODS using cerium metal, which was dissolved into lead metal, oxidized, and extracted as cerium oxide into the glass (Appendix D). Cerium is the preferred chemical substitute for plutonium for conducting initial proof-of-principle experiments.

3.1.2 Glass Refining

After oxidation-dissolution of the PCMs, various glass additives [silicon oxide (SiO₂) etc.] are added to improve the quality of the glass. Optimum glasses for rapid oxidation-dissolution of materials are different in composition from glasses for long-term durability; thus, glass additives that create a more durable glass are introduced after PCM oxidation-dissolution takes place.

Excess PbO can be removed from the final glass by adding carbon (Appendix A). The carbon reduces the PbO to lead metal while producing gaseous carbon dioxide [Eq. (5)]. Lead oxide may be removed from the dissolution glass for multiple reasons: (1) better final glass, (2) reduction of the volume of the glass, and (3) avoidance of the need for added lead oxide reagent in future batches.

Table 2. Representative proof-of-principle experimental data (see Appendix D)

<i>Demonstrated oxidation-dissolution of following metals in lead borate glass</i>	
Cerium (plutonium substitute)	Carbon
Zircalloy	Aluminum
Stainless steel	Uranium (plutonium substitute)

<i>Demonstrated dissolutions of ceramic oxides in lead borate glass (molar ratio = 2PbO:B₂O₃)</i>				
Ceramic	Wt. % in glass	Softening Temperature (°C)	Solid density (g/cm ³)	Relative viscosity
CeO ₂	10	450	6.99	Viscous at 550° C
U ₃ O ₈	20	475	8.14	Fluid at 550° C
ZrO ₂	10	500	6.97	Viscous at 550° C

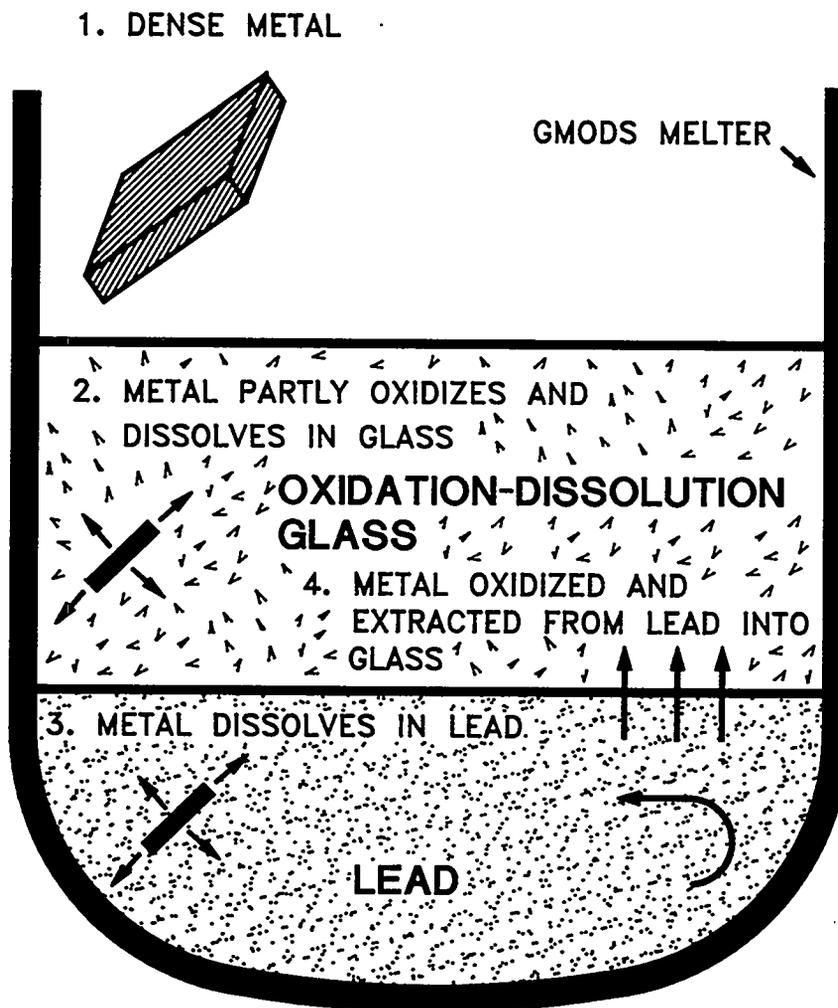
<i>Viscosity measurements of lead borate glass (molar ratio = 2PbO:B₂O₃)</i>			
Clean glass		20 wt. % uranium oxide	
Temperature (°C)	Viscosity (Centipoise)	Temperature (°C)	Viscosity (Centipoise)
620	200	626	1970
710	47.4	768	116
820	21.8	905	22.2

Cerium Loaded Glass



Lead Reaction Product

Fig. 3. Crucible dissolution test of conversion of cerium metal (surrogate for plutonium) in lead borate glass with conversion of cerium metal to cerium glass and production of byproduct lead.



1. HIGH DENSITY METALS ($>11.3 \text{ g/cm}^3$ density of lead) WILL SINK THROUGH LEAD. INTERMEDIATE DENSITY METALS ($>5.5\text{--}8.0 \text{ g/cm}^3$ density of glass) WILL FLOAT AT GLASS-LEAD INTERFACE
2. ALL NON NOBLE METALS PARTLY OXIDIZE AND DISSOLVE WHILE PASSING THROUGH MOLTEN GLASS
3. HIGH DENSITY METALS (uranium, plutonium, etc.) DISSOLVE IN MOLTEN LEAD
4. DISSOLVED METALS OXIDIZED AND EXTRACTED INTO GLASS AT GLASS-LEAD INTERFACE

Fig. 4. High-density metal oxidation-dissolution cycle in GMODS.

3.1.3 Glass Pour

The final waste glass mixture is poured into containers or sent to "marble" production machines, where it is solidified (Appendix H).

3.1.4 Makeup Glass Formulation

The product glass contains both B_2O_3 and PbO. Replacement B_2O_3 and PbO are added to the melter for processing the next batch of PCMs.

3.1.5 Lead Recycle

The lead at the bottom of the melter is reoxidized back to PbO by the addition of oxygen (Appendix E). Lead is an oxygen carrier that does not leave the system. The oxidation reaction is



This lead-oxidation process is a common industrial process used in the manufacturing of car batteries and in other industrial activities (Appendix E). This oxidation creates the new dissolution glass for the next batch of PCMs to be processed.

The optimum quantities of PbO in the oxidation-dissolution glass will usually exceed the quantities of PbO needed to oxidize PCMs and needed for the product glass. This excess lead oxide assists the dissolution process. It is later removed by addition of carbon before the final product glass is poured (Sect. 3.1.2).

Noble metals (gold, silver, rhodium, palladium, etc.) will dissolve and build up in the lead because they can not be oxidized by PbO; thus, they can not enter the glass. The glass does not dissolve noble metals. The lead industry has developed multiple technologies to recover these noble metals and produce pure lead (Appendix E). For small-scale operations, vacuum distillation is often used.

3.2 OFF-GAS SYSTEM

GMODS produces limited off-gas because solid PbO is the oxidizer. The primary off-gases are water and carbon dioxide, by-products of (a) oxidation of organic wastes (if organics are in the feed) or (b) reduction of PbO with carbon in the product glass.

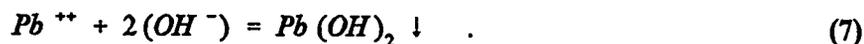
For most applications, GMODS would include an off-gas system similar to the British "Harvest" process for vitrification of HLW. This type of off-gas system uses special glass filters to remove the aerosols from the off-gas. When the filters are blocked, they are used as glass frit in the main process. This minimizes secondary waste generation.

3.3 PROCESSING OF CHLORIDE-CONTAINING WASTES

Many types of PCMs contain chlorides in various chemical forms (salt, plastic, etc.) as a result of metal production and fabrication operations. Many glasses cannot accept significant chlorides within their chemical structure. Furthermore, chloride-containing materials generally have poor performance as a storage or waste form.

GMODS converts PCMs with chlorides into glass and a secondary nonradioactive sodium chloride salt stream (Fig. 5). This separation process avoids chlorides in the glass and their negative impact on product quality. When GMODS processes PCMs with chlorides, the chlorides react with the lead-borate glass to produce lead chloride. Lead chloride ($PbCl_2$) is volatile and exits the melter as a vapor.

The melter off-gas can be sent through an aqueous sodium hydroxide scrubber that removes lead particles, glass aerosols, and the lead chloride. The lead chloride dissolves into the scrub solution. After entering the scrubber solution, the lead ions in solution react with the hydroxide ions and are precipitated from the aqueous scrubber solution as lead hydroxide. The chemical reaction is:



The sodium chloride that remains after lead hydroxide has precipitated is highly soluble in water. This salt solution is either filtered to remove the lead hydroxide, or the lead hydroxide precipitate is allowed to settle from the solution. This solids-liquids separation also separates and removes aerosols scrubbed by the aqueous solution. The lead hydroxide and other solids are recycled back to the melter.

The aqueous solution of sodium chloride is filtered and sent through a charcoal or an ion-exchange system to remove residual dissolved lead and other ions, and the clean salt is disposed of as nonradioactive waste. Filter material, ion-exchange resin, and charcoal are fed back to the melter for disposal. The chloride exits the system separately from the PCMs with which it entered. Appendix J provides a more detailed description of this separation step.

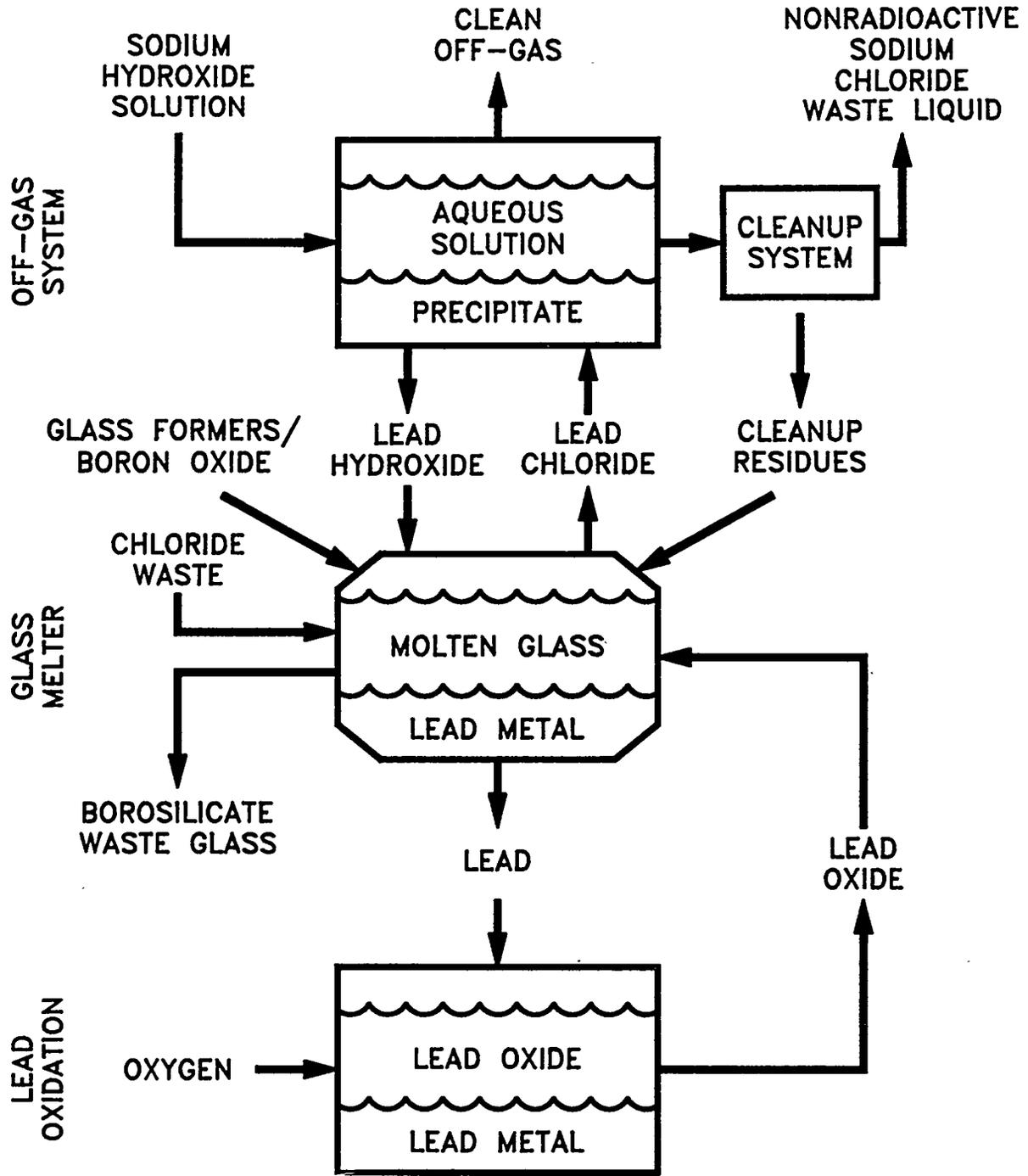
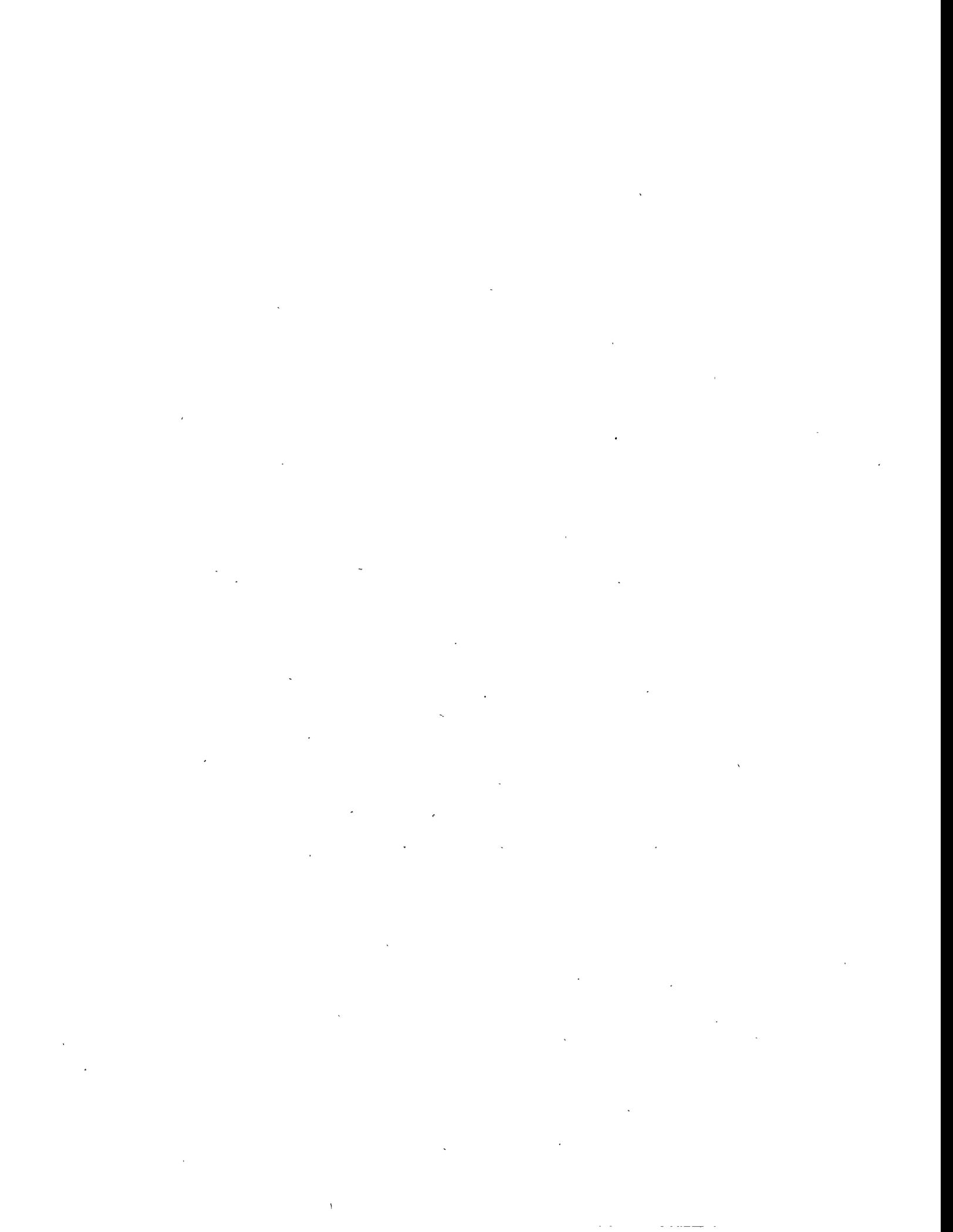


Fig. 5. Separation of chlorides from wastes while converting other waste compounds to glass using GMODS.



4. SYSTEMS

4.1 INTRODUCTION

Systems describe how a mission is to be accomplished using a specific process. Different feed and product requirements imply different systems. Examples of systems are included in this report to provide an understanding of the range of capabilities and options for GMODS and an understanding of how different system requirements alter the process.

4.2 SYSTEM DIAGRAMS

Systems can be described by block flow diagrams. Figure 6 shows the top-level block flow diagram for conversion of PCMs to a plutonium glass for storage or borehole disposal.

For some applications, such as conversion of PCMs to glass for storage, the process facility is not a dominant facility. An example is conversion of PCMs to glass where the PCM storage and receipt facilities may be larger operations than the chemical process.

4.3 INDIVIDUAL PROCESS OPERATIONS AND OTHER CONSIDERATIONS

Each box within a block flow diagram may contain one or more processes. In many cases, there are multiple process or equipment options to accomplish each task. The choice depends upon system requirements.

4.3.1 GMODS Melter Flowsheet Options

GMODS is a process, but there are multiple ways a flowsheet can be constructed from the process. The optimum way depends upon the feed and product requirements. GMODS was described earlier in the form of a batch process (Fig. 2). It can also be operated as a continuous or semicontinuous process with one or more vessels for each process step. One example is shown in Fig. 7, where most of the operations are conducted in a batch mode but the lead oxidation is external to the batch operations and operated continuously.

Such a flowsheet would be preferable if a feed with a high carbon content—such as ion-exchange resin—was being processed. In such a case, large quantities of lead oxide are required to oxidize the carbon to carbon oxides that leave the melter. Simultaneously, only the ash dissolves into the glass. With this flowsheet, the melter can run continuously for long periods of time destroying carbon continuously. Only when the dissolved ash content in the glass builds up would it be necessary to produce and pour a product waste glass.

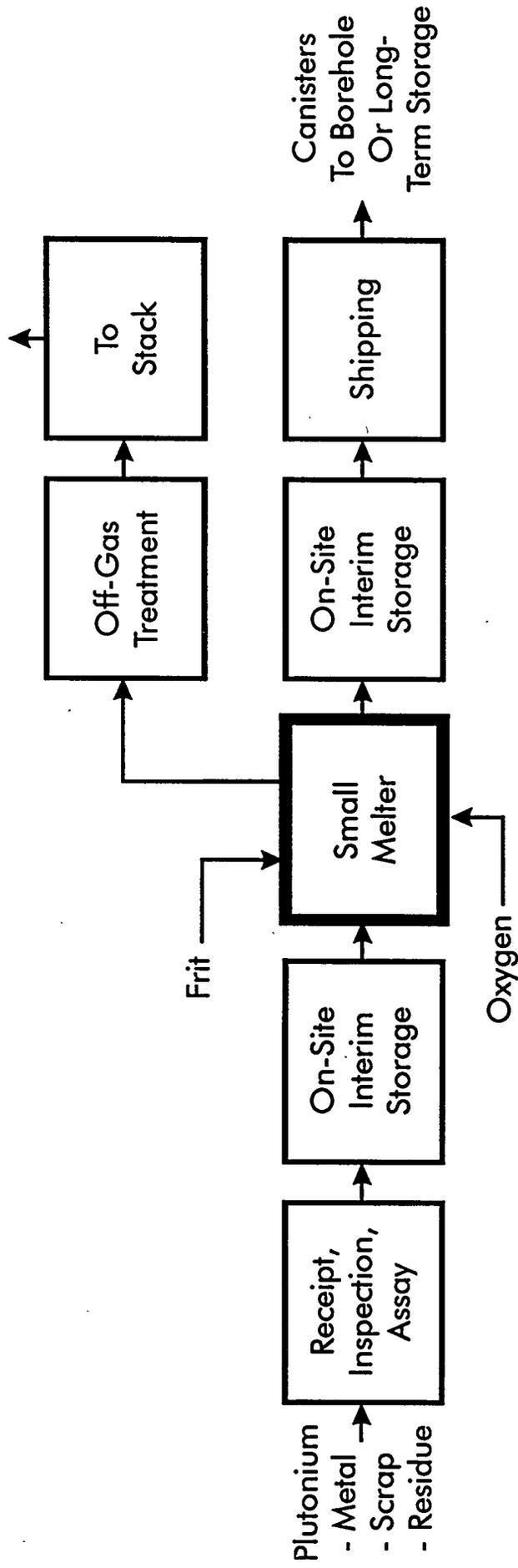


Fig. 6. Block flow diagram: Direct conversion of PCMs to glass.

GLASS-CONVERSION FURNACE

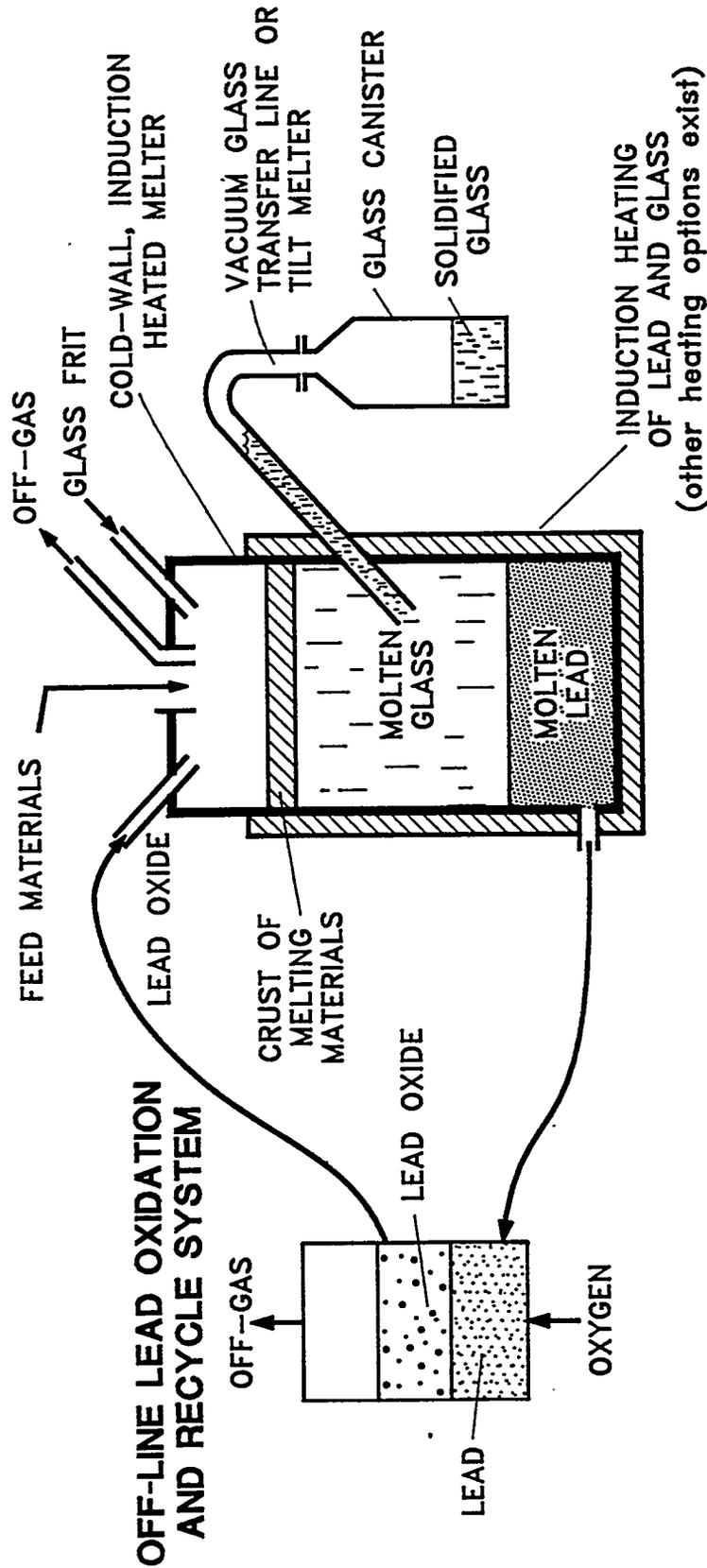


Fig. 7. GMODS—direct conversion of PCMs to glass.

4.3.2 Glass Inspection, Mixing, and Packaging System

After glass production, a glass inspection, mixing, and packaging system is required. There are multiple options with the preferred option dependent upon feed and product requirements. Figure 8 shows some of these options. The basic options are to produce glass logs or glass marbles.

If there is high confidence that the product glass will always meet product requirements, glass logs may be directly produced. If (1) the feed material is highly heterogeneous, (2) product control is difficult, and (3) a high quality product is required, marbles are the preferred waste form because they can be easily inspected. Marbles that fail can be recycled back to the melter. Marbles that pass inspection can be packaged as is, consolidated into glass logs, or encapsulated with some other encapsulation agent.

The marble option also allows mixing of different marble types to produce the final glass. It is not practical to feed many different materials simultaneously to GMODS to produce a glass with a tight product specification. It is feasible to convert different sets of materials to glass marbles and then melt the marbles together to produce a homogeneous final glass product. In some cases, there are strong incentives for such an approach:

- **Glass chemical properties.** There are limits on the concentrations of each element in glass if high-quality glass is to be produced. Different PCMs have widely different chemical compositions. If, for example, one particular PCM is converted to glass, significant quantities of glass may have to be produced to avoid exceeding the glass-concentration limit of one element in that PCM. Furthermore, it is well known that in glass systems, addition of some elements raises the acceptable concentrations of other elements in the glass. By mixing different PCMs with different limiting conditions for production of glass, the total quantity of product glass is reduced for any given amount of plutonium.
- **Nuclear criticality.** Nuclear criticality is avoided with the proper ratios of fissile materials to neutron poisons. Blending different PCMs and other wastes together limits the need to add neutron poisons to the final glass and increase its volume (Appendix B).
- **Thermal control.** Some fissile materials have high heat-generation rates. Blending with low heat-generation-rate materials creates glass waste forms that are easy to handle and acceptable for disposal.
- **Spent fuel standard.** For disposition of PCMs, it is proposed to mix PCMs with highly radioactive materials such as HLW liquid, SNF, and ^{137}Cs . The high variability in available sources of radioactive materials implies blending to meet the Spent Fuel Standard, minimize total glass produced, and ensure sufficient radioactive materials are available.

It is noteworthy that the equipment to consolidate glass marbles into logs is small, cheap, and simple compared to the mainline glass melters. Mainline GMODS melters must allow chemical reactions to occur and provide large-scale mixing to ensure a homogeneous glass. These requirements imply the need for large equipment compared to that needed to melt premixed marbles, convert into a homogeneous melt, and then consolidate the marbles into logs.

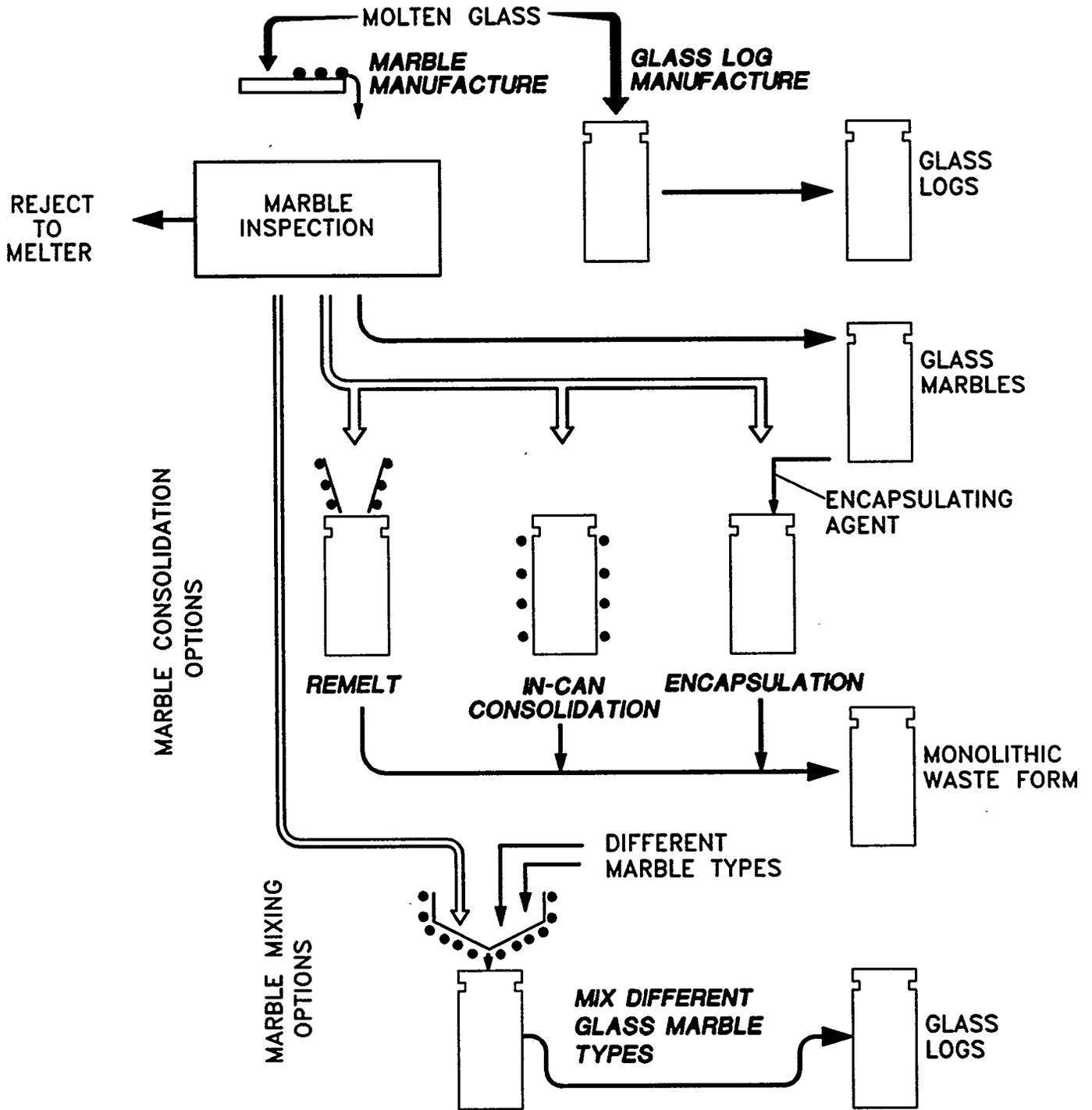


Fig. 8. Glass-form product options.

4.3.3 Nuclear Materials Accountability

GMODS may improve nuclear materials accountability. The conversion of heterogeneous materials with variable or ill-defined compositions into a homogeneous glass in containers of defined dimensions allows an accurate determination of plutonium content. It creates good conditions for nondestructive assay. Small samples of the final glass can also be used to determine the plutonium composition of the bulk glass.

The glass process also provides a mechanism to ensure that secret diversion of plutonium does not occur in storage. Platinum microspheres can be added to the glass when the molten glass is poured into the final package. The microspheres distribute randomly in three dimensions in the glass to create a unique tamperproof identity for each glass package that is determined by X-ray. This in situ system ensures that diversion by substitution of packages can not occur.

4.3.4 Waste Management of Secondary Wastes

All processes generate secondary wastes and require facilities to handle these wastes. GMODS creates unique options for handling these wastes. It is designed to convert metals, ceramics, organics, and amorphous solids to glass. That capability implies that secondary process wastes can be converted to waste glass for disposal. The GMODS melter that produces the primary glass can also produce secondary waste glasses or a secondary GMODS waste melter may be used.

In some cases, secondary wastes may be incorporated into the final plutonium product glass. An example of this would be glass filters from the melter off-gas system. Other secondary wastes may be converted to different glass waste forms.

5. EQUIPMENT DESCRIPTION

5.1 MAINLINE EQUIPMENT

The equipment required for GMODS will depend upon the detailed composition of the feed material, throughput, and product specifications. Different equipment necessarily may be used for plutonium metal vs plutonium residues.

GMODS may use several types of glass melters depending upon scale of operation. For large-scale operations, an induction-heated melter, such as those used for the processing of scrap metal and for certain specialty glass-making operations, may be preferred. Induction heating is rapid compared to most alternatives because (1) the bulk of the material is simultaneously heated and (2) limitations such as electrode corrosion in Joule heated melters are avoided. In waste management, induction-heated melters with capacities up to 20 tons are used to melt radioactive scrap metal. Induction heating will heat both lead and glass. Molten-lead currents help provide uniform bottom heating of the glass.

The melter materials of construction will depend upon the consistency of the feed. Where a consistent feed is expected, ceramic line melters are an option. The ceramic is chosen for the expected conditions. For widely variable feeds (plutonium scrap and residues) with variable chemical compositions, cold-wall, induction-heated melters are preferred (Appendix F). With a cold-wall melter, a thin layer of frozen glass separates the molten glass from the melter wall; thus, concerns about vessel corrosion are eliminated. A cold-wall melter avoids glass corrosion of the furnace lining. High temperatures ($\geq 1400^{\circ}\text{C}$) are possible with such glass melters. Being able to operate at these higher temperatures allows the use of glass formulations with higher PCM loadings and production of more durable glasses (Hrma, 1994). The high throughput per unit volume minimizes cost. The disadvantage of such melters is their lower energy efficiency.

Cold-wall, induction-heated melters are used industrially to melt titanium and superalloys (Fig. 9), melt ultrapure materials such as glass for fiber optics, process refractory metals, and process wastes (Fig. 10). Versions are currently being used and developed for radioactive waste processing in France (Monconyoux and Sombret, 1992; Monconyoux, Boen, Puyou, and Jouan, 1991), Russia (Sobolev et al., 1994), and the United States because of the aforementioned advantages. A cold-wall, induction-heated glass melter is under construction in the United States for treatment of low-level radioactive waste (Mason, September 1994).

The French have an operating melter with a throughput of 50 kg/h and are developing a 200-kg/h melter. Typical wall temperatures are 200°C . For French HLW glasses, the molten-glass operating temperatures are between 1150 and 1380°C . The French melters have operated up to temperatures of 2800°C for melting of uranium dioxide. These melters contain both (a) bottom valves for removing melt materials and (b) gas-

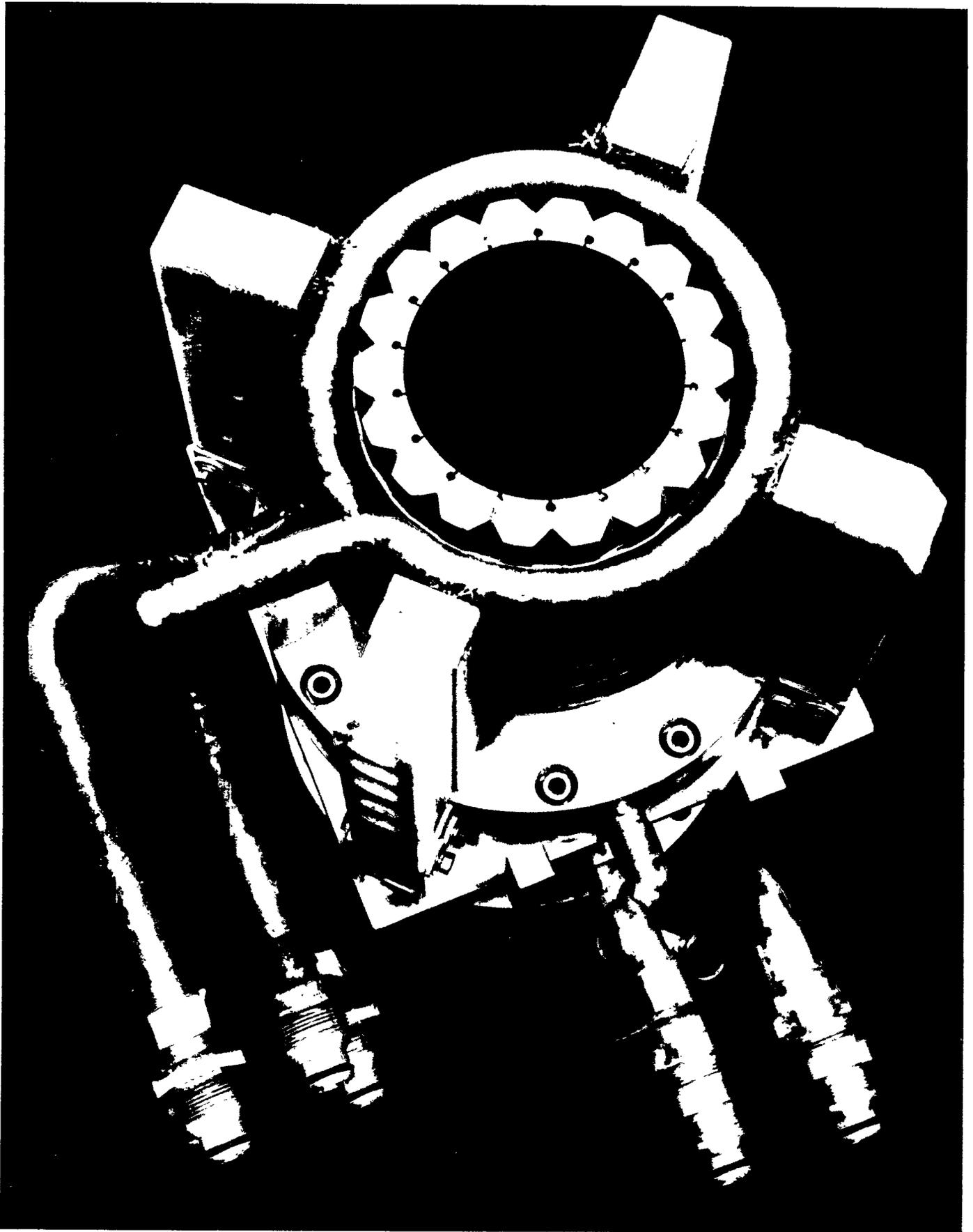


Fig. 9. Small cold-wall, induction-heated melter (*Courtesy of Consarc—New Jersey*).

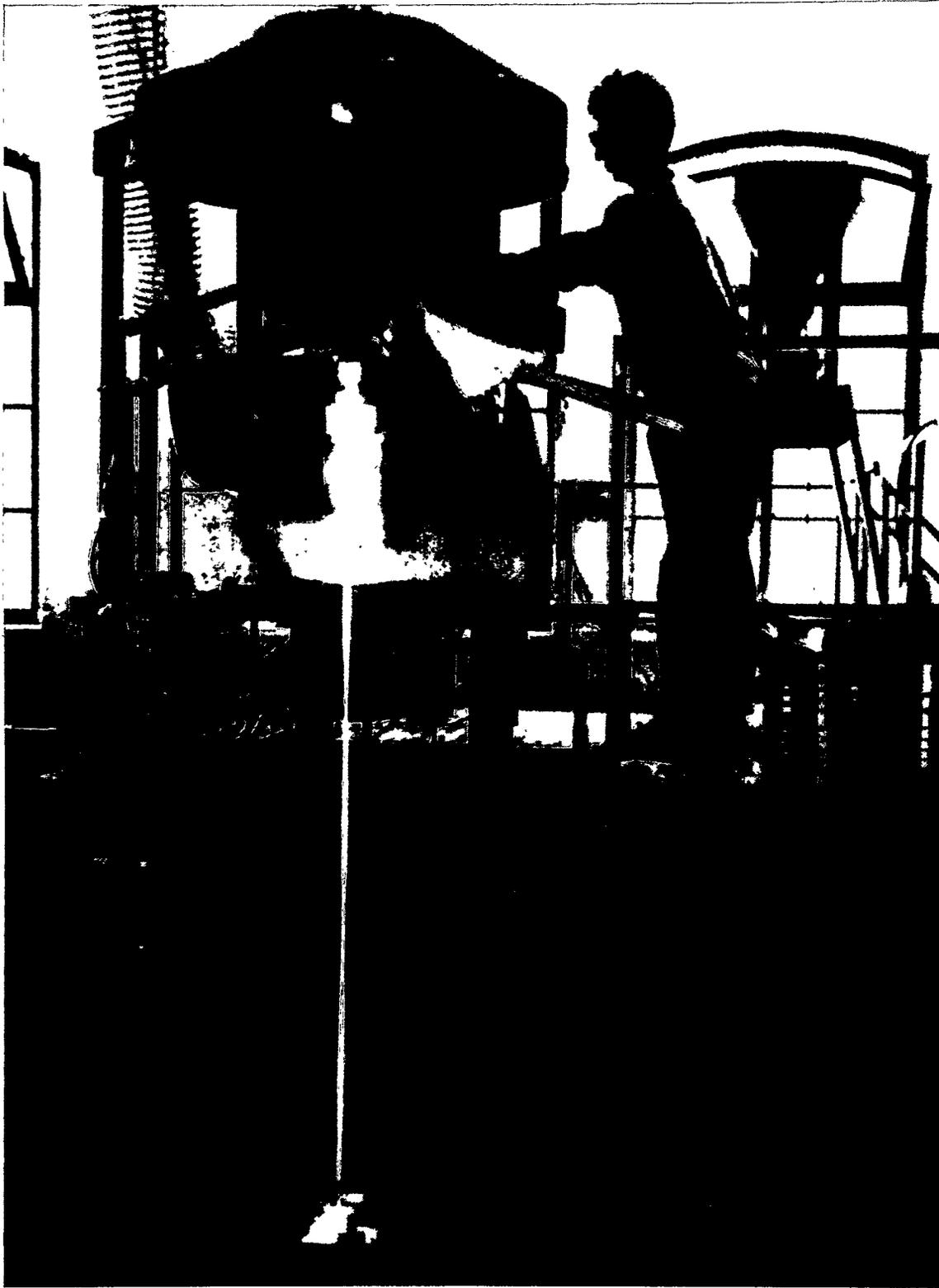


Fig. 10. Cold-skull, induction heat melter: Celes experimental plant (Courtesy of Prométhée, Group Schneider and Celes, Group Fives-Lille, Paris-France).

injection valves for purging the melt material. Some versions of the French melter are designed to process molten zirconium with the zirconium exiting the bottom of the melter. Also, a Russian melter has been recently installed at the HLW solidification facility at Mayak.

In terms of functional requirements, cold wall melter used to process refractory metals are most similar to those required for GMODS. In refractory metal processing the molten metal is kept in contact with a molten slag to extract impurities from the metal into the slag. The two-phase system (metal and slag) is similar to GMODS except for the higher operating temperatures. Much of this type of equipment has been developed in Russia.

It is noted that cold-wall, induction-heated melter for the applications described herein are small (0.1 to 1 m) compared to traditional HLW glass melter used in the United States. This reflects differences in input feed materials and melter design. Many HLW melter are fed nitrate-containing liquids and slurries. This creates high-volume, nitrogen-oxide-and-steam, off-gas flows. Large surface area melter are required to allow a slow exit of the gases from the melter and thus avoid high aerosol loadings in the off-gas system. With low off-gas generation rates from GMODS, small-volume, high-powered glass-melting technology can be used.

For each melter, there is the option of glass or lead transfer to product packages or external lead oxidation loops, respectively, by pouring from the melter or using bottom valves (Roth, Grunewald, and Tobie, 1994). Bottom-placed freeze valves have been specifically designed for glass and metal melter.

5.2 PROCESS CONTROL

GMODS requires process control both to produce the desired product and to ensure safety, which includes both chemical safety and nuclear criticality safety. For control purposes, multiple independent systems will be used to determine the status of the glass in the melter at all times.

The important process parameters are temperature, concentrations of elements in the glass, and assurance of homogeneous glass solutions. Temperatures must be limited to avoid overheating the system. Overheating causes equipment burnout and excess lead-glass component to vaporize and be routed to the off-gas system. Temperatures should be as high as possible (within these constraints) to minimize process time and maximize throughput.

Product requirements necessitate a uniform glass product composition; therefore, the key process parameter is a determination as to when uniform glass compositions *in the melter* are obtained and, thus, when the product is ready to pour. Measurements of glass homogeneity are also needed for safety. To avoid nuclear criticality, each batch of plutonium must be homogeneously dissolved in the glass before new batches

of plutonium are added to the melter when the total plutonium inventory exceeds several kilograms. Plutonium dissolved in glass solution is not a criticality concern because it is diluted with neutron poisons (boron, rare earths, etc.) in the glass. Succeeding plutonium feeds can not be added until the previous plutonium has dissolved into the glass.

Several independent methods can be used to ensure uniform glass compositions to meet product specifications and ensure nuclear criticality safety.

- Experiments and process models can be used to predict operations and, hence, determine the minimum time until the PCMs are fully oxidized and uniformly dissolved in the glass.
- Plutonium in the feed can be used to monitor the degree of glass homogeneity. Pulsed-neutron sources and detectors are used to determine the fissile content of waste packages before processing and disposal (Appendix I). These systems also determine the location of fissile material in waste packages. They can be used to determine the plutonium distribution within GMODS. This allows an on-line independent determination of variations in plutonium concentration in glass and lead.
- Glass samples can measure glass composition, including plutonium content. In normal operations, the amount of plutonium added to the melter will be known. This implies a unique plutonium composition of the glass if the plutonium is homogeneously mixed in the glass. Comparisons of plutonium in glass to total plutonium in the feed determine glass homogeneity.

5.3 CRITICALITY CONTROL AND EQUIPMENT DESIGN

The approaches used to ensure product quality and criticality safety have a major impact on economics. Small quantities of plutonium in certain environments can start a nuclear criticality event. Historical accidents indicate that the consequences do not usually go beyond the facility; however, it is very important to avoid such accidents to protect employee health and safety and to acquire public acceptance.

The allowable batch size will be determined by nuclear criticality considerations (Appendix A). After the plutonium oxide is dissolved in the glass, criticality is controlled by the boron as a nuclear poison. The flowsheet and operating procedures must preclude any excessive accumulations of plutonium separate from the boron. This will require both limitations on the amount of plutonium per batch and measurements to ensure that the plutonium is dissolved into the glass product. There are three approaches to criticality that can be used with this flowsheet.

- **Plutonium mass limit.** Criticality safety can be obtained by limiting the total plutonium in the system to <5 kg so that criticality can not occur.
- **Geometry limit.** In a cylindrical geometry with plutonium metal, the melter size can be limited to about 4.4 cm to ensure that criticality can not occur. The maximum diameter depends upon the plutonium chemical form.

- **Concentration control.** Nuclear criticality can occur with plutonium metal in sufficient quantities, but it can not occur when the plutonium is dissolved in the GMODS glass at appropriate concentrations because of the high concentrations of boron. The maximum allowable concentration of plutonium in the glass to avoid nuclear criticality depends upon the glass composition, but will typically be near 10 wt %. This allows the option to use a larger melter where the plutonium dissolution step is broken into a series of ministeps. During each ministep, several kilograms of plutonium are added to the melter. The plutonium is oxidized and dissolved into the oxidation-dissolution glass. When this is complete, several more kilograms of plutonium are added to the melter and subsequently oxidized and dissolved. These ministeps are repeated until the oxidation-dissolution glass is fully loaded with plutonium; then the product glass can be produced. Concentration control does not limit total plutonium per process batch but does limit rates of plutonium addition to the melter.

Large-scale equipment dramatically lowers cost; thus, criticality control by concentration control is usually preferable. With criticality control by control of fissile concentrations, the quantity of plutonium per batch can safely be many critical masses, thus allowing the use of large-scale equipment. Criticality control by fissile concentrations is used in some parts of the nuclear power industry and widely within the DOE in waste management.

Criticality limitations will apply to any plutonium-processing option. Those process options where neutron poisons are chemically added to the system in the first process step allow a choice of options on how to avoid nuclear criticality in latter operations. This can have a major impact on costs and offers safety advantages. GMODS is in this class of options.

6. PRODUCT DESCRIPTION

The final product composition may depend upon which plutonium disposition option is chosen. Typical ranges of glass composition for one set of plutonium storage glasses are shown in Table 3. These numbers are based on preliminary experimental work at Savannah River Laboratory (Ramsey, 1994) in development of actinide glasses.

The glass product form can be logs or marbles (Appendix H). Logs provide a well-defined product form that fills a product canister. Marbles allow easy inspection of the quality of the plutonium product and easy recycle of off-specification materials. Marbles can also be converted into glass logs using small, simple glass melters or by filling the containers with marbles and heating the marbles to consolidate them at temperatures below normal molten-glass conditions. This option also allows separate production of marbles of plutonium glass and HLW glass with the possibility of combining the marbles and melting them together within the final waste package.

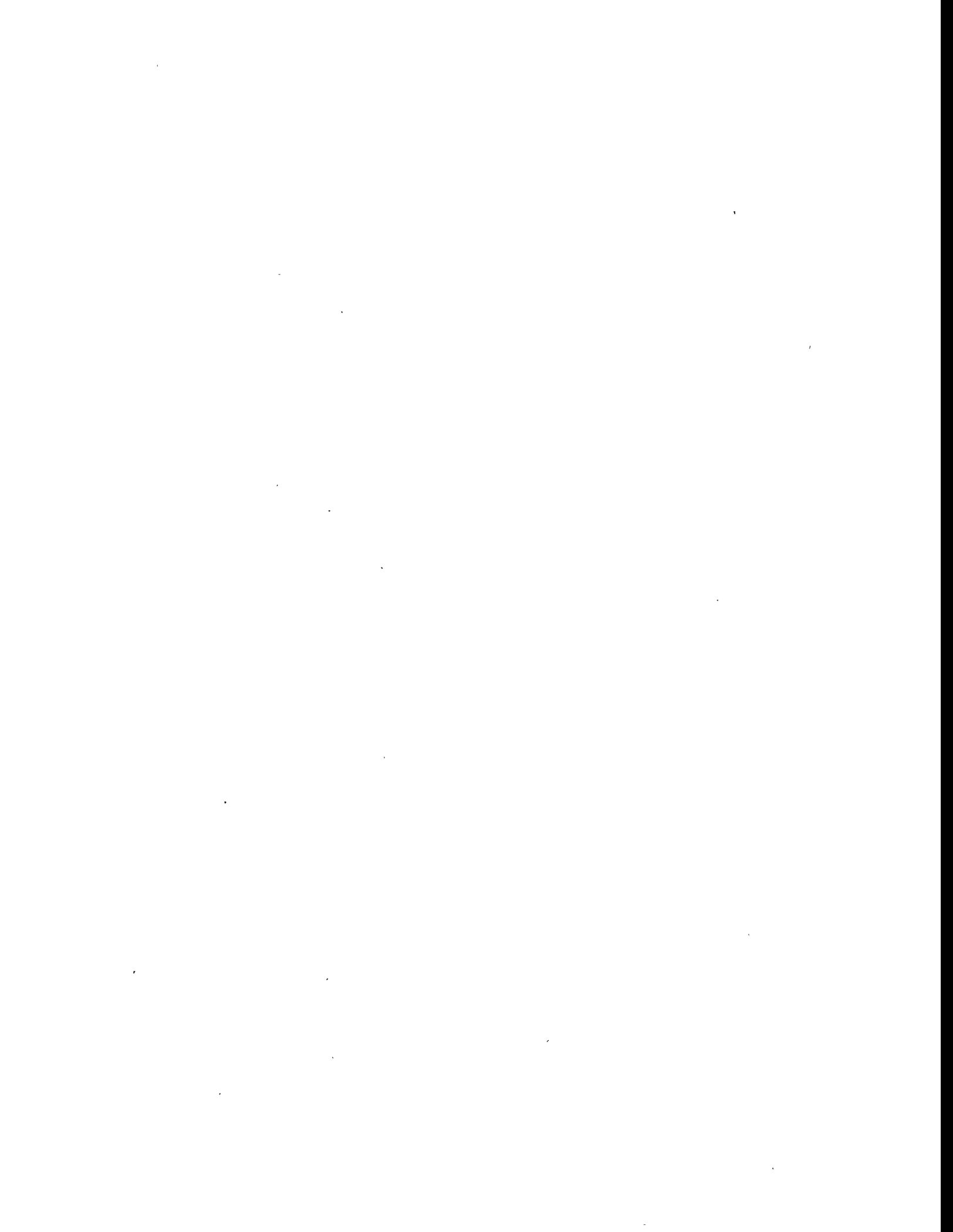
Table 3. Nominal actinide borosilicate glass compositions

Component ^a	Range tested (wt. %)
SiO ₂	21-30
B ₂ O ₃	5-8
BaO	2-4
Al ₂ O ₃	3-13
PbO	8-14
PuO ₂	<i>a</i>
UO ₂	0-20
Am ₂ O ₃	<i>b</i>
Cm ₂ O ₃	<i>b</i>
La ₂ O ₃	0-55
Nd ₂ O ₃	0-55
CeO ₂	0-18

^aCeO₂ and ThO₂ used as surrogates for plutonium in glass when conducting glass formulation tests. Actual plutonium loadings limited to ~10% due to nuclear criticality concerns.

^bNd₂O₃, Eu₂O₃, and La₂O₃ tested as surrogates.

Note: Typical densities for 10 wt. % plutonium glass are 4.8 g/cm³.



7. EXAMPLE FLOWSHEET

Conceptual material balance and equipment flowsheets are needed for preliminary comparisons with other flowsheets for plutonium processing and as a basis for planning a GMODS development program. Because the amount of experimental information available is limited, the conceptual GMODS flowsheets are based on limited experimental data, assumptions, and extrapolations of known information. One major purpose for preparing these preliminary conceptual flowsheets is to identify which of the assumptions or extrapolations are most crucial and, thus, identify which data are most important to validate the GMODS flowsheets for plutonium.

An example flowsheet with mass flows is shown (Fig. 11) for a feed that is predominantly plutonium metal. This flowsheet assumes GMODS operations are conducted in a single vessel in a batch mode (Fig. 12). The product glass composition is shown in Table 4. Each processing step can be operated at the conditions necessary to meet a major processing requirement. Because of the limited information available, chemical and equipment flowsheets for continuous GMODS operations would require added assumptions and additional uncertainties. A more complete discussion of flowsheet considerations is given in Appendix A.

The glass composition requirements and the nuclear criticality limitations are major considerations. The batch type of flowsheet provides the simplicity and maximum flexibility necessary from these considerations. It is assumed that a cold-wall, induction-heated melter is the primary piece of equipment. Appendix G provides additional flowsheets for the option of conversion of SNF and PCMs to HLW glass.

BASIS: 1 kg OF Pu METAL, A GLASS WASTE COMPOSITION SUITABLE FOR STORAGE OR DISPOSAL, WEIGHT IN kg

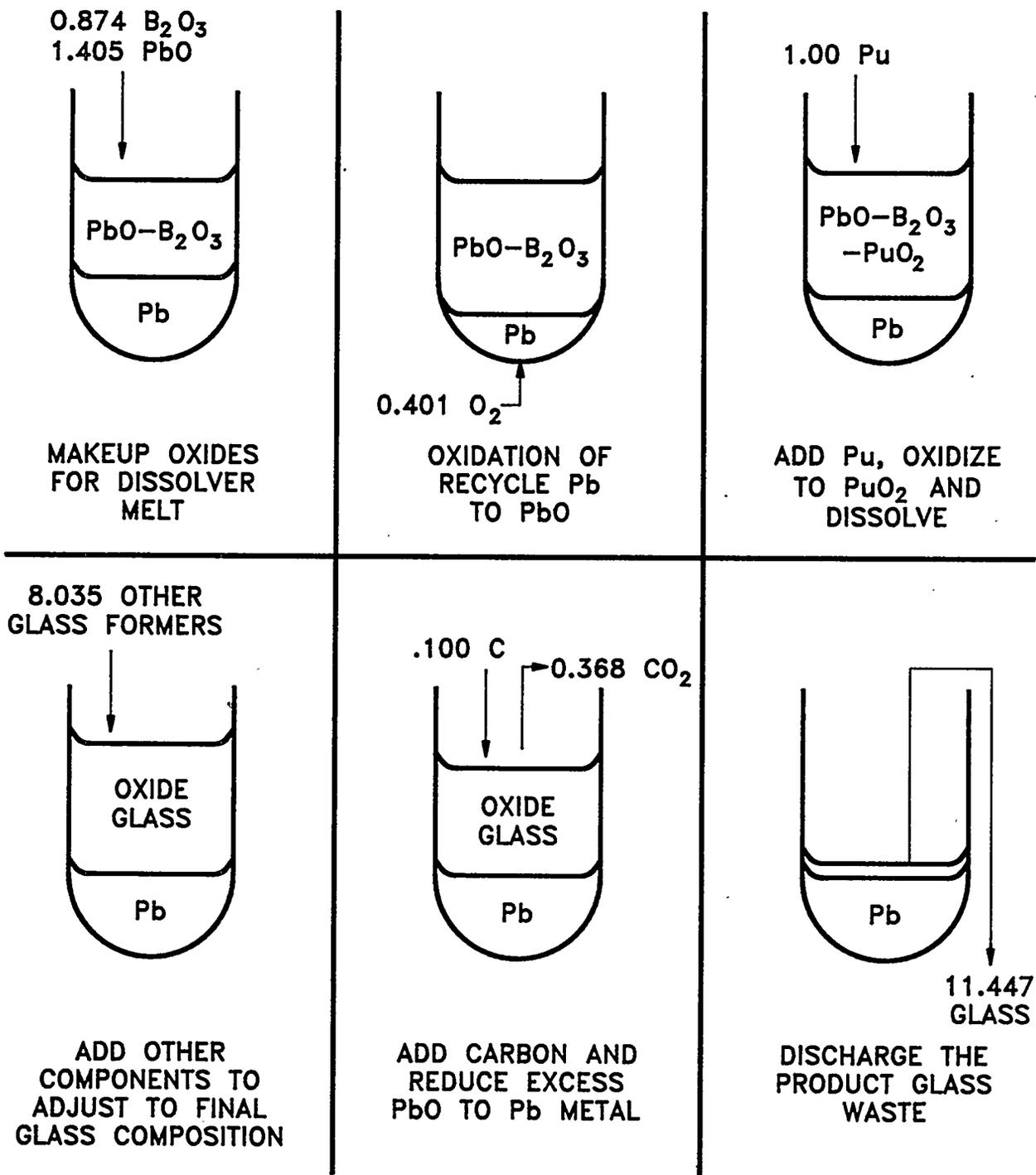
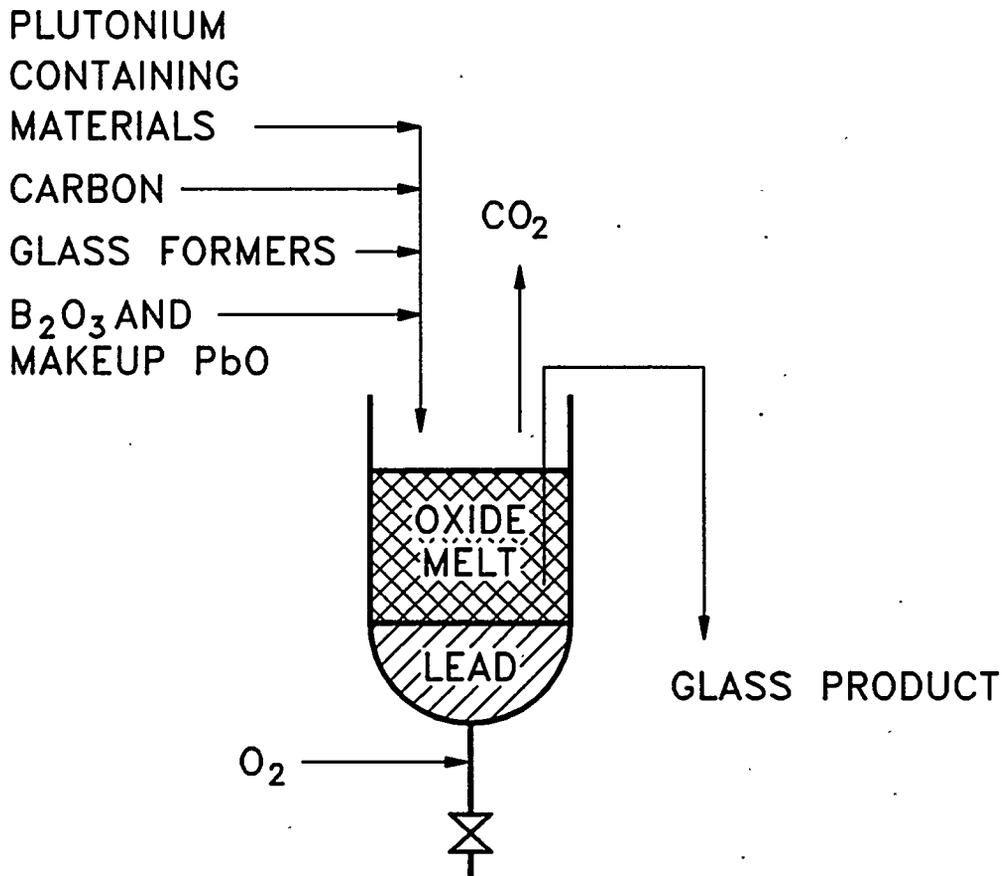


Fig. 11. A material balance for batch GMODS processing of plutonium metal.



BATCH PROCESSING STEPS:

<u>NUMBER</u>	<u>DESCRIPTION AND PURPOSE</u>
1	OXIDATION-DISSOLUTION GLASS IN MELTER
2	ADD Pu METAL, OXIDIZE AND DISSOLVE
3	ADD GLASS FORMERS TO ADJUST MELT COMPOSITION TO FINAL GLASS WASTE COMPOSITION
4	ADD C TO REDUCE EXCESS PbO TO Pb AND CO ₂
5	DISCHARGE GLASS WASTE (10 wt % PuO ₂)
6	ADD B ₂ O ₃ AND MAKEUP PbO FOR ONE BATCH
7	ADD O ₂ TO CONVERT RECYCLE Pb TO PbO

Fig. 12. Batch processing for plutonium metal feed to a GMODS process.

Table 4. Product glass composition, assuming plutonium metal feed

Metal	Metal (Moles per mole Pu)	Metal (g-mol)	Weight (kg)	Weight of oxide (kg)	Oxide (wt. %)
Pu	1.00	4.18	1.000	1.146	10.0
B	6.0	25.1	0.272	0.874	7.6
Pb	1.5	6.27	1.300	1.405	12.3
Si	13.0	54.4	1.528	3.268	28.5
Al	6.0	25.1	0.667	1.280	11.2
Ba	0.6	2.51	0.345	0.385	3.4
Other				3.102	27.1
Total				11.46	100.1

8. OTHER CONSIDERATIONS

8.1 HEALTH, ENVIRONMENT, AND SAFETY

GMODS has a set of characteristics that, in principle, minimize health, environmental, and safety concerns compared to existing processes:

- Direct conversion of plutonium to a glass with minimum plutonium processing and handling operations.
- Minimum off-gas to treat with the use of PbO as a recyclable oxide.
- Potential for single-vessel operation with minimization of secondary waste quantities.
- Conversion of secondary wastes to high-quality-glass waste form.

Detailed hazard and operability analysis will be required to evaluate process safety characteristics when the process is developed. Until process development is farther along and designs are more nearly complete, uncertainties will exist that can not be addressed because of lack of information.

8.2 ECONOMICS

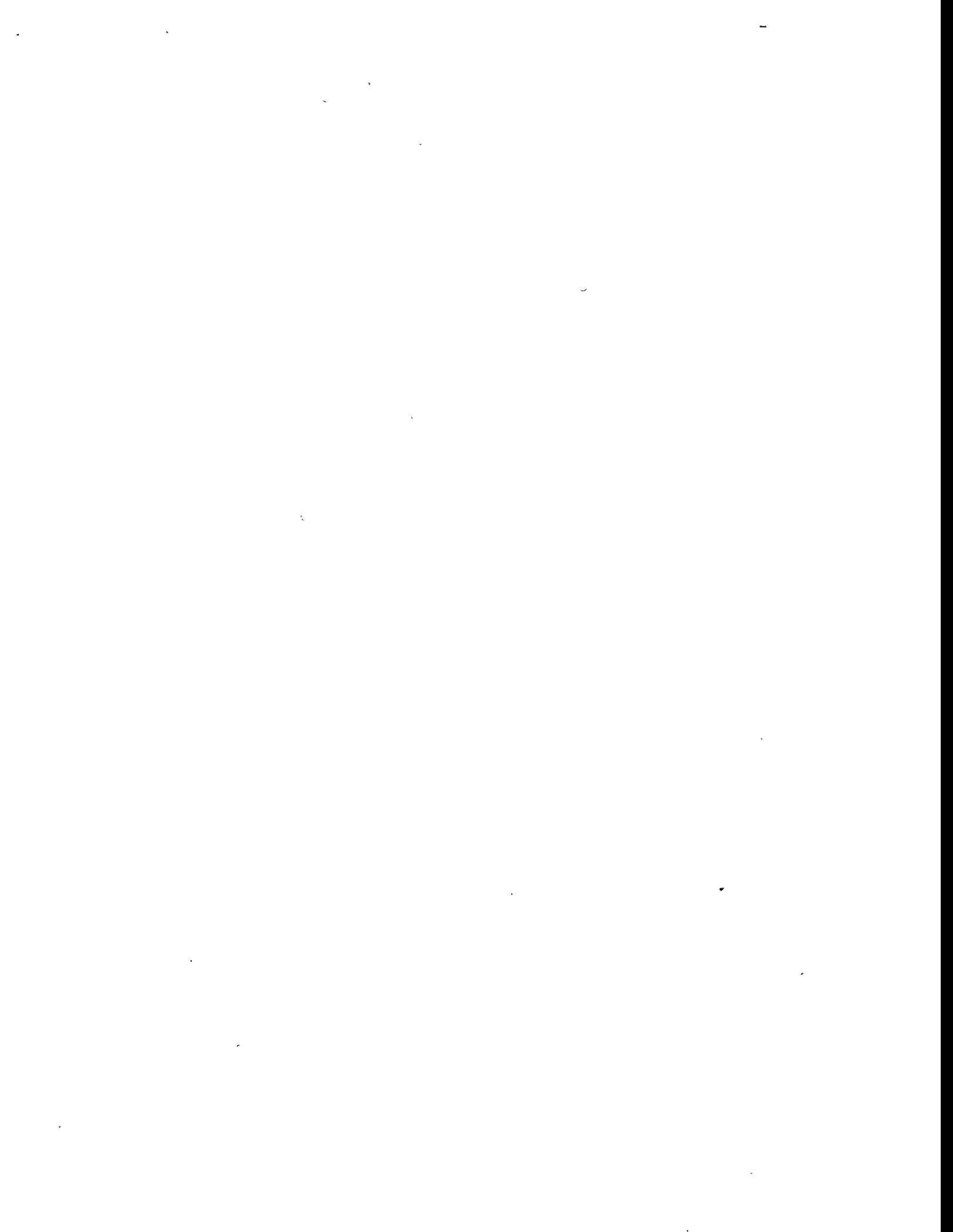
Detailed studies will be required to determine process economics, which is a strong function of the number of process steps and equipment size. Based on theoretical considerations (the limited number of process steps), the GMODS has the potential to be a low cost process.

8.3 UNCERTAINTIES

There has been no industrial experience in converting plutonium to glass with any process—hence, no real baseline process exists as a basis for comparison. There are significant technical uncertainties with GMODS that can be resolved only by process development.

Thermodynamic calculations indicate GMODS's thermodynamic feasibility. Limited proof-of-principle experiments have confirmed key chemical reactions. Flowsheet analyses have identified alternative flowsheet options. However, there are significant uncertainties.

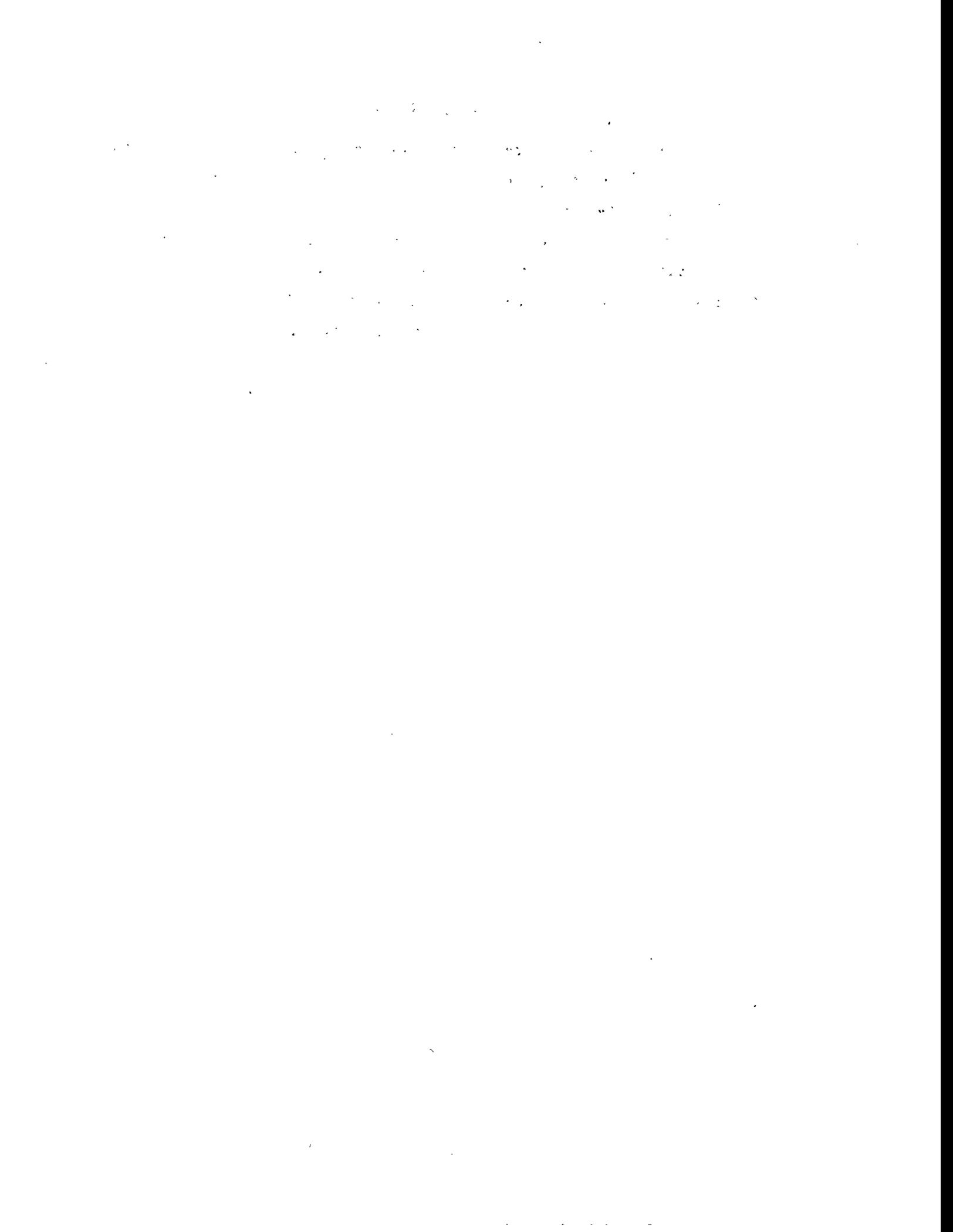
- Only limited chemical reaction rate data exist with limited modeling. Better information is needed to size equipment for any given throughput.
- There are multiple flowsheet options.
- Major engineering issues (e.g., melter design) must be resolved.



9. CONCLUSIONS

A new process to convert plutonium in multiple forms directly to glass has been invented. GMODS may convert PCMs into glass for storage, disposal, or conversion to HLW glass. The major strength of GMODS is its potential capability to address multiple types of PCMs.

Thermodynamic calculations indicate process feasibility. Initial proof-of-principle experiments have confirmed some key chemical reactions using cerium as a substitute for plutonium. Other experiments have shown that the process can accept a wide variety of other feed materials (Zircaloy, carbon, stainless steel, aluminum, chloride, etc.). Significant additional work is required before engineering feasibility can be demonstrated.



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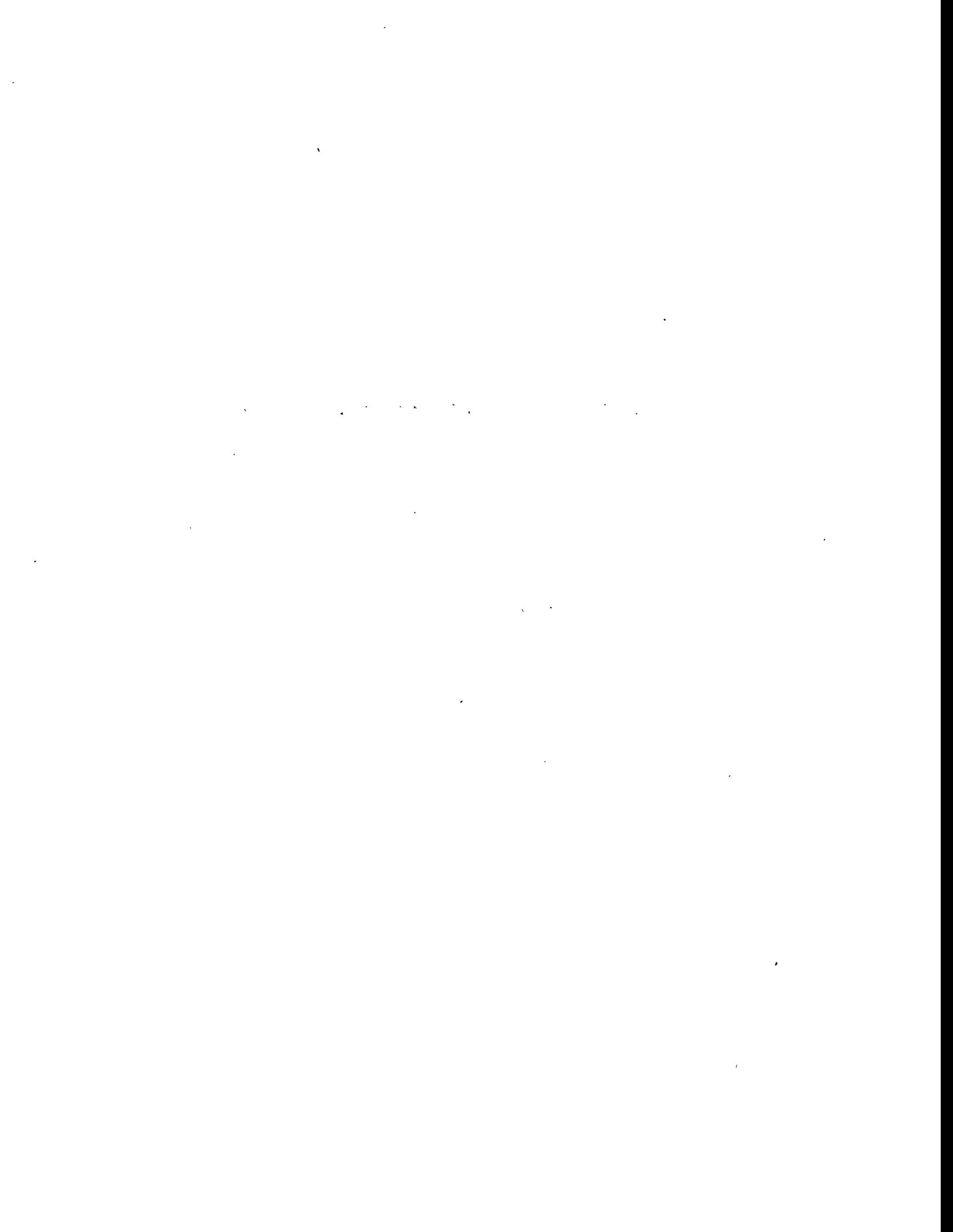
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Appendix A:

DESIGN ISSUES ASSOCIATED WITH GMODS FLOWSHEETS



APPENDIX A: DESIGN ISSUES ASSOCIATED WITH GMODS FLOWSHEETS

GMODS is proposed for conversion of PCMs to an oxide glass for (a) storage, (b) feed to an HLW vitrifier, or (c) a final waste for borehole or equivalent disposal options. There are multiple considerations in design of the flowsheets. Some of these are discussed in this appendix.

A.1 PRETREATMENT OPTIONS

GMODS is a general purpose treatment process that can accept metals, ceramics, amorphous solids, and organics. This implies that most wastes can be handled without any pretreatment. While waste pretreatment is not required, the decision as to whether to pretreat wastes will depend primarily on economic factors. In some cases, specialized single-purpose equipment to reduce waste volumes before they are converted to glass may be more economic.

An example is the processing of Rocky Flats plutonium-containing residues to glass, as shown in Fig. A.1 (DOE, 1992). These residues exist in many chemical forms representing several major groups. All of the materials could be directly fed to GMODS. Alternatively, there are several pretreatment options to reduce the quantities of materials to GMODS:

- **Graphite.** Plutonium-contaminated graphite can be treated as a waste or as a carbon source for GMODS to reduce excess lead oxide in the final glass product.
- **Combustibles.** Combustible wastes can be incinerated with the ash to GMODS or directly fed to GMODS.
- **Salts.** Salts can be processed directly by GMODS or the PCMs extracted from the salts by dissolution of the salts in water, followed by ion exchange removal of PCMs. The ion-exchange resins would then be fed to GMODS. This is an example of GMODS making possible a simple pretreatment system. Ion-exchange resins are good for cleanup of salt solutions, but ion-exchange resins themselves are difficult to process by conventional technologies. The existence of GMODS to process ion-exchange resins makes the use of ion-exchange resins for PCM removal a potentially attractive pretreatment option.

A.2 GMODS GLASS COMPOSITION CONSIDERATIONS

The glass from a GMODS process must satisfy two different requirements. One is that it must effectively dissolve the plutonium metal (oxidize Pu to PuO_2 and be a good solvent for PuO_2). The other is that it must be an acceptable composition for meeting the product glass requirements. It would be a significant process simplification if a single composition of glass (other than the PbO content) could meet both requirements. However, the information currently available indicates much better dissolution by $\text{PbO-B}_2\text{O}_3$ melts without the SiO_2 and other oxides required for the final waste form composition.

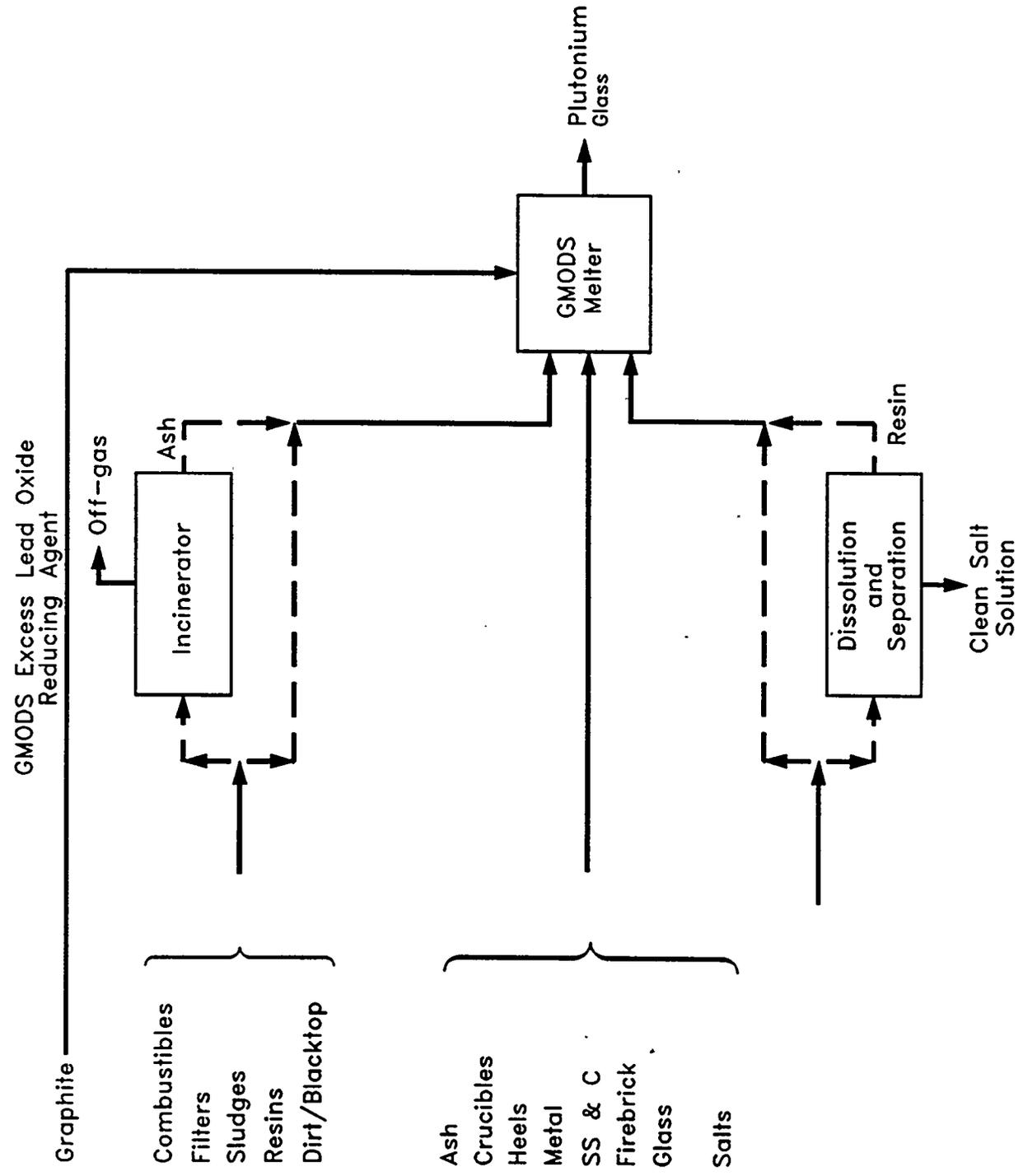


Fig. A.1. Residue treatment options for Rocky Flat's plutonium residues.

The oxidation-dissolution glass composition is chosen to oxidize metals such as Pu, dissolve the PuO_2 , and to allow separation of insoluble lead metal. Lead-borate glasses with high concentrations of PbO are the most promising choices. There are four constraints on the composition of the oxidation-dissolution glass:

- The boron-to-plutonium ratio in the oxidation-dissolution glass must not exceed the boron-to-plutonium ratio in the desired product glass. Boron can be added to the oxidation-dissolution glass after plutonium dissolution, but it can not be removed.
- The boron-to-plutonium ratio in the oxidation-dissolution glass must ensure nuclear criticality safety. In practice, this ratio is usually specified by the product glass composition to ensure no criticality concerns with the product glass. The same ratio ensures criticality safety for the oxidation-dissolution glass.
- There must be sufficient oxidation-dissolution glass with appropriate composition to ensure that all PCMs are fully soluble in the glass after oxidation-dissolution. Limited experimental data indicate that glass with a molar ratio of 2 mol PbO per mole of B_2O_3 has the maximum solubility for actinides. The glass has excess PbO over what is needed to oxidize metals in the PCM to ensure everything remains in solution.
- The composition must ensure reasonably fast oxidation-dissolution rates.

The glasses resulting from dissolution of plutonium metal in lead borate-PbO glasses do not have the compositions and properties needed for final disposal. Addition of SiO_2 and other components and removal of part of the excess PbO are necessary to give the compositions commonly preferred for waste glasses. The Savannah River Site (SRS) experimental studies of glass composition (Ramsey, 1994) were applied to select the composition for the GMODS product. The SRS work indicates that typical glasses should have no more than 10 wt. % plutonium oxide to ensure that nuclear criticality is not an issue under any circumstances. These glass compositions also include some PbO because of the beneficial effects of PbO on glass properties.

A.3 METALS SOLUBILITIES IN LEAD

If large pieces of dense metal ($> \sim 11 \text{ g/cm}^3$) are fed to a GMODS melter, they will sink through the glass into the molten lead. Metals with low melting points, such as plutonium, will also melt while sinking through the glass. Reactive metals (including plutonium and uranium) will be partly oxidized during the descent through the glass. The oxidized materials dissolve into the glass. Small pieces of reactive metals are fully oxidized and dissolved into the glass before reaching the lead.

In the lead, metals will dissolve up to their limits of solubility. Most metals have high solubility in lead. Figure A.2 shows the plutonium-lead-phase diagram. Figure A.3 shows the lead-uranium-phase diagram. In GMODS, reactive metals will be oxidized and extracted back into the glass as metal oxides at the lead-glass interface. This implies that all reactive metals are removed from the lead in time.

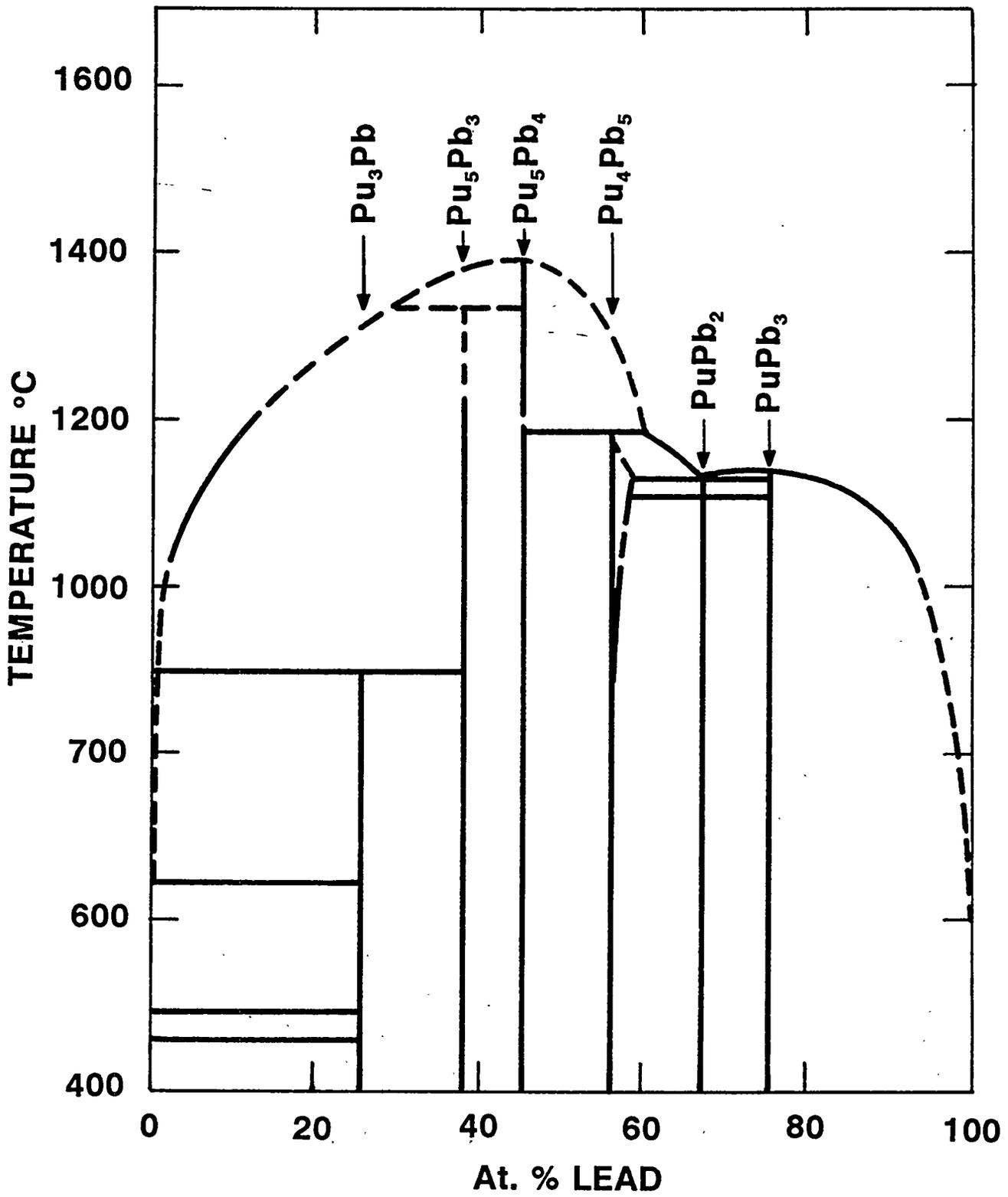


Fig. A.2. Plutonium-lead-phase diagram.

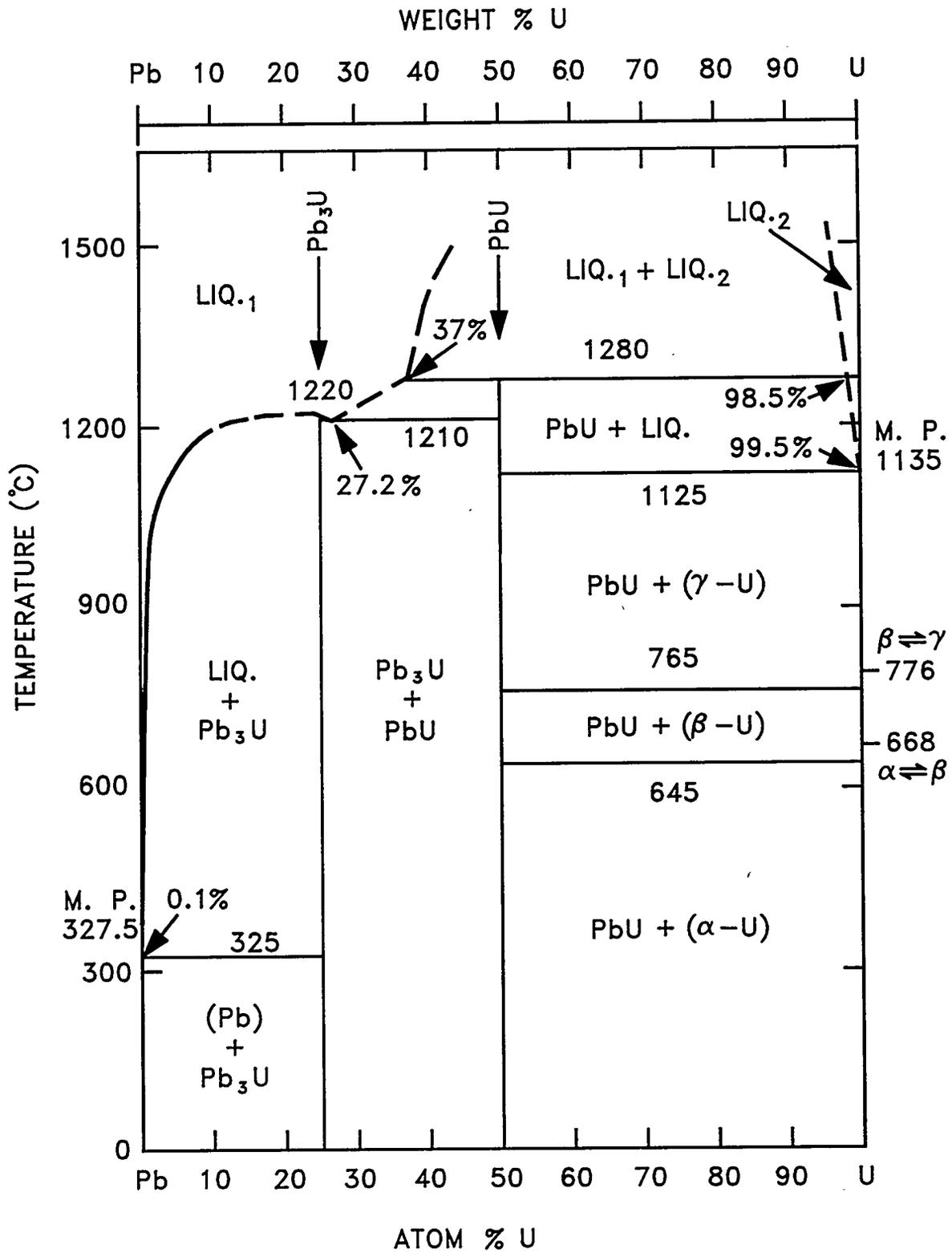


Fig. A.3. Lead-uranium-phase diagram.

For GMODS, there are two modes of operation with dense metals:

- Sufficient molten lead can be maintained within the system to keep all dense metals in solution in the lead at all times.
- Dense intermetallic compounds can be allowed to precipitate out of the lead as solubility limits are exceeded. Examples of such intermetallic compounds include Pu_3Pb and Pu_5Pb_3 . As dense reactive metals are oxidized and dissolved into the glass, the lead is stripped of dense metals, and the dense metal concentrations go below their solubility limits. This, in turn, causes the intermetallic compounds to dissolve back into the lead solution where they can be extracted into the glass.

Nuclear criticality and other considerations determine the preferred mode of operation.

Noble metals in lead are not oxidized by lead oxide in the glass (Appendix C). Instead, these noble metals will build up in solution in the lead. If the concentration becomes excessive, off-line processing of the lead is required to remove the noble metals (Appendix E).

A.4 CRITICALITY CONSIDERATIONS FOR PLUTONIUM PROCESSING

The main criticality problems for this process are associated with the plutonium metal before its dissolution in the glass. The boron is a good nuclear criticality poison. The Pu:B ratio and the final plutonium concentration will be limited to ensure criticality safety for the final waste form. All the B_2O_3 in the final waste should be added to the dissolver because the B_2O_3 is needed to dissolve the PuO_2 and to provide a nuclear poison for control of criticality. It is reasonable to assume that PuO_2 dissolved in the glass will not separate from the boron in the glass. Thermodynamic calculations on plutonium oxides (see Appendix C) show that the oxides are more stable than other glass components and are stable against reduction by carbon. This implies that the plutonium will not separate from the boron due to changes in glass chemical composition under any expected conditions.

The control of nuclear criticality is often specified as limits on (a) geometry (infinite cylinders or infinite slabs), (b) fissile mass, (c) concentration of fissile material, and (d) presence of neutron poisons. The fissionable isotope, the maximum density possible, and the reflection or neutron moderation conditions are also parameters that are considered.

The allowable limits for criticality of plutonium metal are smaller than those for ^{235}U or ^{233}U and may limit the design of the process equipment. The limits for ^{239}Pu metal without moderation are about 5 cm diam for an infinite cylinder, or 4.5 kg mass limit. The mass limit could be approximately doubled if the density cannot exceed 0.5% of the theoretical metal density. If criticality safety is assured by geometry, the GMODS dissolver would have to be limited to a cylinder of about 7.5 cm ID, 15 cm length, or about 5 kg of

^{239}Pu metal with measurements to ensure that the plutonium metal was dissolved before more plutonium metal was added. These values require the absence of neutron reflectors, and these values may not be acceptable when water or other coolants containing hydrogen are used in the dissolver vessel walls. The B:Pu ratio can be selected to make criticality impossible after the PuO_2 has dissolved in the melt containing B_2O_3 .

These considerations define three approaches to criticality control within GMODS.

- **Mass limit.** Batch reaction and dissolution of the PuO_2 in the glass with <5 kg of plutonium in about 18 L of the final glass composition. This batch control requires dependable measurements to ensure that any heel of unreacted or undissolved plutonium is small. The quantities of materials for the various process steps using batches with limited plutonium for criticality control are shown in Table A.1.
- **Geometry control.** A continuous dissolver of small diameter (5 cm for infinite length or 7.5 cm for a limited length) or a continuous dissolver with a pancake geometry (5 cm in height) along with verification of the plutonium in the glass solution.
- **Concentration control with feed batch size limits.** Sequential addition of limited quantities of plutonium to the dissolver with each plutonium addition limited to below the critical mass. Following each addition, the plutonium would react and dissolve into the glass. After confirmation of plutonium dissolution, more plutonium can be added to the system.

It is noted that limiting the quantity of plutonium in a GMODS batch operation in many cases is not a severe constraint. For a plutonium residue with 5% plutonium, 5 kg of plutonium will be in 100 kg of residue. A 100 kg batch of residue may be converted into several hundred kg of glass.

A.5 REMOVAL OF EXCESS LEAD OXIDE FROM DISSOLUTION GLASS

The GMODS process requires removal of excess lead oxide from the dissolution glass to create the final product glass. This is accomplished by the addition of a reducing agent to reduce the lead oxide to lead metal. The lead metal then separates from the glass. There are many options on how this can be accomplished.

The baseline GMODS flowsheet shows addition of carbon to the glass as the reducing agent. The carbon can be graphite, charcoal, or a variety of organics. There is a substantial experience base using various types of carbon to remove lead oxide from glass (Rohrmann and Wick, 1981; Jensen et al., 1984; Jensen, 1985).

In the late 1970s, a series of processes were developed to recover noble metals from HLW borosilicate glass. The basic concept was to add lead oxide to the HLW glass, convert the lead oxide to lead metal, extract the noble metals from the glass into the lead metal phase, and use the lead metal to carry the noble metals from the glass to the lead metal phase below the glass. The process was a technical success, but was never implemented because SNF reprocessing was not implemented in the U.S. The base technology developed for reduction of lead oxide in glass is directly applicable to GMODS.

Table A.1. Batch quantities of materials for converting plutonium metal to glass with criticality control by plutonium mass limits

Description	gmol	kg	Volume, L
Pu metal	20	4.8	0.3
PuO ₂	20	5.4	0.5
PbO reacted	40	8.9	1.0
B ₂ O ₃ (B/Pu = 6)	60	4.2	1.7
200% excess PbO	80	17.9	1.9
Dissolver oxide products		-28	4
Pb metal products	40	8.3	0.7
Final glass (10 wt. % PuO ₂)		54	18

There are several gaseous reagents (CO and H₂) that can be used to remove excess lead oxide from the dissolution glass. Use of gaseous reagents has three potential advantages: (1) simplicity in metering reducing agent to the melter, (2) extra glass stirring by injection of gas into the melt with rapid chemical reactions, and (3) the ability to stop chemical reactions quickly by stopping gas flow to the melter (very small inventory of reducing agent in the melter).

The preferred reducing agent or agents for GMODS will depend upon available feed materials and equipment design characteristics.

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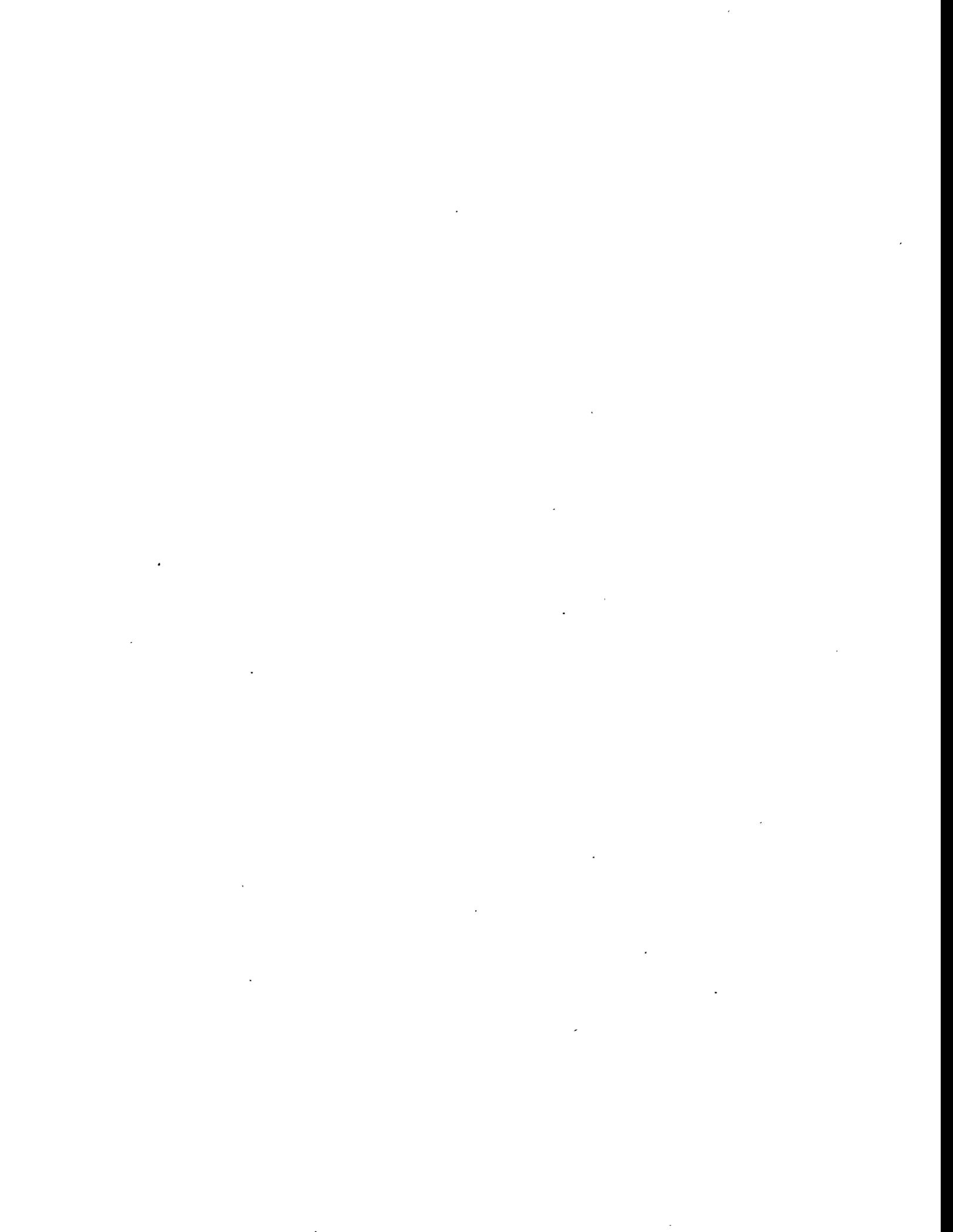
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Appendix B:

WASTE MANAGEMENT DISPOSAL REQUIREMENTS



APPENDIX B: WASTE MANAGEMENT DISPOSAL REQUIREMENTS

B.1 ISSUE DEFINITION

There are three potential sets of plutonium glass performance requirements: (a) national security requirements such as safeguards and potentially a spent fuel standard for PCMs; (b) health, environment, and safety requirements such as chemically stable products and avoidance of nuclear criticality in process facilities; and (c) waste management requirements if the plutonium is to be disposed of as a waste.

The waste management criteria on the final waste form can have a major impact on glass composition. This, in turn, may dominate the choice of GMODS process parameters and equipment design.

- Waste management criteria (long-term avoidance of nuclear criticality) will determine plutonium loading in the final waste form. Depending upon the criteria chosen, the final waste volumes may differ by more than an order of magnitude. Different equipment and perhaps different flowsheets may be selected depending upon waste quantities.
- Waste management criteria will impose waste-form-leachability criteria on the final waste form. This, in turn, determines allowable waste chemical composition that, in turn, determines glass processing temperatures. Glass-processing temperatures strongly impact choice of melter option.

Waste management criteria for disposal of excess plutonium have not been defined; however, there have been major studies of disposal (a) of light-water reactor (LWR) SNF that contains plutonium and (b) of highly-enriched SNF. Because ^{239}Pu decays to ^{235}U , studies of waste management criteria for SNF are directly applicable to plutonium disposal. This appendix is a summary of the issues and criteria from this rapidly growing literature.

B.2 CRITICALITY CRITERIA

B.2.1 Problem Importance

Nuclear criticality is an important issue in the performance and licensing of a geological repository (conventional or borehole). It is a difficult issue to address because of the long time-frames of interest. The U.S. Nuclear Waste Technical Review Board (May, 1994), the Congressionally mandated oversight board for the DOE repository program, in its recommendations to Congress, stated that:

Current Nuclear Regulatory Commission regulations for in-repository criticality control have no explicit time limit; this implies that criticality control over periods of tens of thousands of years requires modeling . . . To complicate things even more, predicting the long-term physical integrity of a waste package and its contents is not easy. It will be difficult to predict, for example, how the waste package contents may become rearranged as a result of phenomena such as rockfalls or long-term corrosion.

It is observed that ^{239}Pu has a half-life of 2.4×10^4 years and decays to ^{235}U , but repository licensing requirements extend over equivalent time periods. This implies that the waste management requirements for a plutonium glass must address criticality issues of both plutonium and its uranium daughter product— ^{235}U . If a waste form contains plutonium as its only fissile and fertile material, in time the plutonium will decay to highly enriched ^{235}U . This suggests that the criticality licensing issues and waste management requirements associated with highly enriched SNF and plutonium will be similar.

The recent Sandia performance assessment studies (Rechard, et al., December 1993) and new production reactor studies (Patrick and McDonell, March 6, 1992) for the disposal of highly enriched SNF showed that assurance of geological repository criticality control will have a major impact on waste form, waste package, and repository designs in order to meet licensing criteria. As summarized by Patrick and McDonell:

The most significant cost question for direct disposal involves nuclear criticality of high-enriched uranium (HEU) spent fuel in the repository for geologic time periods. No nuclear criticality safety criteria exist for HEU in geologic repositories, and the path forward to assure criticality safety is uncertain. Unlike fission products which decay to innocuous levels in ~ 1000 years, HEU has criticality potential for millions of years. Repository criteria must ensure acceptable criticality risk for natural and manmade events for millions of years. The criteria, when accepted, could impose large costs on the direct disposal option.

B.2.2 Scientific Issues

The critical masses of plutonium and HEU are small. If a sufficient quantity of fissile material is concentrated in a small location, it may result in nuclear criticality. In a repository environment, this has two impacts: generation of added fission products and generation of heat. The fission products add to the waste loading of the repository. More importantly, the heat pulse is a mechanism for accelerating chemical reactions, altering water movement in the repository and changing rock characteristics (Michaels, 1994; Buscheck, 1993). These alter the ability of the repository to contain radioactive materials and complicate repository licensing.

While plutonium is a criticality concern, the decay product of plutonium— ^{235}U —may be an equal concern because of the geochemistry of uranium. In a geological environment, over geological time, water flow and other mechanisms can result in uranium dissolution and reprecipitation. In nature, uranium is concentrated into ore bodies because of its chemical dissolution-precipitation chemical behavior. Naturally occurring nuclear reactors have been created by this mechanism in Africa when the uranium enrichment levels exceeded several percent (Smellie, March 1995).

The existence of naturally occurring nuclear criticality events in the past by these mechanisms implies that the issue is not just a theoretical concern and will be a major repository design issue.

B.2.3 Methods of Criticality Control in a Repository

There are four possible approaches to criticality control in a geological repository. The choice of option has a major impact on the waste form, the repository design, and the licensing process.

B.2.3.1 Isotopic Dilution

From a geological perspective, ^{239}Pu decays rapidly to ^{235}U ; thus, nonfissile ^{238}U can be used to isotopically dilute plutonium to prevent long-term nuclear criticality in a repository.

The acceptance of LWR SNF in a repository, in terms of avoidance of nuclear criticality, is based on several factors of which uranium isotopic dilution is one key mechanism. LWR SNF contains plutonium which decays to ^{235}U . The plutonium decay product, ^{235}U is created in a matrix of ^{238}U , which acts as a neutron poison, isotopically dilutes the ^{235}U and minimizes criticality concerns. Because of the chemical integrity of LWR SNF, primarily the ^{238}U oxide, it takes very long times to leach significant quantities of uranium from SNF. Most of the plutonium will have decayed to uranium before large-scale geochemical transport of the uranium. Simultaneously, the repository environment has become saturated in ^{238}U . The LWR SNF enrichment levels are 1 to 2 wt. % when all fissile isotopes, including plutonium, are treated as ^{235}U . With low enrichments, criticality is unlikely in realistic geological repository environments based on calculation and field observation of naturally occurring reactors in the geological past.

The studies of Patrick and McDonell conclude that "HEU dilution with ^{238}U is the only option providing assured nuclear criticality safety for geological time periods and is likely to be the only option capable of complying with more stringent future repository regulations."

One repository criticality control option for plutonium disposal is the creation of an immobilized waste form in which the nonfissile uranium is 98+% of the combined fissile and fertile material. This allows the same logic for criticality control for plutonium as is used for LWR SNF disposal in a repository. This philosophy of criticality control requires glass waste forms with high uranium loadings and relatively low plutonium loadings.

One approach to achieve criticality control with this philosophy is simultaneous processing of PCMs and degraded low-enriched uranium (LEU) SNF to HLW glass (Appendix G). Two problems are solved simultaneously. First, the degraded SNF (primarily Hanford-N SNF) is in a chemical form that may require treatment, such as conversion to HLW glass to meet WAC. Second, the depleted uranium assists in criticality control of the PCMs. The incremental number of canisters of glass for plutonium disposal is very small.

B.2.3.2 Mass and Geometry Control

Fissile material nuclear criticality in a repository environment can be avoided by putting limited quantities of fissile material into each waste package. Limits on fissile content per package prevent nuclear criticality within a package even if the geometry of the package contents changes with time or neutron poisons within the waste package are selectively leached from the waste package. If the packages are sufficiently far apart, the dissolution and, subsequent, precipitation of fissile materials from multiple packages into critical masses are avoided. If the HEU is sufficiently separated and eventually leaches by groundwater movement, it will ultimately be isotopically diluted by the natural uranium in the groundwater and isotopic exchange with natural uranium in the rock. The repository performance assessments of Sandia (Rechard et al., 1993) and others (Evans and Palmer, 1994) indicate that the allowable fissile material per waste package using geometric control depends upon the geology and geochemistry of the particular repository. For HEU, the allowable quantities per waste package vary from 0.7 kg to 10 kg depending upon geology and assuming no interactions between packages over geological time.

The package limits to avoid nuclear criticality within a waste package are determined by the minimum critical mass of material needed to cause nuclear criticality given the chemical composition of the local rock. Many rock formations have relatively few neutron poisons; hence, the allowable fissile material per package is low. A few geological environments such as salt have many neutron poisons; hence, the allowable fissile material per package is higher.

To date, no studies have been completed that determine the minimum separation between packages to avoid long-term nuclear criticality by uranium dissolution and isotopic exchange with uranium in the rock. This separation distance may increase the size of the repository with major impacts on repository cost.

B.2.3.3 Chemical Neutron Poisons

Plutonium criticality can be avoided in a repository by the combination of addition of neutron poisons within the immobilized waste form, very durable waste forms, and uranium leach rates equal or slightly faster from the waste form than the neutron poison. Plutonium criticality in glass for storage is avoided by use of neutron poisons such as boron, cadmium, and certain rare earths.

For geological disposal, the requirement for waste forms with chemical poisons is that a very durable waste form with very low leach rate be used. If the plutonium decay product, uranium, leaches out slowly over very long geological time-frames, it can be diluted by natural uranium in the groundwater. It is known that certain neutron poisons such as boron leach more quickly than uranium from glass; thus, they can not be used. The geochemical requirements probably require use of a rare earth neutron poison. Recent laboratory studies (Ramsey, 1994) have suggested high-performance glasses for plutonium with potentially low leach rates.

B.2.3.4 Nuclear Criticality Acceptance

The fourth nuclear criticality option for plutonium is to show that nuclear criticality is acceptable in a geological environment. The supporting basis for this approach is that naturally occurring reactors have occurred in the past and that geological evidence suggests that the migration of radioactive materials under the appropriate environmental conditions is small.

One of the technical recommendations from the Sandia repository performance assessments (Rechard, 1993) for HEU was that "future work should attempt to determine whether nuclear critical conditions in a repository are noncatastrophic and thus technically acceptable."

B.3 CHEMICAL REQUIREMENTS

There are chemical durability requirements for any waste form to assure no release to the environment. Detailed requirements have been prepared for HLW glass (DOE, January 1993), thus the basic chemical durability requirements are known. Because glass was chosen as a waste form because of its ability to meet these durability requirements, this is not a difficult requirement for glass waste forms.

B.4 CONCLUSIONS

Repository criteria will have a major impact on the GMODS design. If repository nuclear criticality acceptance criteria necessitate a plutonium glass with a high uranium loading (>50 parts uranium per part of plutonium), the glass formulation, glass properties, and processing parameters will be primarily determined by the uranium in the glass. The plutonium content will not strongly impact GMODS processing parameters.

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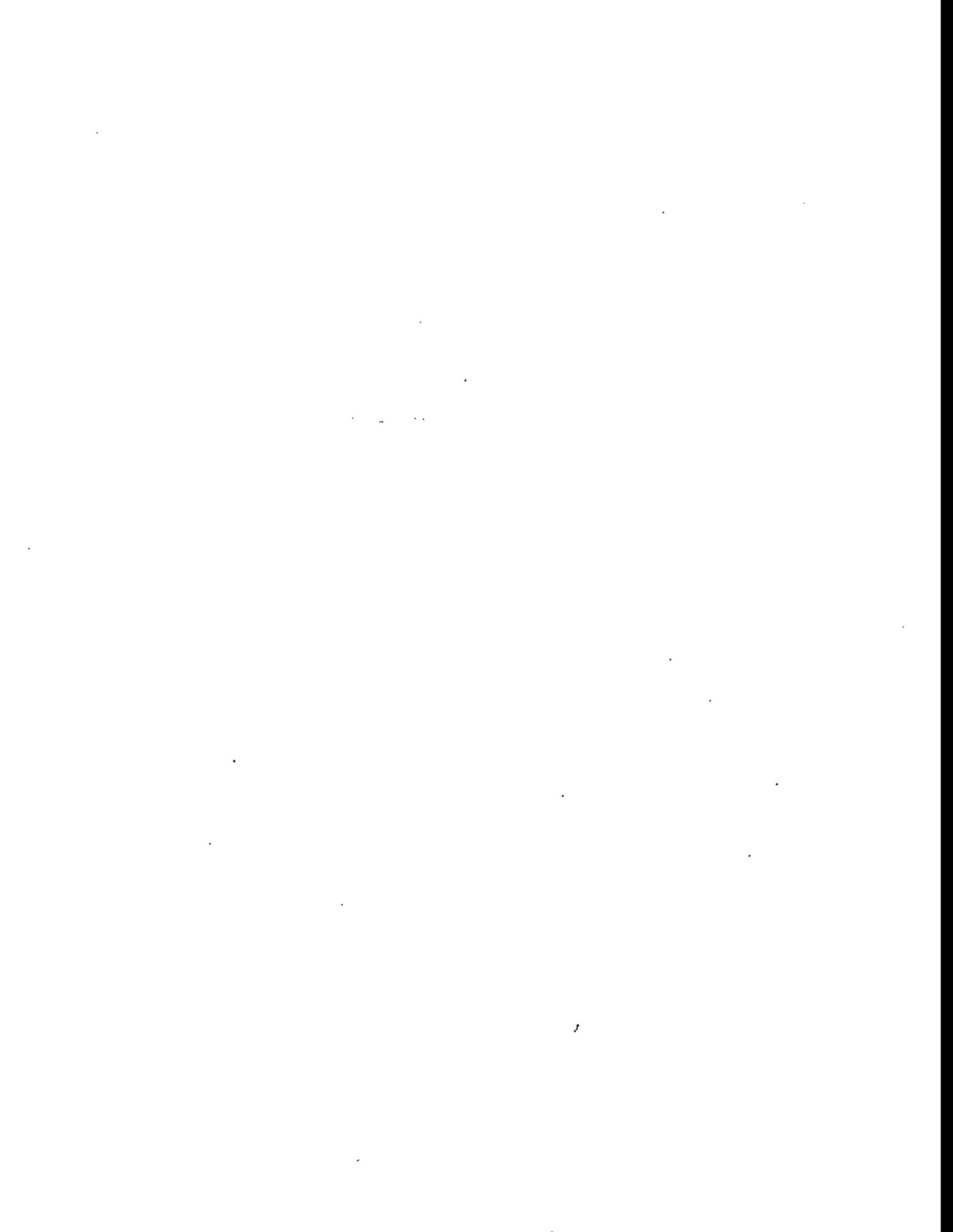
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Appendix C:
THERMODYNAMICS



APPENDIX C: THERMODYNAMICS

C.1 THE PbO-B₂O₃ SYSTEM

The thermochemical properties of the PbO-B₂O₃ system are the basis for GMODS. The abilities to oxidize metals and to dissolve metal oxides are directly related to the thermochemical activity of PbO and B₂O₃. This system was assessed by Slough and Jones (August 1974). These authors used the Gibbs energy values reported by Kapoor and Frohberg (1973). In this work, we also have used the data of the latter authors.

This system shows negative deviation from ideality. In other words, the thermodynamic activities of PbO and B₂O₃ will be less than those in an ideal system. This means that PbO and B₂O₃ interact probably in an acid (B₂O₃) and base (PbO) reaction (Kapoor and Frohberg, 1974):



In this reaction, O⁻² from the PbO is the "Lux-Flood" base, and the boron group is the acid.

The thermodynamic activity of PbO is the key parameter in determining whether a metal will be oxidized in GMODS. Kapoor and Frohberg (1974) expressed the activity of PbO at 1000°C by the following equations:

$$a_{PbO} = N_{PbO} (1 + 2N_{B_2O_3}) \frac{\left[1 + \frac{F-2}{F-1} N_{B_2O_3} \right]^{F-1}}{(1 + N_{B_2O_3})^{F+1}} \quad , \quad (C.2)$$

and

$$F = 1.0005 \left(\frac{1 + 2N_{B_2O_3}}{1 + N_{B_2O_3}} \right) \quad , \quad (C.3)$$

where a_{PbO} is the activity of PbO ; N_{PbO} , and $N_{B_2O_3}$ are the mole fractions of PbO and B_2O_3 , respectively. The F in these equations is the ratio of anionic to cationic sites in the structure. Table C.1 lists activities for some PbO - B_2O_3 compositions that were calculated from these equations, and Fig. C.1 is reproduced from Kapoor and Froberg (1974).

Table C.1. Calculated PbO activities at $1000^\circ C$

Composition	a_{PbO}
$N_{B_2O_3} = 0.762$ $N_{PbO} = 0.238$ (50 wt. %)	1.2×10^{-2}
$N_{B_2O_3} = 0.500$ $N_{PbO} = 0.500$	5.6×10^{-2}
$N_{B_2O_3} = 0.33$ $N_{PbO} = 0.67$	1.4×10^{-1}
$N_{B_2O_3} = 0.25$ $N_{PbO} = 0.75$	2.2×10^{-1}

It is likely that GMODS would be operated in the composition region where the activity of PbO would be ~ 0.1 to 0.2 . At a composition of $N_{PbO} \approx 0.64$ and $N_{B_2O_3} \approx 0.36$, $a_{PbO} = a_{B_2O_3} = 0.12$. The composition can be adjusted to suit the type of waste being treated. In general, higher values of a_{PbO} would enhance the oxidation process, and higher values of $a_{B_2O_3}$ would enhance formation of borates.

Table C.2 lists calculated PbO partial pressures when $a_{PbO} = 0.1$ and 0.2 , respectively. The partial pressures of B_2O_3 will be several orders of magnitude lower than those of PbO .

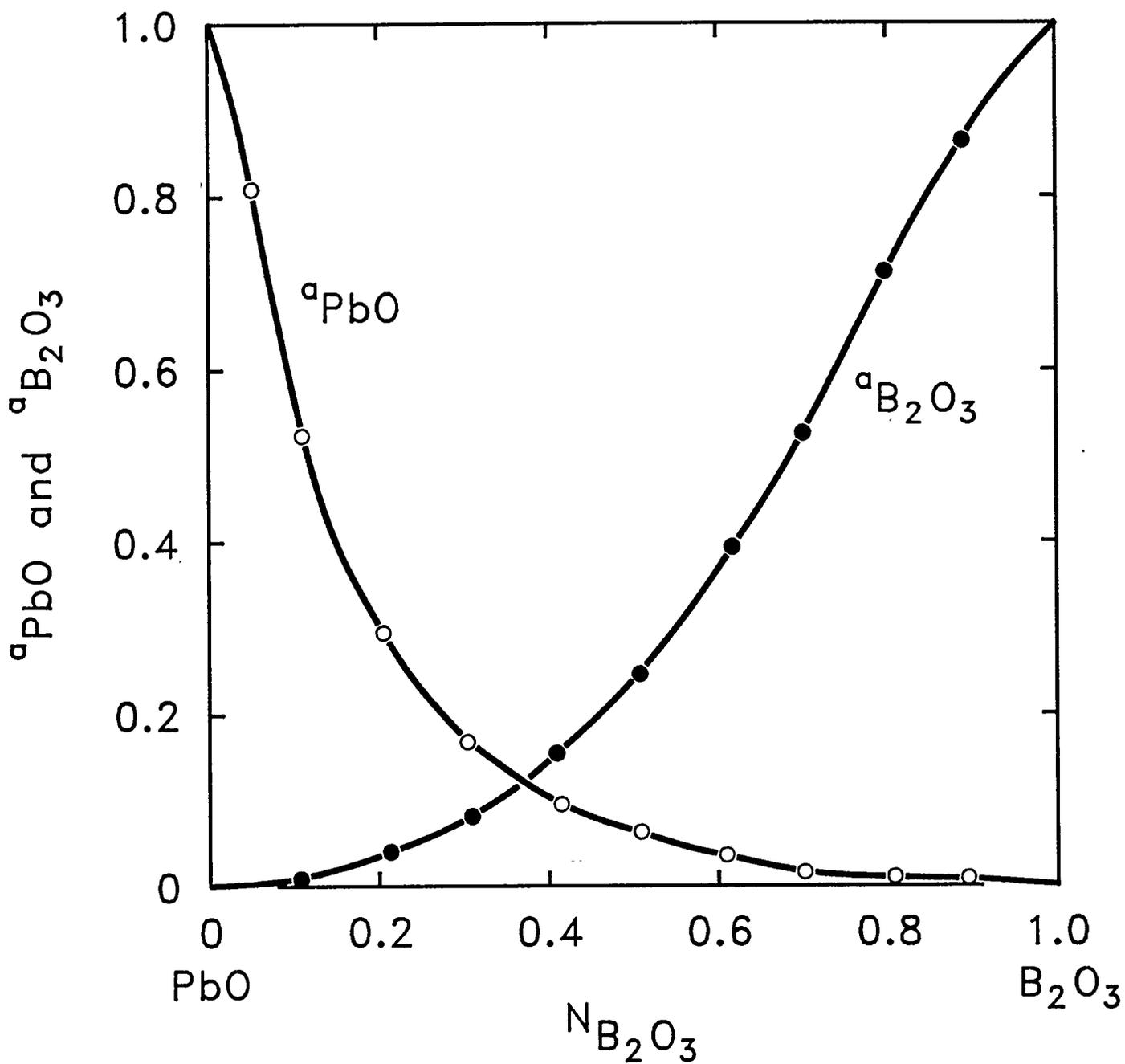


Fig. C.1. Activity of PbO and B₂O₃.

Table C.2. Vapor pressure of PbO in PbO-B₂O₃ system^a

Temperature (°C)	P _{PbO} atm	
	At a _{PbO} = 0.1	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}

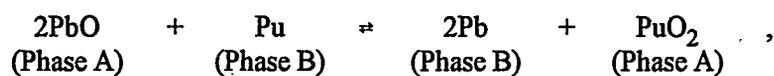
^aSource of free energy data: *HSC Chemistry for Windows*, Outokumpu Research Oy, Finland.

C.2 Pb-Pu ALLOYS AND THE OXIDATION OF Pu

Let us consider a phase containing PbO, PuO₂, and B₂O₃ in contact with a phase containing Pb and Pu. We would like to know if Pu in the metallic phase could attain a mole fraction large enough to be of concern in GMODS. The system being considered can be described by the phases:

Phase A	Phase B
xPbO +	rPb +
yPuO ₂ +	sPu
zB ₂ O ₃	

The reaction to convert Pu in the metallic phase to PuO₂ in the oxide phase can be written:



where Phase A and Phase B are the oxide and metallic phases, respectively. At 1000°C, the equilibrium constant for this reaction is 3.78×10^{25} (see Table C.3), or:

$$\frac{a_{Pu(B)}^2 \cdot a_{PuO_2(A)}}{a_{PbO(A)}^2 \cdot a_{Pu(B)}} = 3.781 \times 10^{25} \quad , \quad (C.4)$$

where $a_{Pu(B)}$ is the thermodynamic activity of plutonium in the metallic phase at equilibrium, and the other activities are labeled in a similar way. Rearranging the above equation gives:

$$a_{Pu(B)} = 2.65 \times 10^{-26} \cdot \frac{a_{Pb(B)}^2 \cdot a_{PuO_2(A)}}{a_{PbO(A)}^2} \quad (C.5)$$

During the process of oxidation and dissolution of plutonium, we will want to maintain $a_{PbO(A)}$ at a value of ~0.1 to 0.2. Here, we will assume a value of $a_{PbO(A)} = 0.1$ because it would give the highest value for $a_{Pu(B)}$ within the range of a_{PbO} that we would operate. From this:

$$a_{Pu(B)} = 2.65 \times 10^{-24} \cdot a_{Pb(B)}^2 \cdot a_{PuO_2(A)} \quad (C.6)$$

To avoid high-melt-temperature compounds in the Pb-Pu system, we will maintain enough lead in the metal to keep the mol fraction of Pu <~0.2. Because the thermodynamic activity of Pb and PuO_2 will be ≤ 1.0 , the activity of plutonium in a Pb-Pu alloy in contact with PbO in the oxide phase will be extremely low. Thus, even if plutonium enters into an alloy with lead, the plutonium should be oxidized and would then enter the oxide phase as equilibrium is approached.

The phase diagram for the Pb-Pu system shown in Fig. C.2 includes intermetallic compounds with relatively high melt temperatures. The researchers who produced this phase diagram stated that alloys which contained more than ~40 at. % Pu had a high-melt-temperature alloy between the two liquid phases and that this prevented reaction (Wood, Cramer, Wallace, and Ramsey, 1969). To avoid the high melt temperature alloys in GMODS, it is recommended that the Pu be <20 at. % in the Pb. There are other reasons to maintain a relatively low Pu at. %. It may be necessary to avoid criticality problems, and it may be desirable to maintain an excess of lead for operation of the induction heating system.

Table C.3. Oxidation of Pu by PbO^a

Temperature (°C)	ΔH (kJ)	ΔS (J)	ΔG (kJ)	K (equilibrium constant)
600	-615.198	11.646	-625.367	2.597E+037
700	-618.326	8.234	-626.339	4.188E+033
800	-619.089	7.489	-627.126	3.368E+030
900	-671.251	-37.543	-627.207	8.488E+027
1000	-673.279	-39.202	-623.369	3.781E+025
1100	-675.202	-40.657	-619.374	3.656E+023
1200	-677.004	-41.925	-615.243	6.561E+021

^aSource of free energy data: *HSC Chemistry for Windows*, Outokumpu Research Oy, Finland.

C.3 OXIDATION OF METALS BY PbO

The processing of metals in GMODS involves both oxidation and dissolution into a PbO-B₂O₃ glass. The overall free energy change for the process will include the free energy change for the oxidation plus the free energy change for the dissolution. The final dissolution product will be at least a ternary system involving PbO-B₂O₃-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 a material by GMODS is the oxidation of the metal by PbO.

Oxidation of metals will result in oxides that have different metal-to-oxygen ratios (i.e., 2:3 in Al₂O₃, 1:2 in PuO₂). The best way to compare the relative ease of oxidizing a given metal is to use oxygen potentials. Oxygen potential has a unit of energy and is defined as $RT \ln P_{O_2}$. A single example will show what is meant by oxygen potential and how they are used. Consider the oxidation of Al:



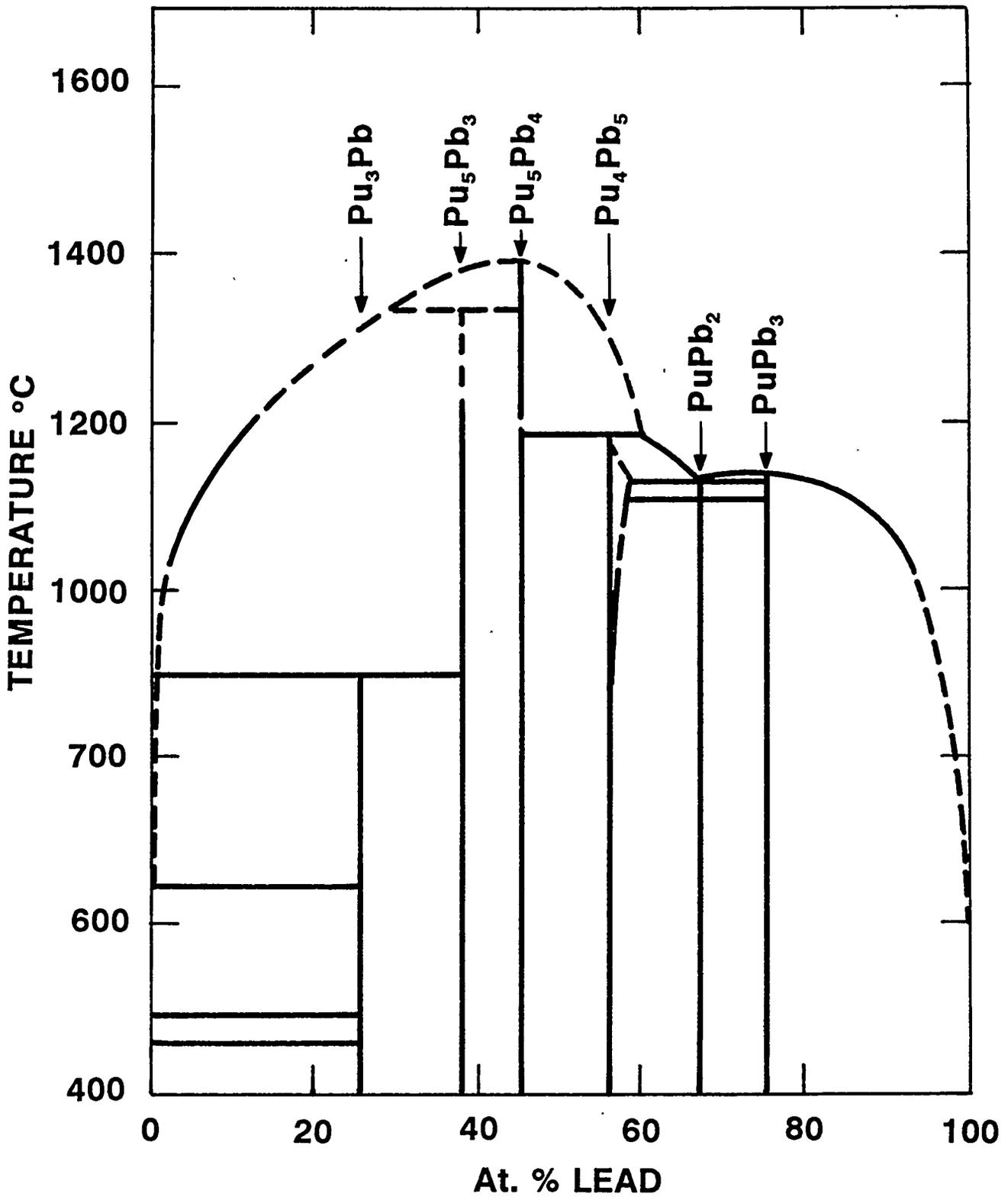


Fig. C.2. Plutonium-lead phase diagram. (Courtesy of Wood, D. H., Cramer, E. M., and Wallace, P. L., 1969. *J. Nuclear Materials* 32, 193-207.)

The overall free energy change for this reaction, ΔG_T° , can be written as:

$$\Delta G_T^\circ = -RT \ln \frac{1}{P_{O_2}^{3/2}} = 3/2 RT \ln P_{O_2} \quad (C.8)$$

or

$$RT \ln P_{O_2} = 2/3 \Delta G_T^\circ \quad (C.9)$$

Note that the stoichiometric factor for O_2 is accounted for in calculating $RT \ln P_{O_2}$, the oxygen potential. Figure C.3. shows plots of oxygen potentials for forming a number of metal oxides. This type of figure has the important feature that any metal oxide that is higher than another can oxidize the metal in a lower position. Here, we are concerned about the ability of PbO to oxidize metals. Figure C.3 shows that any metal, Zn, Cr, U, Pu, Al, etc., that lies below the $PbO: a_{PbO} = 0.1$ line will be oxidized when the activity of PbO is 0.1. 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 CuO, is stable in $2PbO \cdot B_2O_3$ glass. The stability of oxidized copper in this glass must be due to the combination of oxidation and dissolution and not oxidation alone. Other metals, such as Ag, Au, Pt, and Pd, do not form oxides that are stable at high temperatures and they are not included here. The oxygen potentials for the formation of ZrO_2 are similar to those of Al_2O_3 .

Some metals, such as U and Pu, have more than one oxide that may form. The highest oxide of Pu, PuO_2 , is thermodynamically stable as far as oxidation is concerned. However, the overall oxidation and dissolution may result in a lower oxide in the borate glass.

Carbon may be introduced into GMODS either as waste to be treated or to reduce PbO to Pb:



The equilibrium constant for this reaction is $\sim 3 \times 10^8$ at $1000^\circ C$; therefore, even when the PbO activity is quite low, carbon will be oxidized.

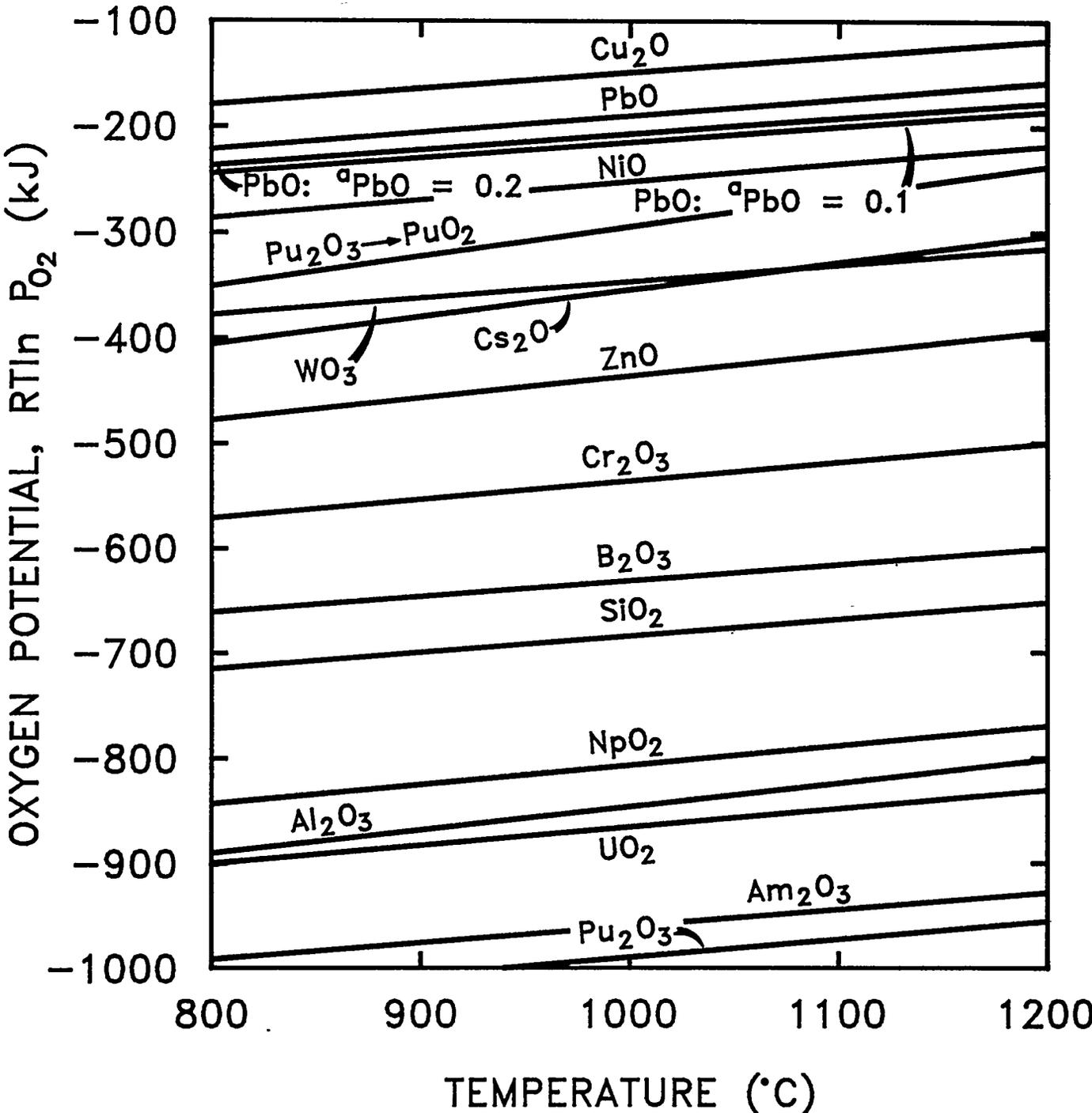


Fig. C.3. Oxygen potential diagram.

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Appendix D:

EXPERIMENTAL DATA



APPENDIX D: EXPERIMENTAL DATA

D.1 INTRODUCTION

This appendix presents a summary of the experimental data collected on the lead borate system that are applicable to GMODS. This includes information collected for the plutonium immobilization program and information generated for other programs.

The GMODS proof-of-principle experiments are designed to answer the questions below. Note that the characteristics of lead borosilicate glass (fine dinner crystal) and borosilicate glass (laboratory glassware and HLW glass) are reasonably well known over wide ranges of chemical compositions. In contrast, the characteristics of lead borate glass—the initial dissolution glass—are not well known. This is reflected in the experiments that are conducted and the experimental emphasis on lead borate glasses. The experimental questions are:

What are the solubilities of different oxides in lead borate glass as a function of chemical composition and temperature?

Higher solubilities minimize equipment size. Reasonable oxide solubilities are required for practical systems.

Under what conditions (temperature and composition) will metals react and dissolve into lead borate glasses?

Thermodynamics clearly shows most metals (except noble metals) will react with a lead borate glass. Practical dissolution systems require reasonably fast kinetics that, in turn, require the avoidance of formation of passivating oxide layers on the metal surfaces in the glass. Dissolution strongly depends upon composition.

Can lead oxide be removed from the lead borate glass with carbon?

The lead oxide content of the molten glass must be altered within the process. The proposed approach is the addition of carbon.

What are the viscosities of lead borate systems as a function of temperature and chemical compositions?

Homogeneous glass solutions are required to meet product quality requirements. Maximum loading of wastes in the glass are desired. Both of these goals require the ability to mix the glass into a homogeneous solution. The corrosive characteristics of the glass make mechanical glass stirring systems problematic. Potential stirring mechanisms are by thermal convective currents, electromagnetic, and gas injection. All require reasonably low glass viscosities. Thermal convective mixing (the simplest option) also requires reasonably large glass thermal expansion coefficients.

Can plutonium and uranium metal that enter the lead phase be easily oxidized and transferred at the lead metal/glass interface?

Plutonium and uranium metals are more dense than the lead borate glass. When they enter the melter, much of the material will react and dissolve into the glass while descending through the glass. If the pieces are sufficiently large, some metal will enter the molten lead phase. Uranium and plutonium dissolve in lead and theory predicts that they will be oxidized and extracted from the lead phase to the glass phase at the interface. This must be shown not to be kinetically limited.

What are the reaction rates for each chemical reaction?

Chemical reaction rates may be limited by local kinetics or mass transfer. With high temperature systems, mass transfer (mixing) is usually limiting but this must be shown.

What limits are there to adding glass frit?

After waste dissolution, glass frit (primarily SiO_2) is added to create a durable glass. Frit addition will change glass properties. It must be shown that no precipitates are generated locally during this process that are slow to redissolve as the glass is homogenized. (Note: Lead borosilicate glasses have been produced in large quantities for household glassware for 200 years; hence, there is a very large industrial data base for this operation. The concerns herein are with elements not normally found in household and industrial glasses.)

What are the limits for removal of lead oxide from the final borosilicate glass?

The final process step is to reduce the lead oxide content of the glass to desired levels (lead oxide must remain during frit addition to keep wastes in solution until frit is dissolved and frit glass formers hold wastes in solution). It must be shown that no precipitates are generated locally during this process that are slow to redissolve as the glass is homogenized. (It is noted that removal of lead oxide from some borosilicate glasses by reaction with carbon has been studied elsewhere as part of a process for removal of noble metals from HLW glasses.)

Each of the above questions has been partly demonstrated as described below. The order that the experiments have been performed depended partly upon the sequence of key questions listed above and experimental apparatus. In some cases, certain sets of experiments were performed together because the same equipment could be used to obtain multiple sets of information.

Each question can be answered in different levels of detail. In most cases, this implies more experimental data over a wider range of chemical compositions and temperatures representing wider operating conditions. The experiments herein are proof-of-principle experiments. This implies measurements were over a limited range of conditions. Because plutonium is one of the materials of interest, cerium and uranium have been used in many experiments as substitutes.

D.2 EXPERIMENTAL METHODS

The methods used are typical of those of glass-industry experimentalists in that most of the work required the use of platinum ware in place of ceramics.

Using a standard 3-in. high by 2.75-in. wide crucible, weighed amounts of powder mixes of PbO and boric oxide (B_2O_3) in the whole number ratio of 1:2 up to 4:1 gmol of PbO to boric oxide are mixed and poured into the crucible, which is placed in a vertical quartz thimble being heated in an open-top nichrome furnace with standard chromal thermocouple controls (Fig. D.1). While inside the crucible, a platinum-rhodium thermocouple is used to follow the temperature of the melt. Through the open top, the melt is stirred frequently with an extended platinum rod, which is then withdrawn from the furnace to avoid oxidation of the extension material above the platinum. An open-top furnace thimble is normally used with all oxide melts; however, a closed system is available for oxidizable compositions such as added metals. When the melt is judged completely homogeneously melted, the crucible is retrieved with surgical tongs, the crucible is tilted, and the melt is poured into a platinum dish (Fig. D.2). This procedure is duplicated when solubility studies are made with added oxides, such as those of alumina, zirconia, ceria, magnesia, and uranium.

After cooling, the vitrified products are examined for complete solution of all components, and a clear sample is then removed (made easy by the spontaneous cracking of the glass melt as it cools) and weighed in air and then under toluene to reveal the glass density.

D.3 MATERIALS USED

Table D.1 lists the amount of material used in the formation of 2:1 PbO: B_2O_3 base glass as well as the amount of oxides used for solubility experiments. The only difference in preparing glasses of differing ratios is the amount of PbO used.

Table D.1. Lead borate mix for the 2:1 type solvent glass

Experimental inputs	Weight (g)
Lead oxide (PbO), 2 gmol	446.0
Boric oxide anhydride (B_2O_3), 1 gmol	69.6
Total weight	515.6
Oxide to mix at 10 wt. % of Al_2O_3 , ZrO_2 , CeO_2	51.6
U_3O_8 to mix at 20 wt. %	103.2

- ① Open-Top Oxide Melting Furnace at 900°C
- ② Sealed Furnace for Inert Gas Cover
- ③ Platinum Thermocouple Temperature Indicator
- ④ Platinum Cooling Dish for Oxide Melts

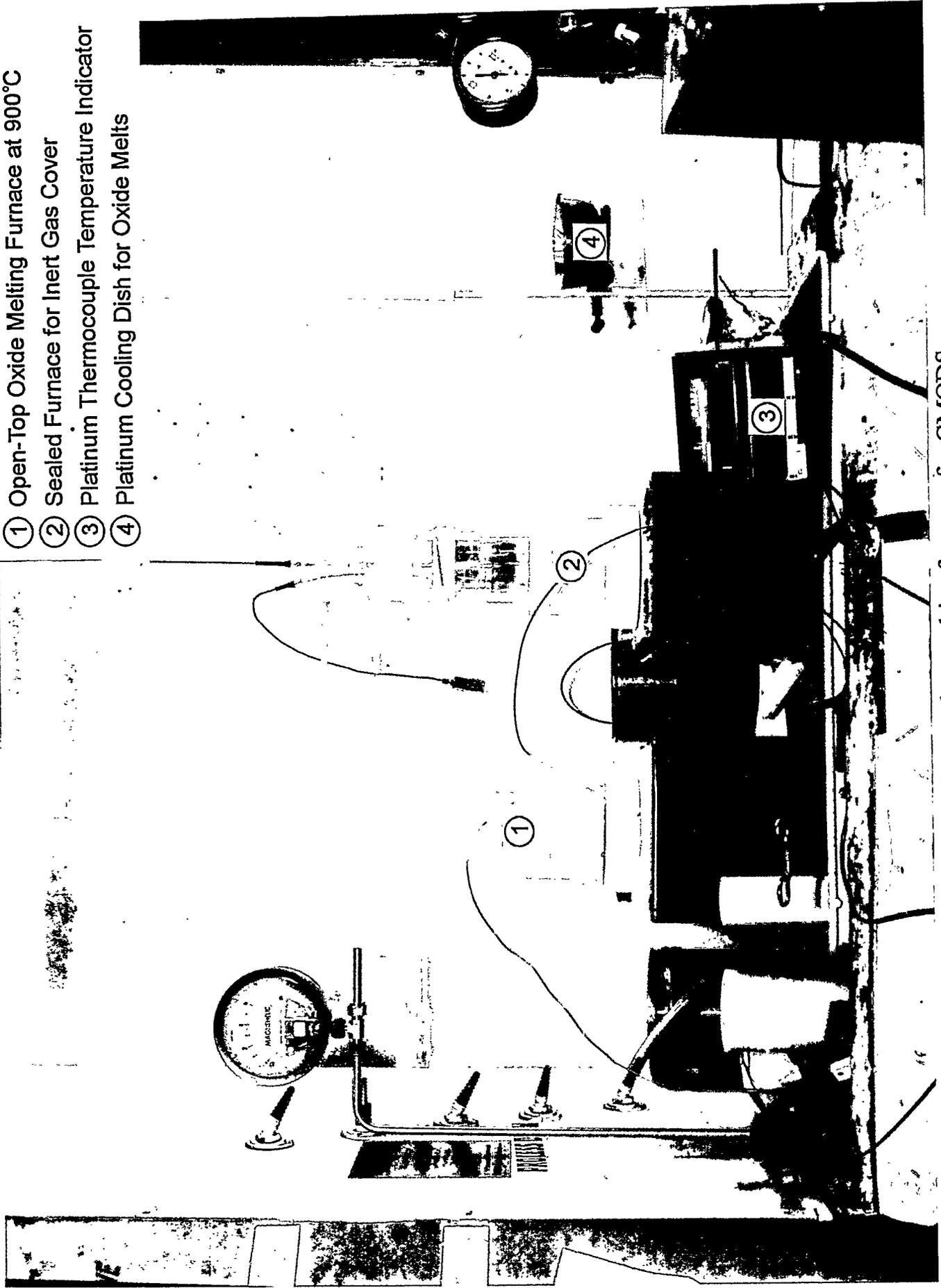


Fig. D.1. Lead-borate glass-melting furnaces for GMODS.

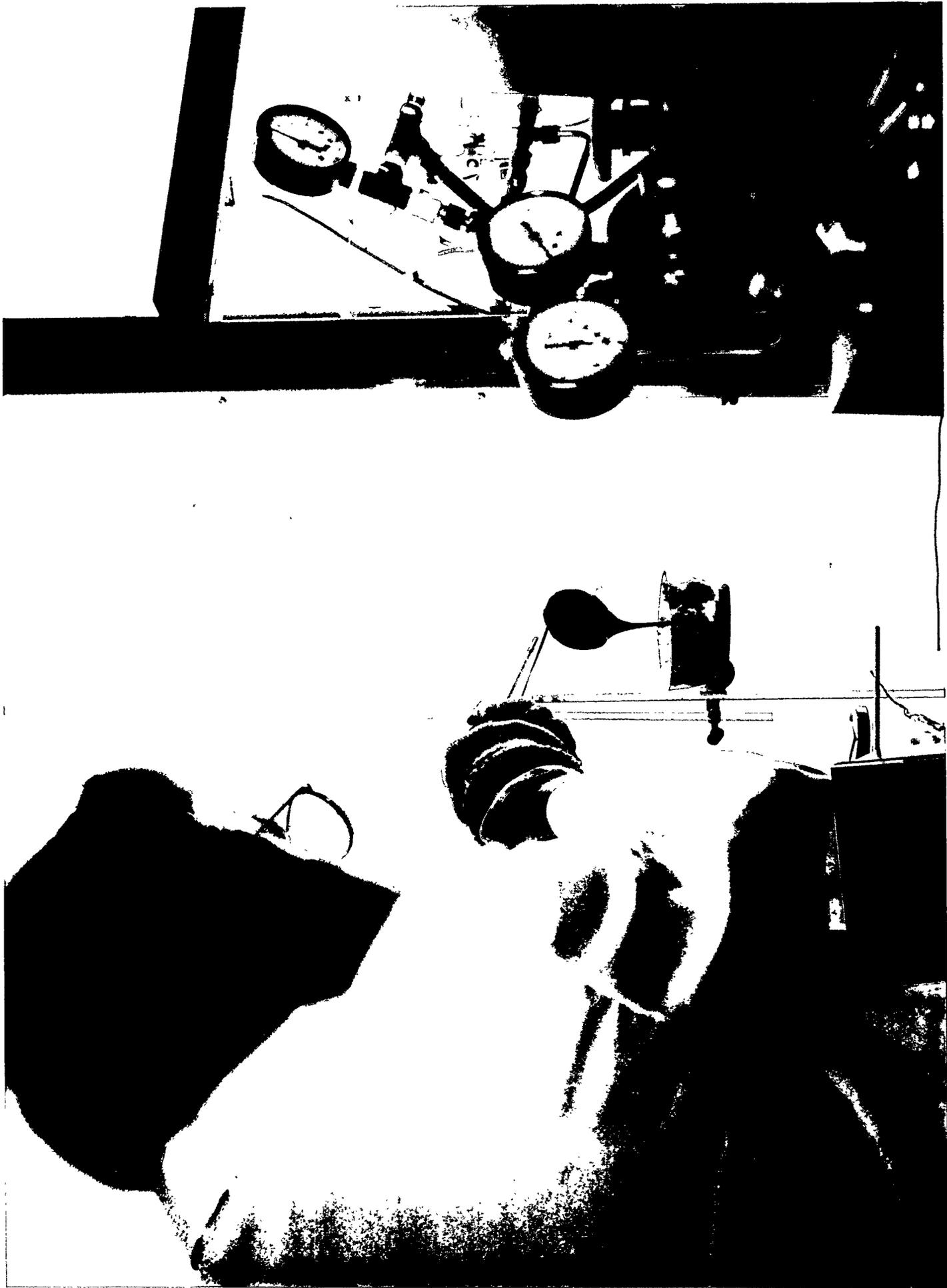


Fig. D.2. Pouring of lead borate glass into platinum dish.

D.4 SCOPING EXPERIMENTS

Scoping experiments are proof-of-principle tests designed to demonstrate that some phenomena occur. By definition, they are conducted with the minimum equipment and measurements to confirm or disprove a particular hypothesis. The experiments are not designed to obtain detailed design information.

Bench-scale tests (~500–600 g) with lead borate glasses were used to evaluate four important characteristics: (1) solubility of UO_2 , ZrO_2 , and Al_2O_3 in the glass; (2) oxidation of Zr or Al and then dissolution in the glass; (3) cracking of the glass on cooling; and (4) disintegration of the glass in water.

D.4.1 Solubility of Selected Oxides in Lead Borate Glasses

These tests were run at $\sim 1020^\circ\text{C}$. Several tests were run to determine the solubility of UO_2 , Al_2O_3 , or ZrO_2 in a glass with the initial composition $1\text{PbO}\cdot 1\text{B}_2\text{O}_3$. Both the UO_2 and Al_2O_3 readily dissolved in this glass. The limit of solubility for UO_2 was >30 wt. %, and for Al_2O_3 , it was 20 wt. %. The dissolution of 30 wt. % Al_2O_3 was hampered by the very high viscosity of the melt rather than by a solubility limit.

An attempt to dissolve 10 wt. % ZrO_2 was not successful. However, with a glass composition of $2\text{PbO}\cdot 1\text{B}_2\text{O}_3$, 20 wt. % ZrO_2 , and 20 wt. % UO_2 were dissolved. The results of the solubility studies are listed in Table D.2. Several glasses are shown in Fig. D.3.

Table D.2. Solubility of UO_2 , Al_2O_3 , and ZrO_2 in lead borate glasses

Glass composition	Solubility at 1020°C
$1\text{PbO}\cdot 1\text{B}_2\text{O}_3$	>30 wt. % UO_2 <10 wt. % ZrO_2
$1\text{PbO}\cdot 1\text{B}_2\text{O}_3$	>20 wt. % Al_2O_3
$2\text{PbO}\cdot 1\text{B}_2\text{O}_3$	20 wt. % UO_2 plus 20 wt. % ZrO_2
$3\text{PbO}\cdot 1\text{B}_2\text{O}_3$	Incomplete dissolution of 20 wt. % UO_2 plus 20 wt. % ZrO_2

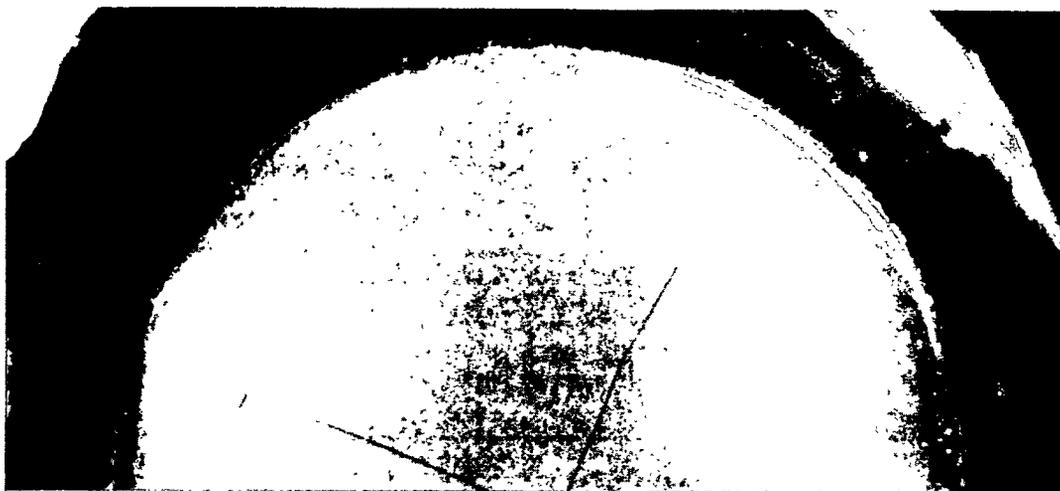
A material containing $1\text{Al}_2\text{O}_3\cdot 2\text{B}_2\text{O}_3$ with 10 wt. % UO_2 was prepared and heated to 1020°C . The product contained both a solid and a liquid. When the B_2O_3 content was increased to $1\text{Al}_2\text{O}_3\cdot 4\text{B}_2\text{O}_3$, there were still some solids. Significantly, the only way that this material could be removed from the platinum crucible was to add PbO.



Al_2O_3 Dissolved in 2:1 Lead Borate Glass
(10% by Weight)



CeO_2 Dissolved in 2:1 Lead Borate Glass
(10% by Weight)



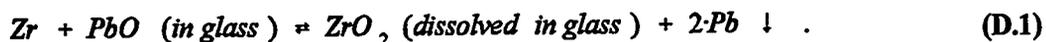
ZrO_2 Incompletely Dissolved in 2:1 Lead
Borate Glass (20% by Weight Incomplete)

Fig. D.3. Different lead-borate glasses.

From these studies, it is clear that PbO enhances the solubility of oxide in these borate glasses. The optimum composition for dissolution of UO_2 together with ZrO_2 is $2\text{PbO}\cdot 1\text{B}_2\text{O}_3$.

D.4.2 Oxidation of Nuclear Metals and Carbon by Lead Borate Glass

A central feature of GMODS is that the glass will contain a sacrificial oxide, PbO, that can react with metals. For example, the reaction with metallic zirconium to form ZrO_2 and Pb is:



This reaction would result in the zirconium's being dissolved in the glass as ZrO_2 .

All tests with metals and carbon were performed in high-fired ceramic alumina because the lead product of this reaction readily forms alloys with platinum metals. This is satisfactory as long as the melt is not allowed to solidify and then be reheated. Pouring the melt into an open silica dish is the most satisfactory way of recovering the sample and examining it for the lead product. All experiments were performed under argon without stirring to prevent oxidation from air. Tests were run at 1000°C with an initial glass composition of $4\text{PbO}\cdot 1\text{B}_2\text{O}_3$ to provide ample PbO for the oxidation of Zr or Al and to give a resultant $\text{PbO}\cdot\text{B}_2\text{O}_3$ ratio of $2\text{PbO}\cdot 1\text{B}_2\text{O}_3$ after reaction.

This reaction has been investigated qualitatively with powdered zirconium, strips of aluminum, Zircaloy, cerium chunks, and with a solid-carbon rod. The reaction with powdered zirconium metal was very rapid; the energy released resulted in a flash of light, an audible report, and a broken crucible and quartz sleeve. Further experiments used 1/8 in. to 1/16 in. strips of metal without further difficulty. Figure D.4 shows the partial dissolution of Zircaloy-2 at the half-way point. At the start of the experiment, the crucible contained no lead.

Stainless steel was discovered to be rapidly attacked when a standard stainless-steel-clad thermocouple was inserted into the melt and soon thereafter was found to be shortened because of the complete dissolution of the immersed portion. Examination showed that these metals readily reacted with the lead borate glass to form lead and to dissolve the newly formed metal oxide. Lead globules were seen in the sample specimens after they were cooled.

For conversion of plutonium, spent fuel, radiation sources, and other materials to glass, dissolution is critical. Oxides dissolve in glass, but metals are insoluble. The experiments show the feasibility of direct conversion to glass. Separate tests were carried out with cerium metal, which is a substitute for plutonium.

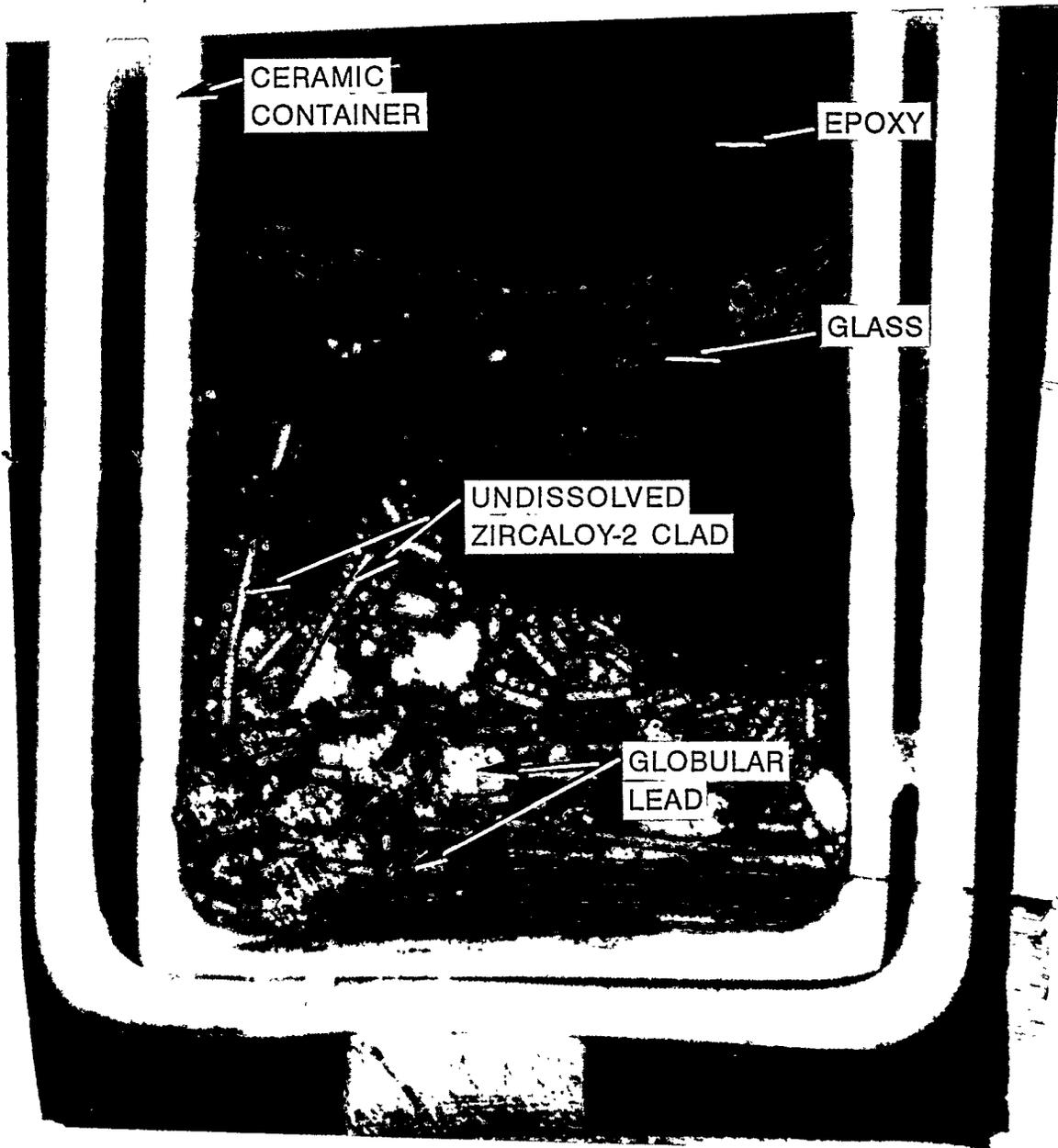
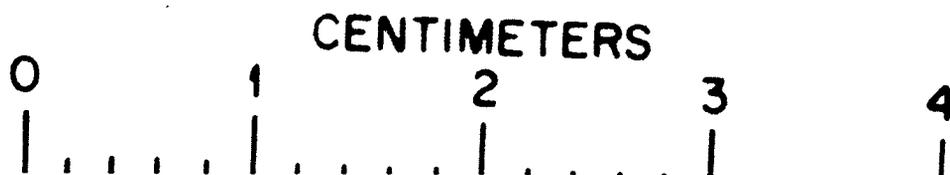


Fig. D.4. Dissolution of Zircaloy-2 in lead borate glass at half-way point.



D.4.3 Cracking of Glass

Tests with a $2\text{PbO}\cdot\text{B}_2\text{O}_3$ glass and a similar glass loaded with 20 wt. % UO_2 plus 20 wt. % ZrO_2 resulted in significant cracking during air cooling from 1020°C to room temperature. This suggests a significant coefficient of thermal expansion of glass.

D.4.4 Leach Test of $2\text{PbO}\cdot\text{B}_2\text{O}_3$ with Boiling Water

Lead borate glasses dissolve incongruently in water; that is, they break down into soluble B_2O_3 and insoluble hydrated PbO . Tests with the glass $2\text{PbO}\cdot\text{B}_2\text{O}_3$ found that the rate of loss of glass in boiling water was $35\text{ mg/cm}^2\cdot\text{h}$.

D.4.5 Scoping Experiment Conclusions

The optimal glass composition of $2\text{PbO}\cdot\text{B}_2\text{O}_3$ was found for dissolution of materials UO_2 and ZrO_2 . The oxidation and dissolution of Zr, Al, and Ce by the sacrificial oxide PbO in the glass were demonstrated. In addition, the glasses readily cracked during cooling.

D.5 DENSITY MEASUREMENTS OF GLASS

Small-scale experiments were conducted with the proposed GMODS glass system to measure density of the mixtures over the range of potential system compositions (Table D.3). The range of compositions of the proposed GMODS dissolution mixture is between the mole ratios of 1:1 up to 4:1 $\text{PbO}:\text{B}_2\text{O}_3$. Over this range, a fairly uniform vitrified glass is obtained, and the measurement of freezing temperature ambient glass density has been partially completed and is summarized herein.

It has been found that density of the solid glass closely follows the empirical calculated range of densities (Table D.4) based on simple mole ratio average from 1:1 up to 4:1 PbO to B_2O_3 . The high-ratio 4:1 mix always crystallizes on solidification and appears to expand, thus leaving voids in the solid—hence a lower density. The 3:1 mix is variable, that is, mostly a clear vitrified phase with crystalline inclusions—hence a variable density.

D.6 PHYSICAL PROPERTY MEASUREMENTS OF MIXED 2:1 LEAD BORATE AND CANDIDATE CERAMICS

A relatively high degree of importance is attached to thermal hydraulic properties of the most likely candidate ceramic materials expected to occur in the GMODS vitrification processes. The most important of these, of course, is plutonium, which, for experimental purposes, is replaced by the surrogates uranium and cerium. In addition to these, zirconium and aluminum have been included because of their likely presence in processing chemistry and the PbO reduction to metal.

Table D.3. Measured lead borate densities

Mix	Observed freezing temperature (°C)	Density (g/cm ³)
1:1	500	6.35
1.5:1	440	6.82
2:1	480	7.63
2.5:1	500	7.60
3:1	530	7.22–7.70 ^a
4:1	550	6.57 ^b

^aClear, vitrified phase.

^bSolid phase (mostly crystalline).

Table D.4. Calculated vitrified lead borate densities

PbO:B ₂ O ₃ mix	Sum of mole weights × density (No. moles)	Calculated density (g/cm ³)
1:1	11.34 (2)	5.67
1.5:1	16.10 (2.5)	6.44
2:1	20.87 (3)	6.95
2.5:1	25.63 (3.5)	7.32
3:1	30.4 (4)	7.60
4:1	39.93 (5)	7.98

An experimental characterization of these materials in the preferred lead-borate mixture of 2:1 PbO:B₂O₃ includes the solubility limits. The freezing temperature and the product solid density measurements have been completed. Mixtures were made at the relatively modest temperature of 1000° C (Table D.5), a temperature which is dictated by the limited capability of our laboratory ware and furnaces.

Table D.5. Physical property measurements of various materials in lead borate glass with molar ratio 2:1 PbO:B₂O₃

Compound	Concentration ^a (wt. %)	Temperature		Solid density (g/cm ³)	Relative viscosity
		Maximum	Freezing		
U ₃ O ₈	20	1000	475	8.14	Fluid at 550° C
ZrO ₂	10	950	500	6.97	Viscous at 550° C
Al ₂ O ₃	10	1000	500	6.50	Very Viscous at 550° C
CeO ₂	10	1000	450	6.99	Viscous at 550° C

^aWeight percent of combined 2PbO+B₂O₃.

D.7 VISCOSITY MEASUREMENTS

D.7.1 Description of Apparatus for Viscosity Measurements of Lead Borate Glasses

One important physical characteristic of the starting material and the final mixture is the fluid viscosity. Viscosity is important in determining fluid flow, chemical reactor mixing characteristics, and heat-transfer information.

A standard Brookfield (Model RVDV III)TM rheometer is the central component of the experimental setup (Fig. D.5). The principle of operation is relatively simple: a spindle is attached to a motor and is then immersed into the liquid to a specified depth. The motor is started and set at a constant speed [in revolutions per minute (RPM)]. This induces a torque on the spindle which is measured. The viscosity is directly related to the torque and inversely related to the speed. A constant based on the system geometry (determined by using standardized Newtonian fluids) is used to convert these readings to a viscosity in centipoise.

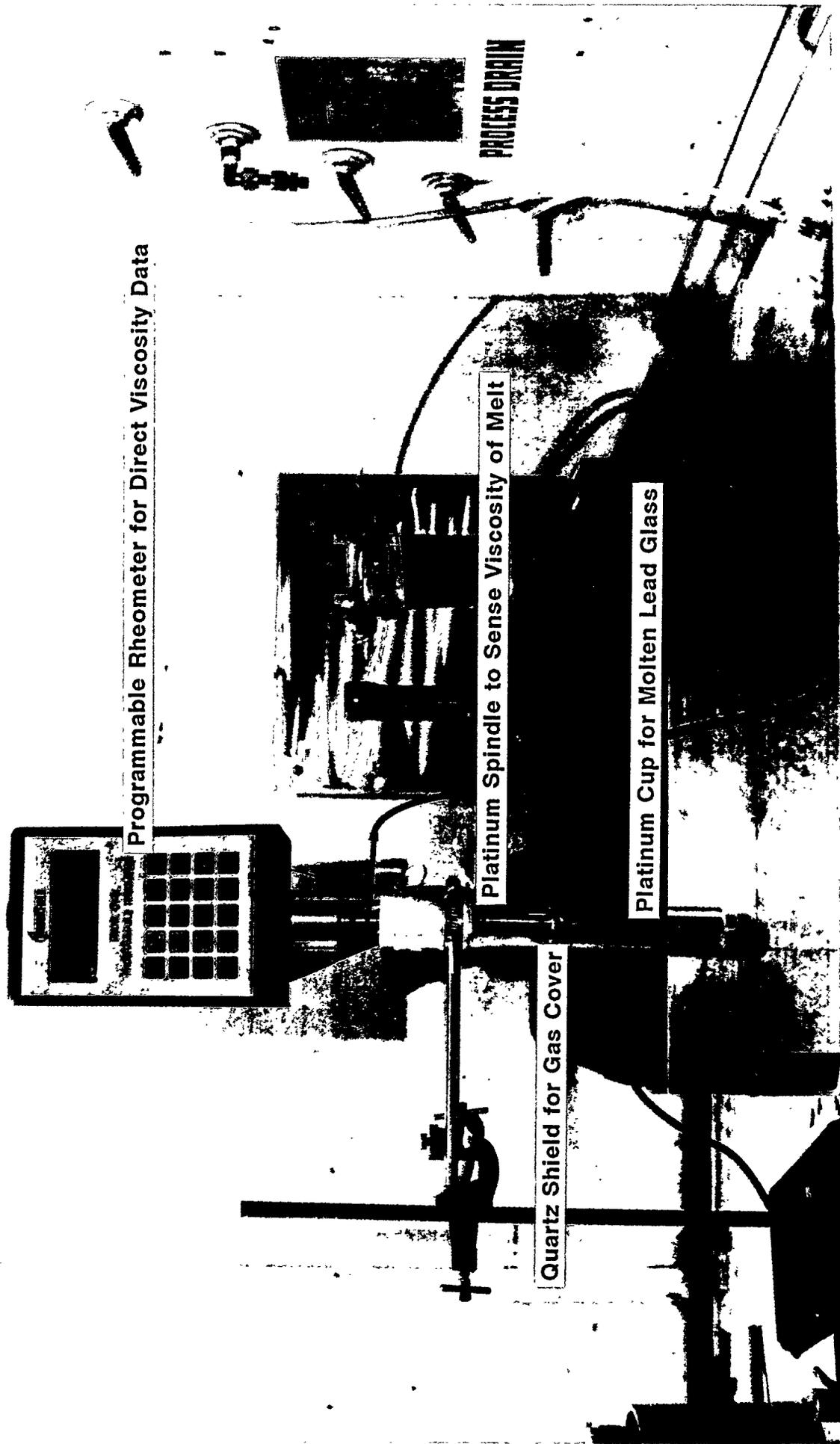


Fig. D.5. Standard Brookfield viscometer fitted with a platinum cup and spindle (furnace removed).

The standard spindles which accompany the rheometer will not withstand the extreme oxidizing conditions present in the molten glass. A platinum spindle (0.375 in. diam at the measuring point) and a platinum cup (0.75 in. diam and 5 in. high) were therefore constructed. The cup and the spindle are enclosed in a quartz shield to capture the gases emitted when the glass is heated. It is covered with a Teflon™ lid, which has a central hole large enough such as to allow the spindle to rotate freely. The lid also has a second opening from which a suction is drawn to remove the gases.

The quartz tube is placed into a platinum furnace (not shown in the figure). The temperature of the molten glass is taken with a platinum thermocouple until the temperature stabilizes. The thermocouple is then removed, and the rheometer is started. Viscosity measurements can then be recorded over a range of speeds.

D.7.2 Calibration of Brookfield Rheometer

To calibrate the rheometer, some standardized fluids (silicone oils) were purchased from Brookfield and were first tested with standard stainless steel spindles. Calibrations with these spindles indicated that the rheometer was out of tolerance. Although this was unfortunate, tolerance was achieved by using a calibration curve. Eventually the rheometer will need to be returned to Brookfield for recalibration.

After checking the rheometer's accuracy, the platinum spindle and cup were used with standard fluids to determine the constant which is specific to the geometry of the experimental apparatus (i.e., diameter of container, diameter of spindle, and depth of immersion). This calibration was reproducible to within 5% error.

Table D.6 provides viscosities of some standard substances to compare with the data on the glass systems to come:

Table D.6. Viscosities of common substances

Substance	Temperature (°C)	Viscosity (cP)
Castor oil	25	986
Glycerin	25	954
Machine oil, heavy	15.6	660.6
Machine oil, light	15.6	113.8
Oliver oil	20	84
Antifreeze	20	19.9

D.7.3 Viscosity Measurements of Initial Glass Compositions

Viscosity measurements of 1:1, 2:1, 3:1, and 4:1 PbO:B₂O₃ were taken (Table D.7 and Table D.8) from a range of 620–800° C. The sample sizes measured were between 100–150 g. The measurements taken were at the low end of the viscosity range for this particular geometry (the spindle's circumference is small; therefore, it does not produce much torque in low-viscosity fluids). This procedure gives a relatively large degree of error.¹ However, this data show that at temperatures considerably lower than the suspected temperature in this system, 600–820° C compared to 1000–1100° C, the glass viscosity is very low—≤100 cP over 750° C, or less viscous than light machine oil. The data also show Newtonian fluid behavior (constant viscosity with increasing shear rate). A correlation could be obtained to predict the change in viscosity with the change in temperature. However, this correlation would require more accurate low viscosity readings which are not considered necessary at this time because the final glass composition is predicted to have a much higher viscosity which will be a much more limiting condition for the process.

D.7.4 Viscosity Measurements of 20% U₃O₈ in 2:1 PbO:B₂O₃

Uranium oxide was expected to raise the viscosity of the glass greatly, thereby causing heat and mass transfer in the liquid to decrease substantially; however, this did not occur (Table D.9). While the mixture is very viscous near its melting point (≈600° C), it drops quickly over the range 600–900° C to a viscosity approximately equivalent to antifreeze.

D.7.5 Viscosity Measurements of 10% ZrO₂ in 2:1 PbO:B₂O₃

A solution of 10% ZrO₂ showed high viscosities (Table D.10), relative to 20% U₃O₈. The viscosity is very well defined by the Bingham model². The Bingham model is used to model “viscoplastic” materials,

¹More accurate data could be obtained in a larger experimental setup, but because platinum equipment is required, it may become rather expensive. Also, because the viscosity of the glass is expected to increase significantly with the addition of other oxides, it was decided to maintain our present configuration.

²The Bingham model is described by the equation:

$$\eta = \mu_o + \frac{\tau_o}{\gamma}$$

with η = viscosity, μ_o = viscosity at infinite shear, τ_o = yield stress, and γ = shear rate.

Table D.7. Viscosity (in cP) of 1:1 and 2:1 PbO:B₂O₃ glass at low temperatures

		Composition						
		1:1 PbO:B ₂ O ₃			2:1 PbO:B ₂ O ₃			
		Temperature ($\pm 10^\circ\text{C}$)						
Spindle (RPM)	Shear rate	706	750	810	620	710	820	Viscosity error (cP)
100	27.5	261			205			± 58
125	34.4	262	102	47	201	52.6		± 48
150	41.3	265	99.3	48.7	200	48.3	23.3	± 40
175	48.1	267	103	55.1	202	50	18.8	± 35
200	55	262	99.9	53.6	199	44.8	17.5	± 30
225	61.9	262	101	50	197	42.6	20.5	± 27
250	68.8	264	99.5	54.9	197	45.9	29.1	± 24
Average		263	101	51.6	200	47.4	21.8	

Table D.8. Viscosity (in cP) of 3:1 and 4:1 PbO:B₂O₃ glass at low temperatures

		Composition							
		3:1 PbO:B ₂ O ₃			4:1 PbO:B ₂ O ₃				
		Temperature ($\pm 10^\circ\text{C}$)							
Spindle (RPM)	Shear rate	603	665	713	803	615	705	822	Viscosity error (cP)
125	34.4	107	59.7			76	65		± 48
150	41.3	104	62	46.7	22	75	62.5	20.5	± 40
175	48.1	105	60.4	39.2	27	76	52.8	18.7	± 35
200	55	105	60.2	40.6	32	77	55.3	16.1	± 30
225	61.9	101	57.2	42.9	31	76	56	22.7	± 27
250	68.8	101	54.8	42	30	76	53.2	28.3	± 24
Average		104	59.1	42.3	29	76	57.5	21.3	

Table D.9. Viscosity (in cP) of 20% U_3O_8 in 2:1 PbO: B_2O_3 glass at low temperatures

Composition					
20% U_3O_8 in 2:1 PbO: B_2O_3					
Temperature ($\pm 10^\circ C$)					
Spindle (RPM)	Shear rate	626 ^a	768	905	Viscosity error (cP)
150	41.3	2070	121	19.3	± 40
175	48.1	2040	116	20.8	± 35
200	55.0	1980	113	24.2	± 30
225	61.9	1940	109	24.4	± 27
250	68.8	1825	110	22.4	± 24
Average		1970	116	22.2	

Table D.10. Viscosity (in cP) of 10% ZrO_2 in 2:1 PbO: B_2O_3 Glass

Composition		10% ZrO_2 in 2:1 PbO: B_2O_3			Viscosity error (cP)
Temperature ($\pm 10^\circ C$)		810	1000	1100	
Spindle RPM	Shear rate (1/s)				
150	41.3	651	---	246	± 40
175	48.1	600	450	221	± 35
200	55.0	553	406	202	± 30
225	61.9	511	370	181	± 27
250	68.8	484	346	174	± 24
Average		560 ^a	393 ^a	205 ^a	

^aGlasses at these conditions behaved as Bingham fluids. Common in fluids with suspended solids.

meaning, materials that have an infinite viscosity (no flow) until their yield stress is reached. This is typical of thick slurries and is a likely indication of incomplete dissolution of ZrO_2 . If a material conforms to the Bingham model, one would expect to observe high viscosities when the viscometer is started, but the yield stress for the ZrO_2 is low enough that the decrease in viscosity is too rapid to note. This phenomena is observed in the 10% U_3O_8 / 10% ZrO_2 described in Section D.7.6.

D.7.6 Viscosity Measurements of U_3O_8 / ZrO_2 Mixtures in 2:1 $PbO:B_2O_3$

Replacing 10% of the U_3O_8 with ZrO_2 caused the viscosity to increase sharply at lower temperatures. The glass appears to act as a Bingham fluid up to at least $960^\circ C$. The viscosity starts off very high (7000–8000 cP @ $850^\circ C$, 3000–3500 @ $960^\circ C$) and then decreases quickly with mixing. The steady state values are shown in Table D.11. The glass is also shear thinning, as the Bingham model predicts, which again suggests incomplete dissolution. There is a relatively large degree of error due to spindle slippage (see Section 1.2). When the temperature was raised to $1160^\circ C$ the glass no longer behaved as a Bingham fluid. Normal Newtonian behavior was observed. This shows that complete dissolution has probably occurred. Whether or not the glass will remain homogeneous as the temperature is lowered is not clear. One should note that while the 10% U_3O_8 / 10% ZrO_2 mixture is relatively viscous at low temperatures, this is an extreme condition. More than likely, the ratio of U_3O_8 / ZrO_2 will be 2/1 or 3/1 or greater.

Viscosities for the 13.3% U_3O_8 / 6.7% ZrO_2 mixture were much lower even though overall weight loading is equivalent. This is due to the much greater fluidity of U_3O_8 . However, the high initial viscosities are still noted at temperatures under $1000^\circ C$. The non-Newtonian behavior is still observed in this glass even at $1100^\circ C$, but is a very small effect. Another interesting fact is that the viscosities were lower as the temperature was ramped down, than they were as the temperature was increased. This would indicate that the oxide dissolved at higher temperatures stays in solution as the glass is cooled down. Viscosity data (Table D.12) is given in the order the measurements were taken.

Table D.11. Viscosity (in cP) of 10% U₃O₈ / 10% ZrO₂ in 2:1 PbO:B₂O₃ Glass

Composition		10% U ₃ O ₈ / 10% ZrO ₂ in 2:1			Viscosity error (cP)
Temperature ($\pm 20^\circ\text{C}$)		850	960	1150	
Spindle RPM	Shear rate (1/s)				
150	41.3	2100 ^b	1300 ^b	-----	± 40
175	48.1	-----	-----	248	
200	55.0	2000 ^b	1110 ^b	240	± 30
225	61.9	-----	-----	240	
250	68.8	1800 ^b	950 ^b	230	± 24
Average		1970 ^{a,b}	1120 ^{a,b}	240	

^aGlasses at these conditions behaved as Bingham fluids. Common in fluids with suspended solids.

^bThese viscosity measurements have a greater error (± 200 cP) than indicated in the far right column. This was due to difficulty with the experimental equipment at high viscosities. When there is an opportunity to send the rheometer back for recalibration this problem should be corrected.

Table D.12. Viscosity (in cP) of 13.3% U₃O₈ / 6.7% ZrO₂ in 2:1 PbO:B₂O₃ Glass

Composition		13.3% U ₃ O ₈ / 6.7% ZrO ₂ in 2:1					Viscosity error (cP)
Temperature ($\pm 20^\circ\text{C}$)		955	1060	1100	895	790	
Spindle RPM	Shear rate (1/s)						
150	41.3	545	188	107	---	---	± 40
175	48.1	503	167	99	330	743	
200	55.0	462	150	92	307	719	± 30
225	61.9	432	140	86	295	694	
250	68.8	399	135	84	283	673	± 24
Average		468	156	94 ^a	304	707	

^aGlasses at these conditions behaved as Bingham fluids. Common in fluids with suspended solids.

D.7.7 Literature Values for Viscosity of 1:1 PbO:B₂O₃

Table D.13 shows measurements of up to 50 mol % PbO in B₂O₃.

Table D.13. Comparison of literature and experimental viscosity data for 1:1 PbO:B₂O₃

Eagan et al. (1:1 PbO:B ₂ O ₃) ³		Experimental (1:1 PbO:B ₂ O ₃)	
Temperature (°C)	Viscosity (cP)	Temperature (°C)	Viscosity (cP)
780	20–100	810	52
725	150–250	750	100
680	500–700	706	263
635	2000+–300		
600	8000+–1000		
560	40,000+–5000		

As shown, it correlates relatively well with our experimental results. The data was taken off a log plot which is the reason for the range in values. In addition, Eagan shows values for lower concentrations of PbO and there is a large decrease in viscosity as PbO content increases. This is the same trend we find until approximately the eutectic point of the PbO:B₂O₃. From the eutectic point up to 80 mol % lead, the viscosity levels off. A summary of glass viscosity data is shown in Table D.14.

D.8 CHEMICAL REACTION RATE MEASUREMENTS

Dissolution rates for lead borate glasses are being investigated systematically for all the candidate metals, including carbon. Quantitative data are incomplete; however, qualitative observations for Zircaloy, aluminum, stainless steel, and carbon confirm that satisfactory rates in the 2:1 PbO:B₂O₃ can be expected. Of these, only carbon (using the rate of weight-loss from a cylindrical rod) has shown an estimated reaction rate of 0.1 g/cm²/h. By measuring the weight of the lead regulus that results from the reaction, similar rates are indicated for aluminum and Zircaloy. The surrogate metal, cerium, which simulates plutonium, also produced a similar amount of lead in the form of a lead pellet (Fig. D.6).

³Robert J. Eagan et al., *Crystal Growth in the System PbO-B₂O₃*, J. Amer. Ceramic Soc., 53, No. 4, p. 214–216.

Table D.14 Summary of viscosity measurements (in cP) vs temperature for several GMODS glasses

	Temperature (°C)	600	650	700	750	800	850	900	950	1000	1050	1100	1150
PbO:B ₂ O 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 ₃ O ₈			2000*		125			22					
2:1 w/10% ZrO ₂						560*				390*		200*	
2:1 w/10% ZrO ₂ and 10% U ₃ O ₈									1150*				240
2:1 w/6.7% ZrO ₂ and 13.3% U ₃ O ₈						710*		300*			150*	100*	

*These viscosity measurements have a greater error (± 200 cP). This was caused by the difficulty with the experimental equipment at high viscosities.

Cerium Loaded Glass



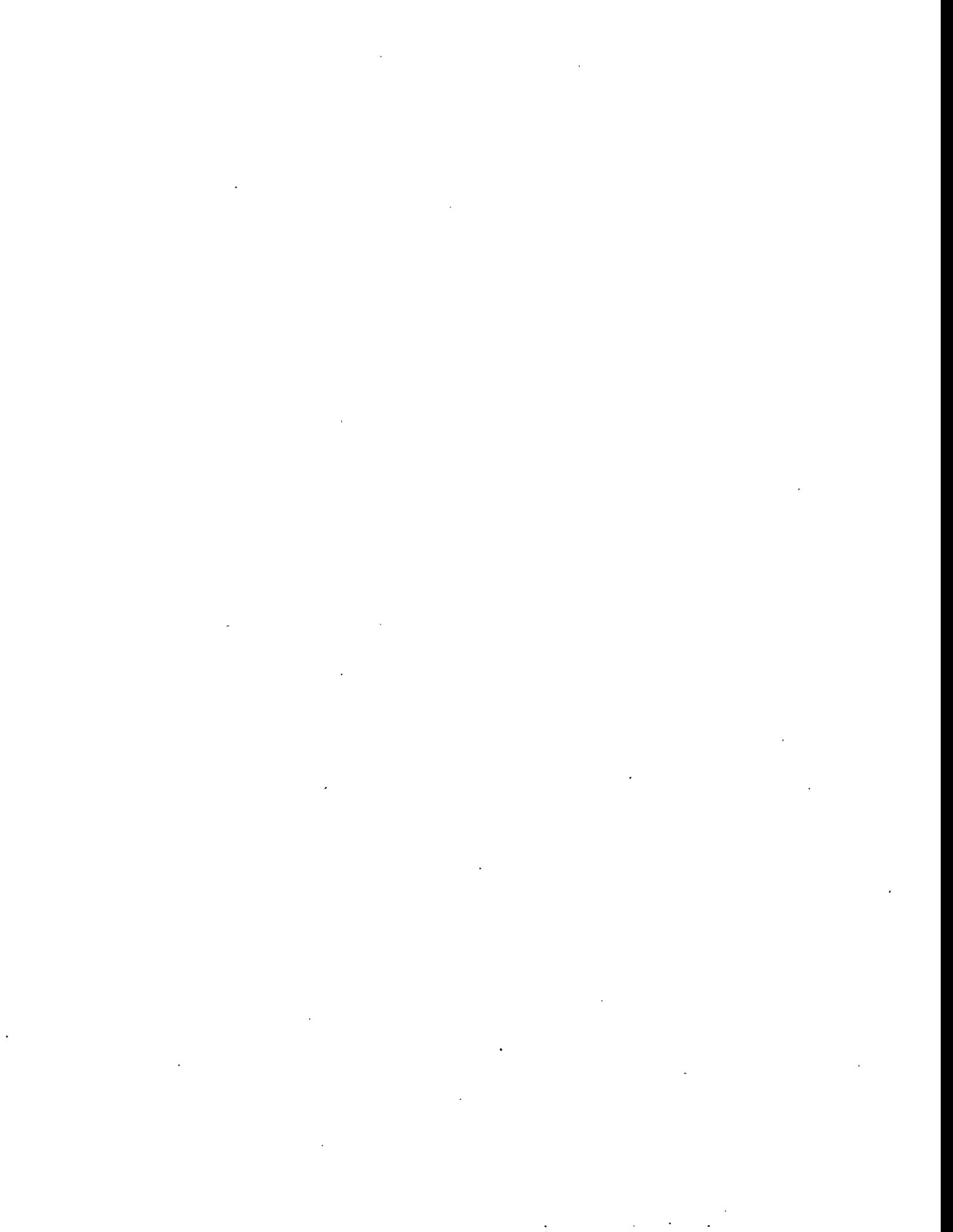
Lead Reaction Product

**Crucible Dissolution Test of
Cerium Metal (Surrogate for
Plutonium) In Lead Borate Glass**

Fig. D.6. Lead pellet formed by the reaction between cerium metal and lead borate.

Appendix E:

LEAD RECYCLE PROCESSING FOR GMODS



APPENDIX E: LEAD RECYCLE PROCESSING FOR GMODS

E.1 PRODUCTION OF LEAD AND LEAD OXIDE FOR GMODS

GMODS is a new process for the direct conversion of a wide variety of wastes, including excess plutonium, to glass.

An integral element of the GMODS process involves (a) the reoxidation of molten lead to lead monoxide and (b) a purification step, the removal of noble metals from the molten lead. In the treatment of many wastes, the latter purification may be needed only at infrequent intervals. Fortunately, there is extensive large-scale industrial lead-processing experience available relating to the performance of these tasks; no new, untried technology needs to be developed. Only adaptations are needed. This appendix reviews industrial experience and suggests some appropriate applications of existing technology for use with GMODS.

E.2 PRODUCTION OF LEAD METAL FROM ORE CONCENTRATES

Lead is found in a number of ore forms. The most important is galena, which is lead sulfide (PbS). Other ore forms include lead carbonate (cerrusite) and lead sulfate (anglesite). Usually associated with galena are zinc sulfide, iron sulfide, and a copper-iron sulfide (CuFeS₂). Gold and silver may also be present.

The primary methods of ore concentration is flotation. The ore is crushed and wet ground to ~375 mesh. Flotation chemicals are added, and the lead minerals are collected in a froth. Copper, silver, and gold (when present) remain with the lead. This ore concentrate contains about 70% lead.

E.2.1 Refining

E.2.1.1 Primary Refining

Ore concentrates are pelletized and then fed to a roasting furnace to burn off most of the sulfur (Fig. E.1) and to produce sintered pellets, which will not blow out of the blast furnace in the next stage of processing. The ore concentrate and coke are added to the blast furnace. Air (or oxygen) is injected, the coke is burned, and a reducing gas (CO, CO₂, or N₂) is formed. The CO reacts with the PbO to produce lead metal. The lead bullion that is produced contains Ag, Au, Cu, Bi, Sb, As, and Sn. The slag from the blast furnace contains Fe, Si, Zn, lime, and other materials.

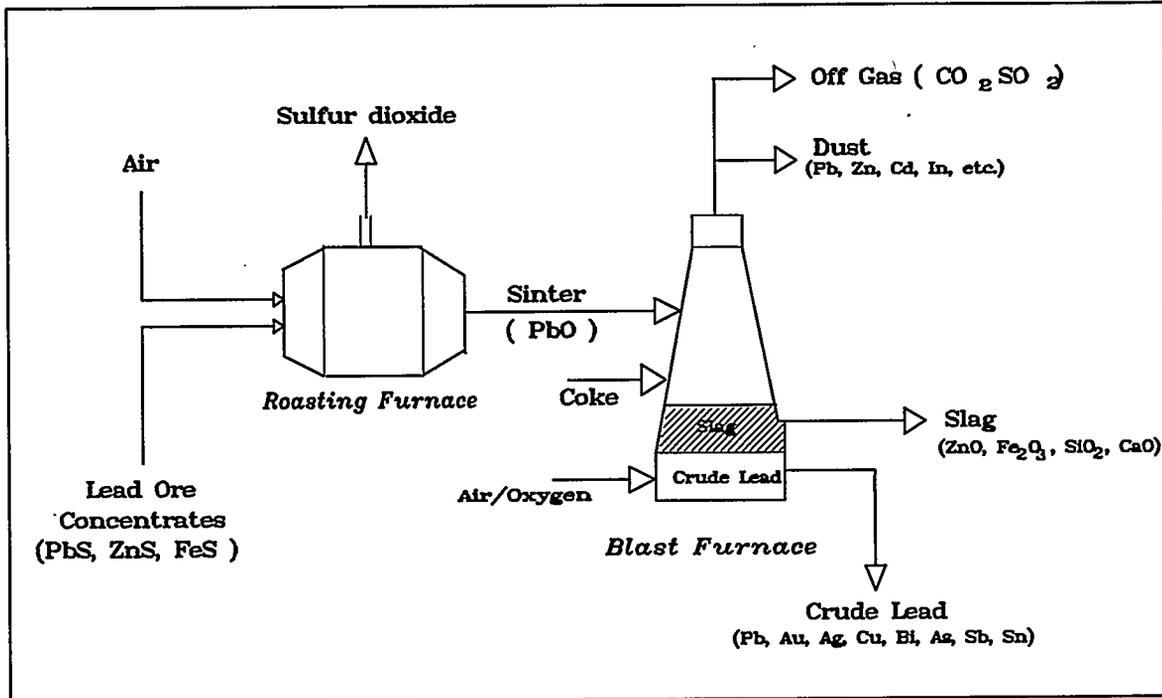


Fig E.1. Production of crude lead from ore concentrates.

A new variant of this refining step is the Queneau-Schuman-Lurgi process:

Pelletized lead concentrates are continuously fed to the melt in the reactor. Oxygen is directly injected continuously to the melt by submerged injectors, oxidizing the ore-concentrate sulfides (literally burning the sulfides). Reduction of the lead monoxide so formed is by addition of pulverized coke or coke breeze. Reportedly, fossil fuel costs are reduced by one-third and a much more concentrated sulfur dioxide is produced (as compared to that produced by air oxidation), which is more suitable for recovery as sulfuric acid by-product. A 30,000-ton/year demonstration plant based upon this process became operational in 1981 in Duisburg, Germany (McKetta, 1988).

In another new variant, the Siros melt submerged combustion process, ore concentrates, and air are injected under a slag cover into a first-stage reactor. Slag, with high lead content, is reduced in a second stage by coal and air (Davey, 1986). This process is particularly suited for ore concentrates having a high sulfur content.

E.2.1.2 Secondary Refining

The impure lead bullion produced in the blast furnace is transferred to furnace kettles for several sequential processing steps referred to as *drossing*, *softening*, *desilvering*, and *retorting* (Fig. E.2). These kettles contain 100–200 tons of lead, and they are constructed of mild steel.

E.2.1.2.1 Drossing

The lead bullion is cooled to about 350°C, forming a dross in which most of the copper is removed. (Note that at or near the melting point of lead, the solubility of copper in lead is very low.) A second stage is reached (when silver and tin are at low levels) by adding sulfur to react with the remaining copper.

E.2.1.2.2 Softening

The softening process step removes antimony, tin, and arsenic by blowing compressed air through the molten charge, thus forming an oxide slag containing large amounts of lead oxide in addition to the antimony, tin, and arsenic. Alternatively, as shown in Fig. E.2, sodium hydroxide and sodium nitrate (Harris Process) may be added to the kettle containing 100–200 tons of lead to produce complex salts (NaSbO_3 , Na_2SnO_3 , Na_3AsO_4 , and Na_2PbO_3) which can be removed (Prengaman, 1981).

E.2.1.2.3 Desilvering

After softening, impurities still remaining in the lead are silver (about 0.2 wt. %), bismuth (up to 0.1 wt. %), gold (about 0.006 wt. %), copper, tellurium, and platinum metals. These metals can be removed by electrolytic refining, but pyrometallurgical techniques are preferred in the United States.

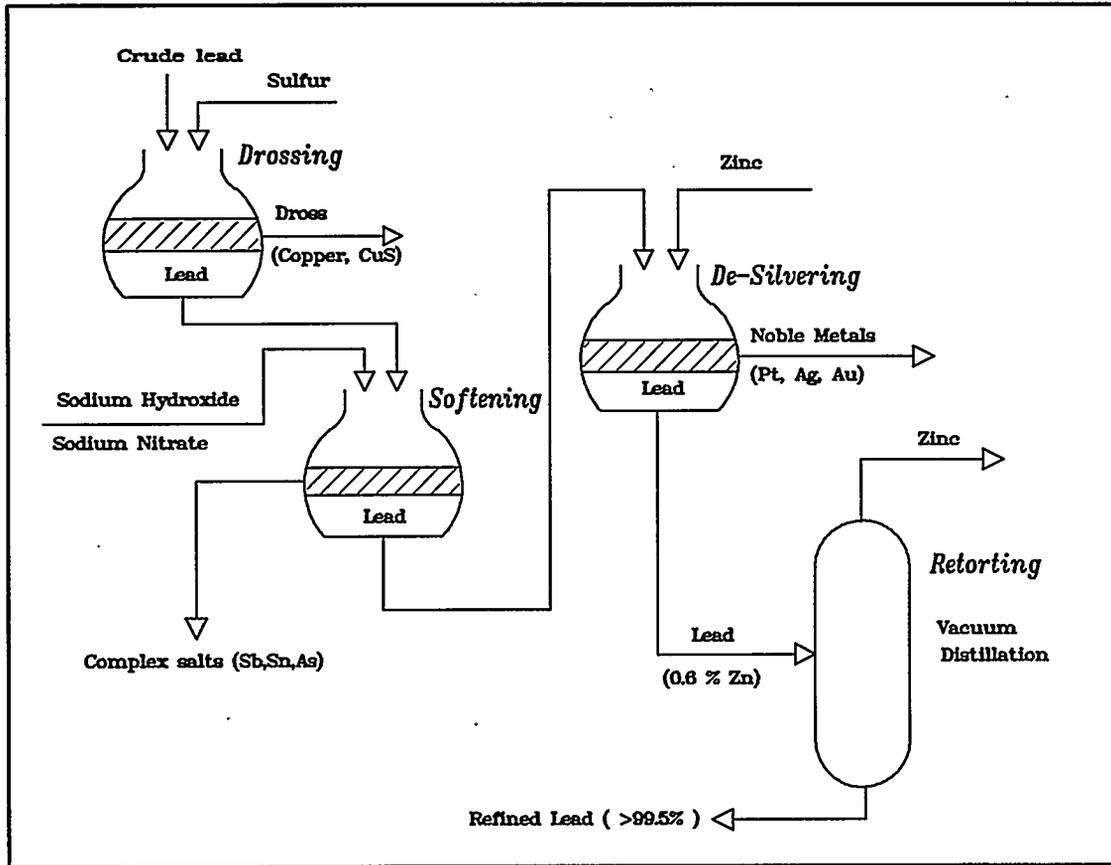


Fig. E.2 Commercial refining of crude lead.

The solubility of the noble metals in lead is lowered by the addition of zinc to saturation, which is 0.55% at 326° C (Parkes De-silvering Process). Typically, 1–2% zinc in excess of saturation is added, forming insoluble intermetallic compounds which separate from the lead upon cooling and then rise to the surface as a dross containing zinc intermetallic compounds. Arsenic and antimony impurities must be low, or they will interfere with this process.

E.2.1.2.4 Retorting

Lead from the desilvering step contains 0.5 to 0.6% zinc, which can be removed by chlorination, oxidation using caustic soda, or by distillation. Vacuum distillation has the advantage in that over 90% of the zinc is recovered as the metal.

The equipment for this step consists of a steel kettle and a steel dezincing chamber suspended inside of the kettle. The temperature is raised to 600° C, and the top of the suspended chamber is water-cooled; zinc then condenses at the top of the chamber. In effect, this is a single-stage Rayleigh distillation.

E.2.1.2.5 Bismuth Removal

Bismuth, if present, remains in the lead. If present at >0.05%, it must be removed to meet commercial specifications. Calcium and magnesium metal can be added to the impure lead to form an intermetallic compound, CaMg_2Bi_2 , which is insoluble in the lead and which rises to the surface as a dross (Betterton-Kroll process).

E.2.2 Corrosion Behavior During Processing

The corrosion resistance of steel to molten lead, zinc, and zinc-bearing lead is discussed by Davey (1986). All of these metals cause corrosion by intercrystalline attack, with zinc-bearing lead (as in the desilvering step) being the most severely corrosive. Kettles used in the desilvering step rapidly develop cracks; they seldom take more than 100 charges before a leak appears.

E.3 PRODUCTION OF LEAD MONOXIDE

Lead forms three oxides, PbO , PbO_2 , and a mixed oxide Pb_3O_4 . A black oxide, a mixture of 60–80% PbO , the balance being finely divided lead, is used for electrodes in lead-acid storage batteries.

Lead monoxide is produced by reaction of molten lead with air or oxygen in a furnace. Black (or grey) oxide for batteries is made by the Barton process (see Sect. E.3.3), by the oxidation of atomized molten lead in air, and by ball milling. The properties of the PbO produced are highly dependent on the method of production and specific process conditions.

Batteries are the largest market for PbO—400,000 MT in 1982. The next large market is the ceramics industry, which uses lead oxides in glasses, glazes, and enamels. Other uses include paints, ferromagnetic, and ferroelectric materials. Large quantities of PbO (8,600 MT in 1979) were used as a heat stabilizer for polyvinyl chloride resins.

E.3.1 Physical Properties

Lead monoxide, also known as litharge, occurs as a reddish alpha form which is stable up to 489°C. Above this temperature, it transforms to a yellow beta form, known as massicot, which is stable up to high temperatures. The beta form is relatively unreactive and undesirable for battery use or for oxidation to form red lead for use in corrosion-resistant paints. The alpha form converts to the beta form over the range of 489 to 600°C, the conversion being complete at 600°C. Conversely, the beta form of PbO changes only very slowly to the alpha form below 488°C. However, mechanical grinding below 488°C will transform the beta form to alpha.

E.3.2 Production by Milling in Air

Lead oxide has been produced by milling 15-mm-diam lead balls in a standard 1-m-diam ball mill using wire mesh for screening the oxide (Williams, 1965) (Fig. E.3). The mill is heated (temperature unspecified) and air is circulated to oxidize the surface of the lead balls. A tumbling action removes the oxide. The product is collected in a cyclone separator. This technique has been scaled up to over 200 tons/week using a 2.1-m-diam drum. Normally, the PbO content of the product is 55 to 65%, the rest being metallic lead.

E.3.3 Production by Oxidation and Stirring of Molten Lead

In the Barton pot process, PbO is produced by partial oxidation of molten lead by air during mechanical stirring. Removal of the product (PbO/Pb mixture) is by the air that induces the oxidation. Collection is by a cyclone separator (Fig. E.4). No heat is added, because the reaction is exothermic and liberates 52.4 kcal/mole of oxide formed (Brachet, 1969).

It is claimed that vigorous mechanical stirring serves to break up oxide particles into fines of 300 mesh or less ($<53 \mu\text{m}$) which are easily carried by the air stream. A portion of the PbO is collected in bag filters (not shown in Fig. E.4). Both fractions of lead monoxide are transferred to storage bins by means of an Archimedes Screw conveyor.

Lead oxide produced by this method, when kept in a dry state, is stable in air. In contrast, abrasion produced PbO/Pb (produced by milling) further oxidizes and also forms carbonates by reacting with atmospheric carbon dioxide.

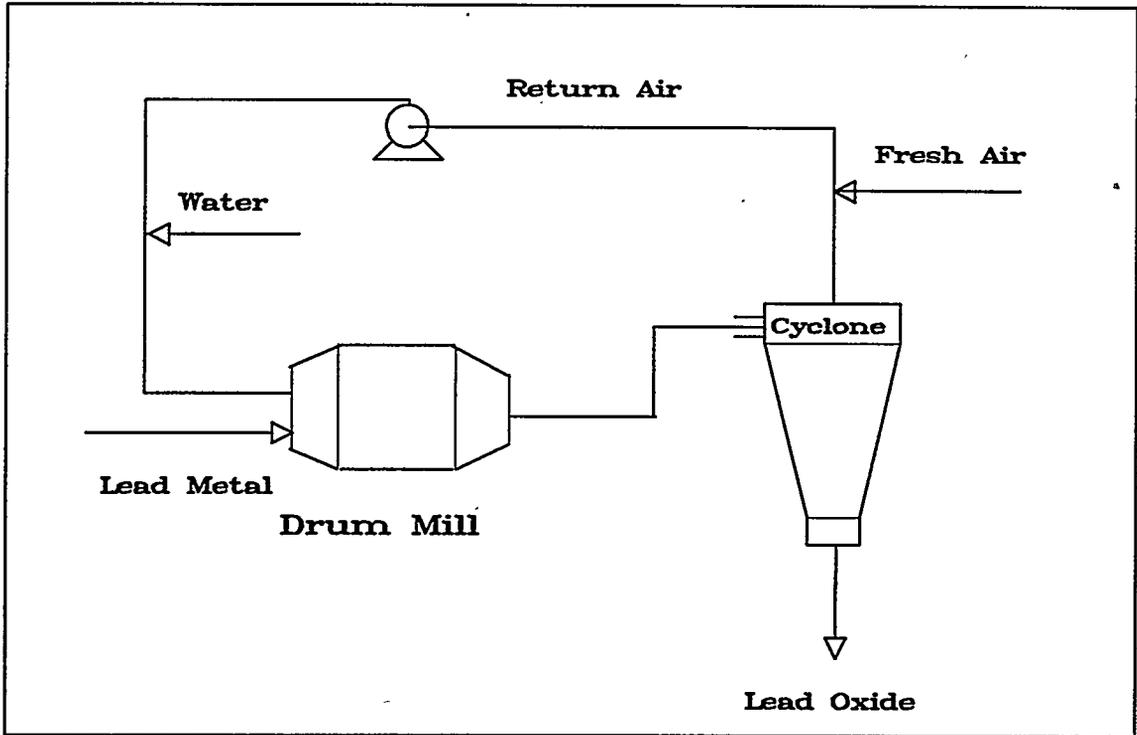


Fig. E.3 Production of lead monoxide by milling.

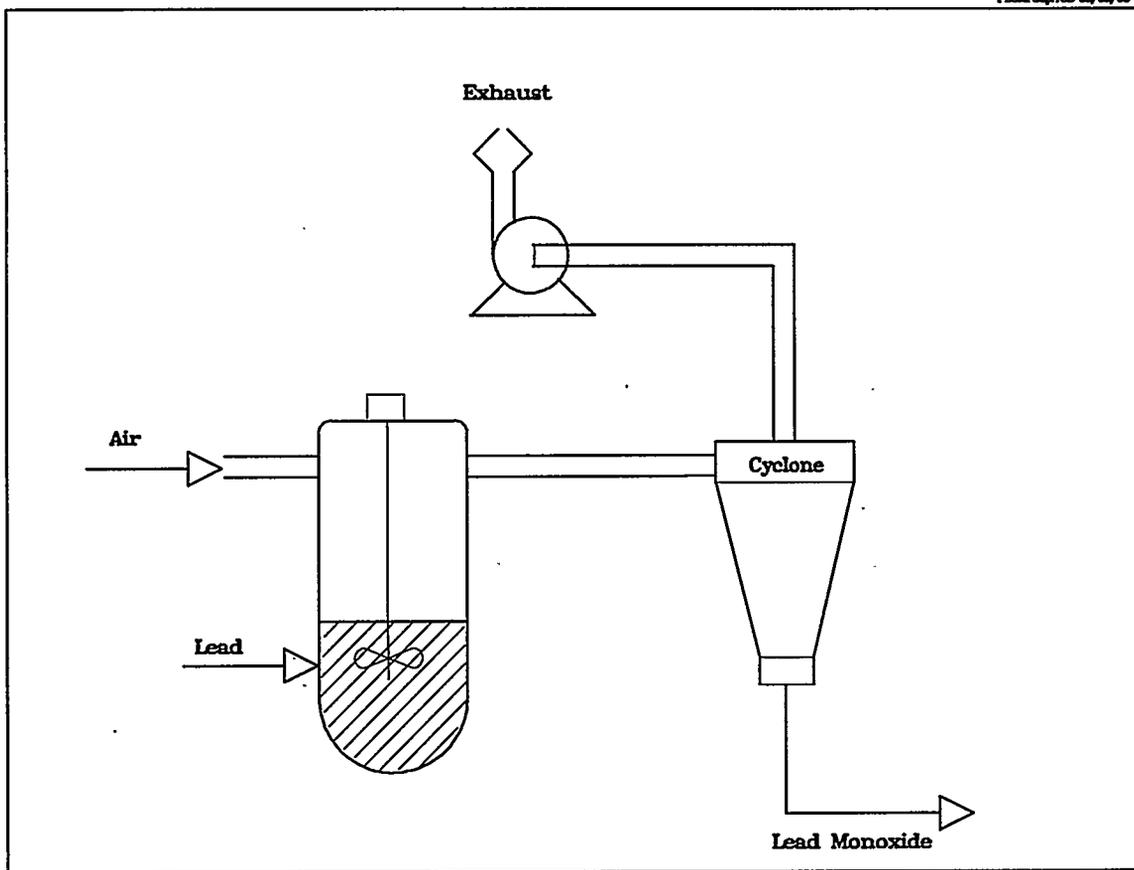


Fig. E.4. Production of PbO in a stirred reactor.

E.3.4 Other Methods for Production of Lead Monoxide

Lead monoxide can be produced from elemental lead by many different techniques, in addition to air oxidation. Some of these are as follows (Hegner and Ritchie, 1974; Brown, 1985):

1. Chemical

- Precipitation of PbO from aqueous solution by, for example, adding ammonium hydroxide to solutions of lead acetate.
- Vapor-phase hydrolysis of lead chloride

2. Pyrochemical

- Burning lead metal in a mixture of 80% oxygen and 20% argon.
- Air or oxygen injection into a melt [see Sect. E.2.1.1, "Primary Refining" and McKetta (1988) and Davey (1986)].

3. Electrochemical

- Anodization of lead metal

Of particular interest to GMODS is oxygen injection into a melt, as mentioned in Sect. 3, because this would permit lead conversion to PbO within the GMODS furnace. No additional equipment would be needed.

E.4 LEAD PURIFICATION AND LEAD MONOXIDE PRODUCTION

Recycling lead in the GMODS process involves two main tasks: (a) purification of lead and (b) reoxidation of lead to form PbO. Each of these tasks can be accomplished in a variety of ways, as discussed below. Processing can be done "batchwise" within the GMODS furnace or in separate auxiliary process equipment

E.4.1 Purification of Lead

Lead metal, formed by reaction of PbO with wastes, will eventually become contaminated with the noble and near noble metals (Au, Pt, Ir, Os, Tc, Re, Ru, Rh, Pd, Ag, and Bi) and, possibly, Cu, As, Sb, and Sn. The extent of contamination and the materials present will determine which of the following process steps may be needed. Copper, for example, may not be present in most of the wastes to be processed. In that case, the step described in Sect. E.4.1.1 may be omitted. Likewise, for most wastes Bismuth will not be present, and the

step described in Sect. E.4.1.4 is not necessary. Most common metals (e.g., Fe, Cr, Zr, Ni, Al) will not be present in the lead metal because they are sufficiently reactive, to form, for example, stable oxides, which remain in the lead borate glass. Optional process steps are shown in Fig. E.5 and are discussed in the following sections.

E.4.1.1 Removal of Cu, As, Sn, and Sb

Cu, As, Sn, and Sb can be removed from lead, as discussed in Sect. E.2.1, by cooling the lead to slightly above its freezing point (350° C) and skimming off the dross. Then, oxygen (or air) is introduced to oxidize As, Sb, and Sn, and the oxide slag formed is skimmed from the surface.

E.4.1.2 Removal of Noble Metals by Zinc

The noble metals can be removed as discussed in Sect. E.2.1.2.3 by adding zinc to the molten impure lead. Zinc, which is soluble to the extent of 0.55% in lead, forms intermetallic compounds with the noble metals; these compounds are less dense than lead, and they float to the surface. In most cases envisioned, further purification of the lead will not be necessary. The lead containing only a small amount of zinc can be oxidized directly. Zinc oxide concurrently formed is easily incorporated into the lead borate glass. Bismuth, if present, is not removed in this step.

E.4.1.3 Removal of Noble Metals by Distillation

Vacuum distillation of lead can be used for purification of the lead when bismuth is not present.

E.4.1.4 Removal of Bismuth

Bismuth can be removed, as discussed in Sect. E.2.1.2.5. Calcium and magnesium (as a calcium-magnesium-lead alloy bar) is added to the molten lead. This forms CaMg_2Bi_2 , which floats to the surface. The lead does not need to be purified further to remove traces of calcium and magnesium because the oxides of these metals, formed when the lead is subsequently oxidized, are incorporated into the lead borate glass. Note that bismuth is likely to be a component of spallation wastes generated by high-energy particle interactions with lead. Thus, the GMODS process can also handle wastes of this type.

E.4.1.5 Disposition of Lead Impurities

Slags and drosses, which result from the above processing steps, can be set aside and oxidized, if necessary, for subsequent occasional batch processing into glass forms not containing PbO , forms which are also suitable for disposal. This glass processing can be done in the same GMODS melter that is used for lead borate glass waste treatment.

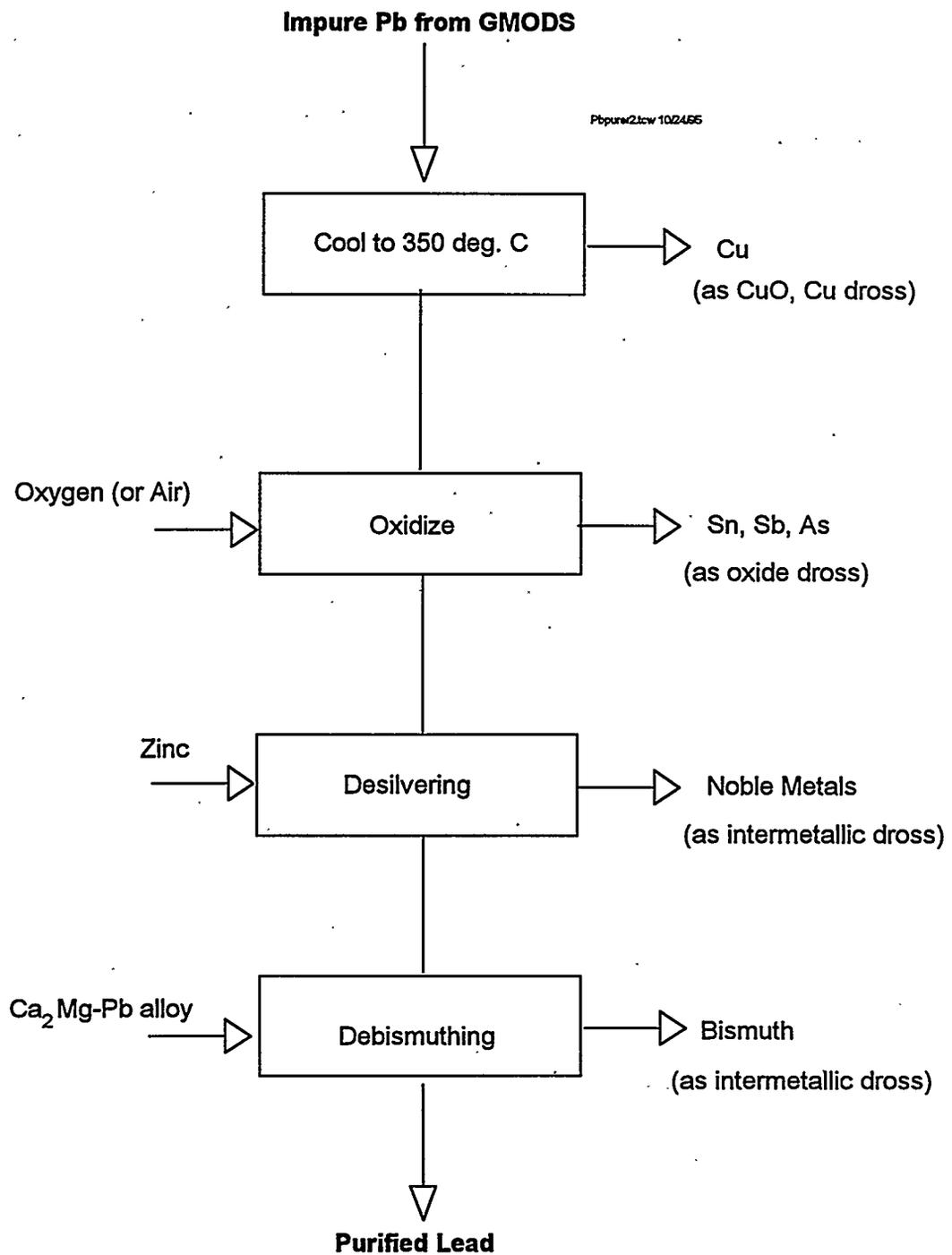


Fig. E.5. Optional lead purification steps for GMODS recycle system

E.4.1.6 Oxidation of Lead to PbO

Oxidation of lead to PbO can be accomplished by a number of ways: (a) direct injection of oxygen into the molten lead within the GMODS furnace, (b) direct injection of oxygen into molten lead in an auxiliary vessel, (c) air or oxygen reaction in a ball mill (see Sect. E.3.2 and Figs. E.3 and E.6), or (d) stirring (or atomization) and reaction with air (Figs. E.3 and E.7). None of these technologies need to be developed because they are established practice in the lead monoxide production industry.

E.5 PRODUCTION OF LEAD MONOXIDE FOR USE WITH GMODS

The system chosen for lead recycle with GMODS processing (as well as the main GMODS module configuration) can be expected to depend upon the type of waste being processed. For example, in the processing of highly radioactive or fissile compact wastes, the amount of contaminated process equipment and the off-gases and other effluents generated need to be minimized. For these highly radioactive compact wastes, lead recycle processing entirely within the GMODS furnace is desirable (Fig. E.8). For less hazardous, high-volume wastes, continuous recycle processing in auxiliary equipment is indicated (Figs. E.6, E.7, and E.9).

Commercial processes for PbO production and noble metal removal from molten lead can be adapted for use with GMODS. Here, we consider recycle processing which is (a) effected within the GMODS furnace and (b) effected external to the GMODS furnace.

Table E.1 considers 5 waste forms: waste high in organic materials; high-volume waste; medium-level waste; SNF; and plutonium.

E.5.1 High-Volume Wastes and Wastes High in Organic Materials

For processing wastes high in organic materials or high-volume wastes, large quantities of lead must be reoxidized to PbO. This suggests the need for a continuous process such as that shown in Fig. E.7. Here, lead is oxidized in a stirred (or atomized) lead reactor by reaction of oxygen with lead in an argon-oxygen mixture. The oxide is collected and removed from the surface of the molten lead with a screw conveyor. The reaction rate may be easily controlled by adjusting the oxygen content of the argon-oxygen gas mixture. An advantage of this process is that the type of PbO produced can be a very reactive alpha form (which is formed at low temperatures) and can have a very small particle size.

GLASS CONVERSION FURNACE

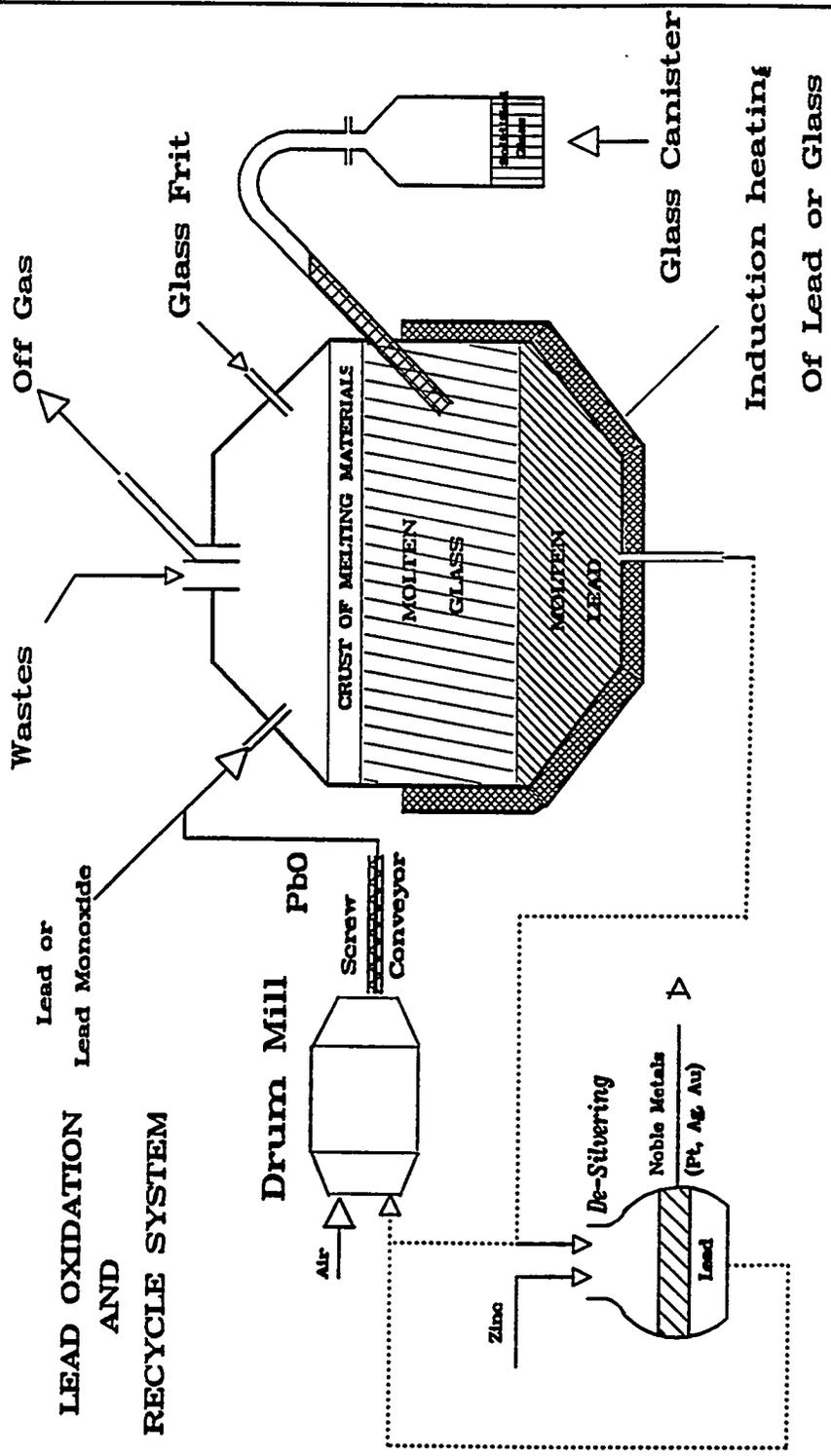


Fig. E.6. Batch or semicontinuous lead recycle.

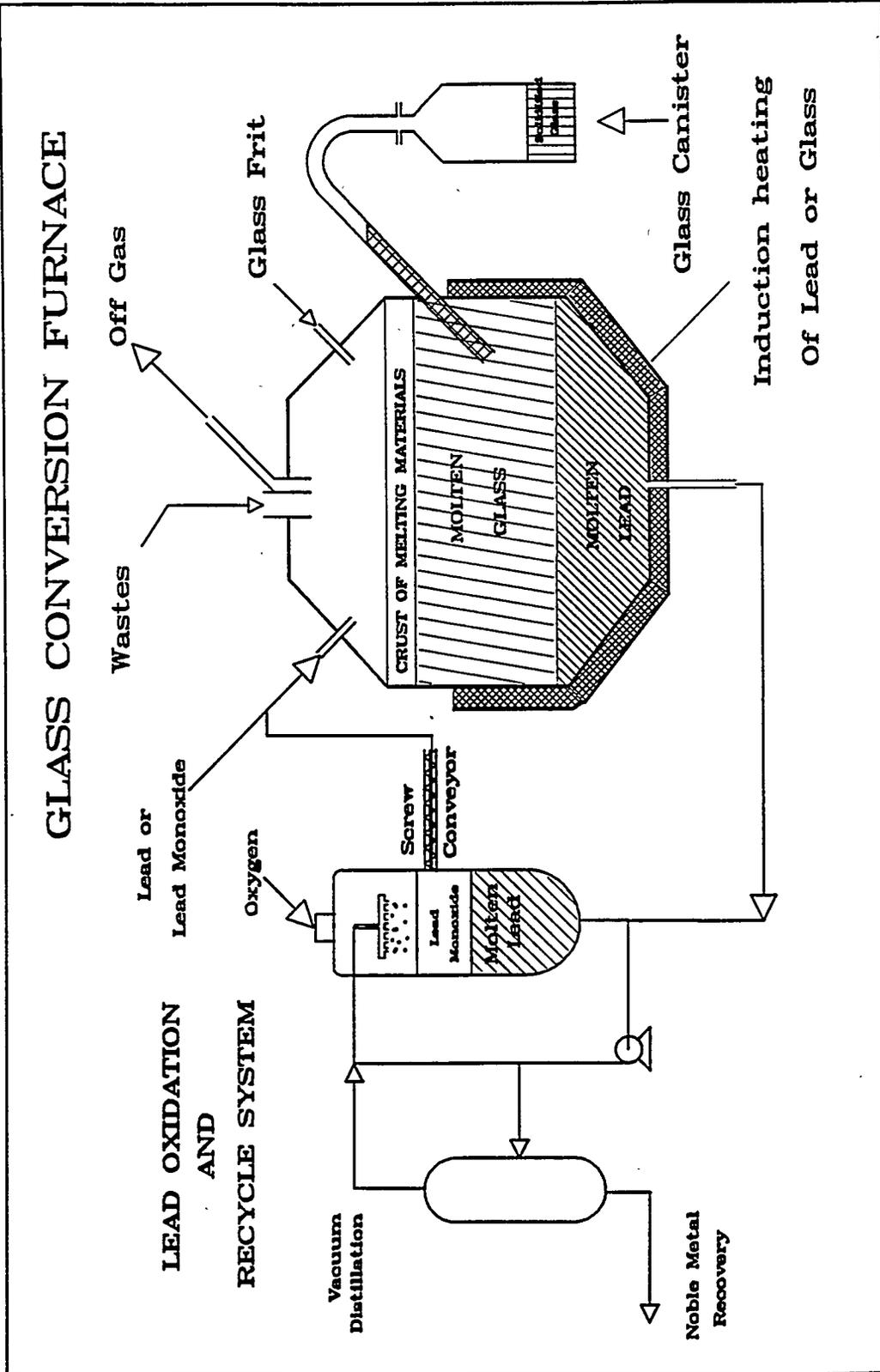


Fig. E.7. Lead recycle for large volume waste processing.

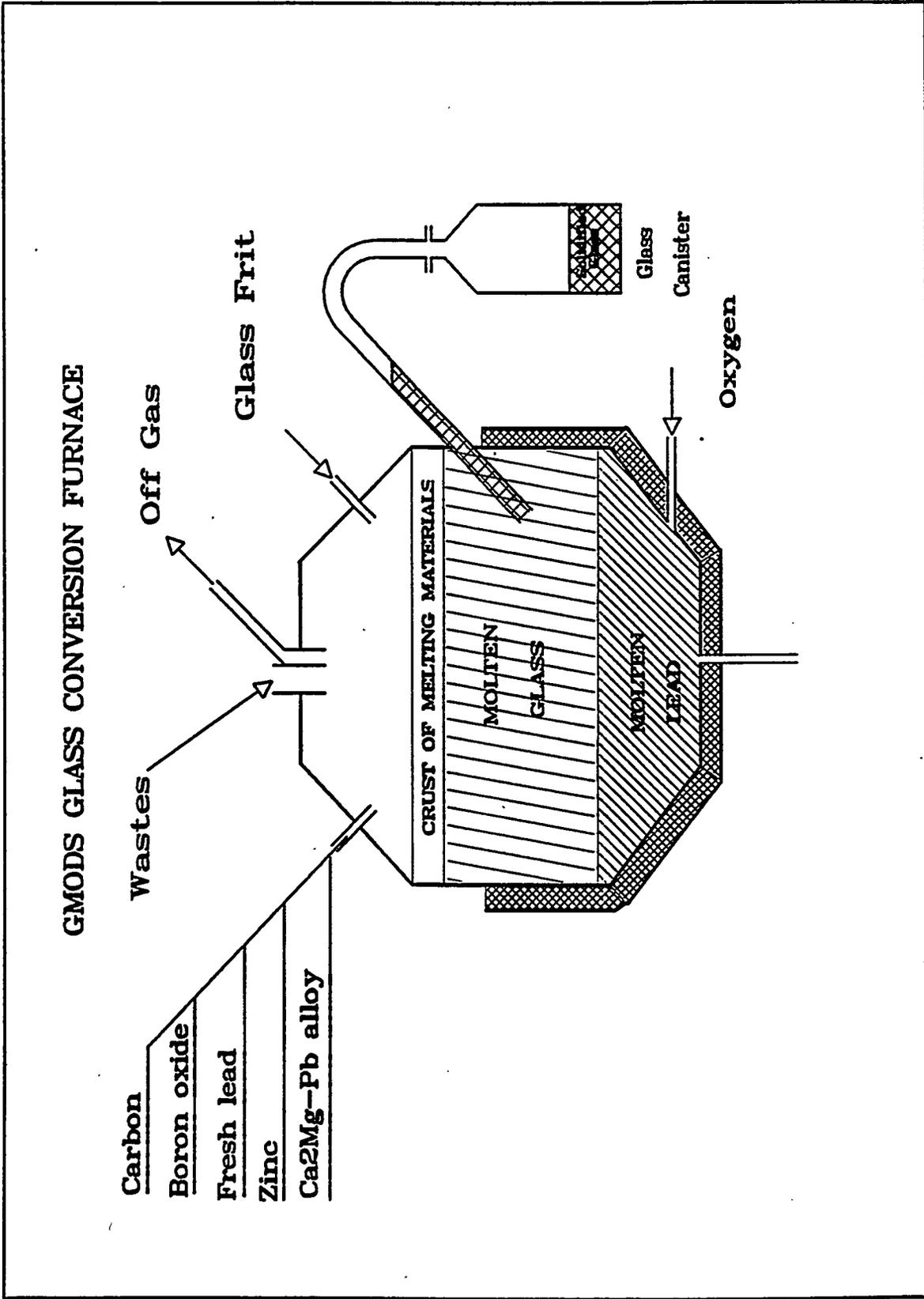


Fig. E.8. Batch lead oxidation and recycle in GMODS furnace.

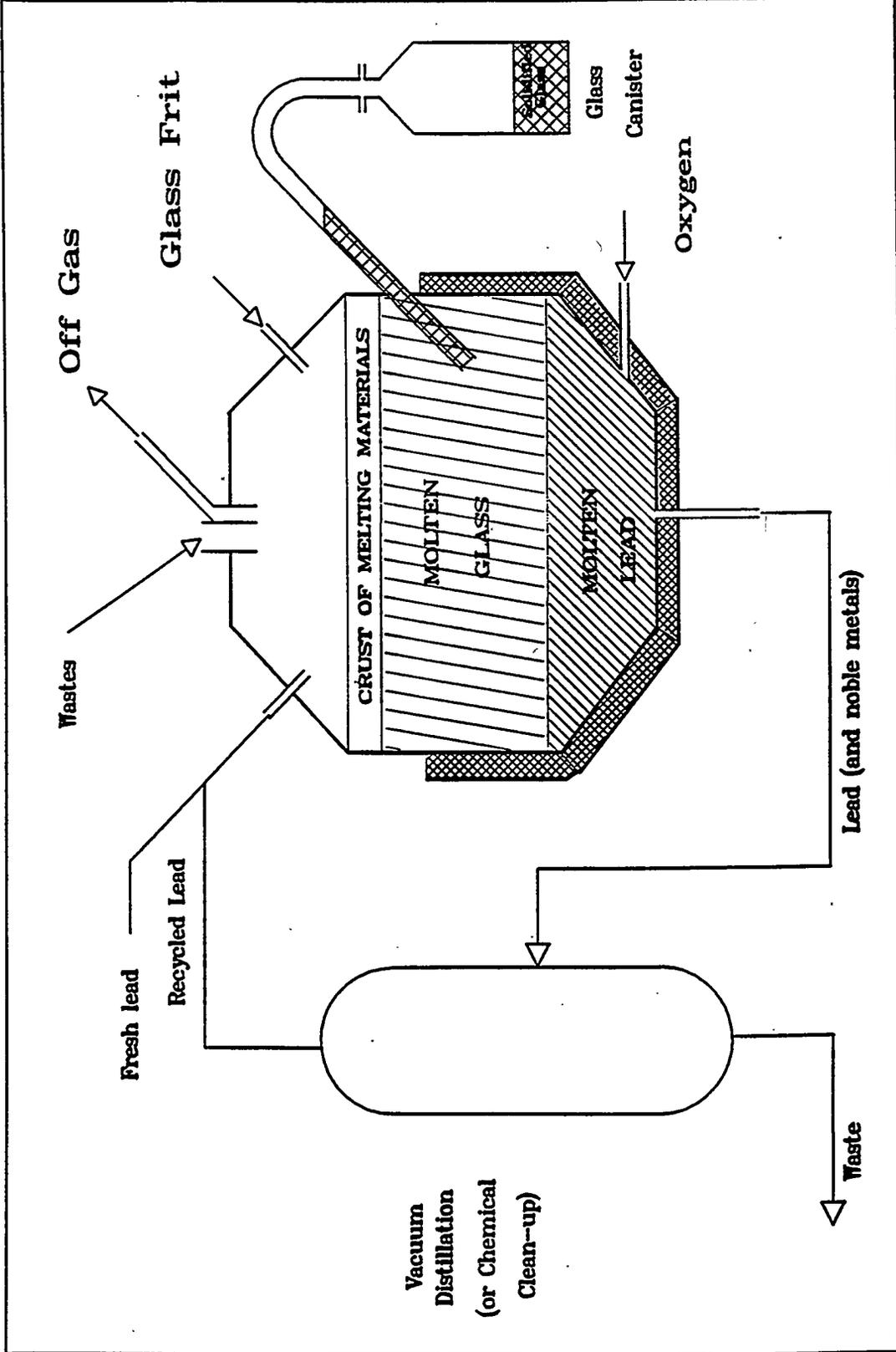


Fig. E.9. Lead recycle for large volume waste processing (GMODS internal oxidation of Pb).

Table E.1. Lead recycle processing for different waste types

Waste type	Lead recycle process	Comments
High-volume waste	Continuous lead recycle processing	Same as above, but less hazardous
Waste high in organics	Continuous lead recycle processing	Lead oxide consumption will be very large for high-organic wastes
Medium-level waste	Semicontinuous or continuous processing. Production of large volumes of lead oxide by spraying lead into an argon-oxygen mixture	Larger volume, less hazardous waste processing requires a larger lead regeneration system
Spent nuclear fuel	Batch: Oxygen injection into glass-making furnace	Batch processing minimizes the amount of highly contaminated equipment
Plutonium	Batch: Oxygen injection into glass-making furnace	Waste form is concentrated. Batch processing is feasible

E.5.2 Medium-Level Wastes

Lead recycle systems for medium-level waste processing can be either fully integrated (Figs. E.7 or E.9) or semi-continuous (Fig. E.6). In either case, modest-to-large amounts of lead need to be reoxidized to PbO. Lead may be oxidized on a continuous basis, stored in a holding vessel, and added to the GMODS glass-making furnace as required.

E.5.3 SNF or Plutonium

For SNF or plutonium wastes, batch processing is advisable. As shown in Fig. E.8, oxygen is injected directly into the lead at the bottom of the GMODS furnace. The use of pure oxygen will minimize off-gases and reduce the amount of auxiliary equipment. If the process temperature is below 888°C, the PbO produced will be a solid, probably in a beta form, which is much less reactive than the alpha form, which could be produced in separate equipment at a lower temperature. Given the reactivity of the lead-borate glass, however, the beta form is likely to be suitable.

The technology of direct oxygen injection into a melt, which is discussed in Sects. E.2.1 and E.3.4 (2), does not involve new technology which needs extensive development.

As to the issue of purification of the molten lead, one could simply add zinc metal in a batch step, similar to the commercial production practice for noble metal stripping. The stripping could be done in the primary glass melter, and the resultant noble metal phase could thus be poured into a separate package for disposal or for secondary processing. No glass would be in the melter during this stripping operation. The removal of residual zinc in the lead (0.5% solubility) by distillation may not be necessary or cost effective. The zinc would be oxidized and incorporated into the next batch of glass that was produced in the melter. Recycle of the lead containing small amounts of zinc would result in negligible amounts of zinc oxide in the GMODS glass product.

E.6 REFERENCES

E.6.1 General References

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Other general references for Sect. E.2: McKetta 1988, Prengaman 1990, Baralis 1965.

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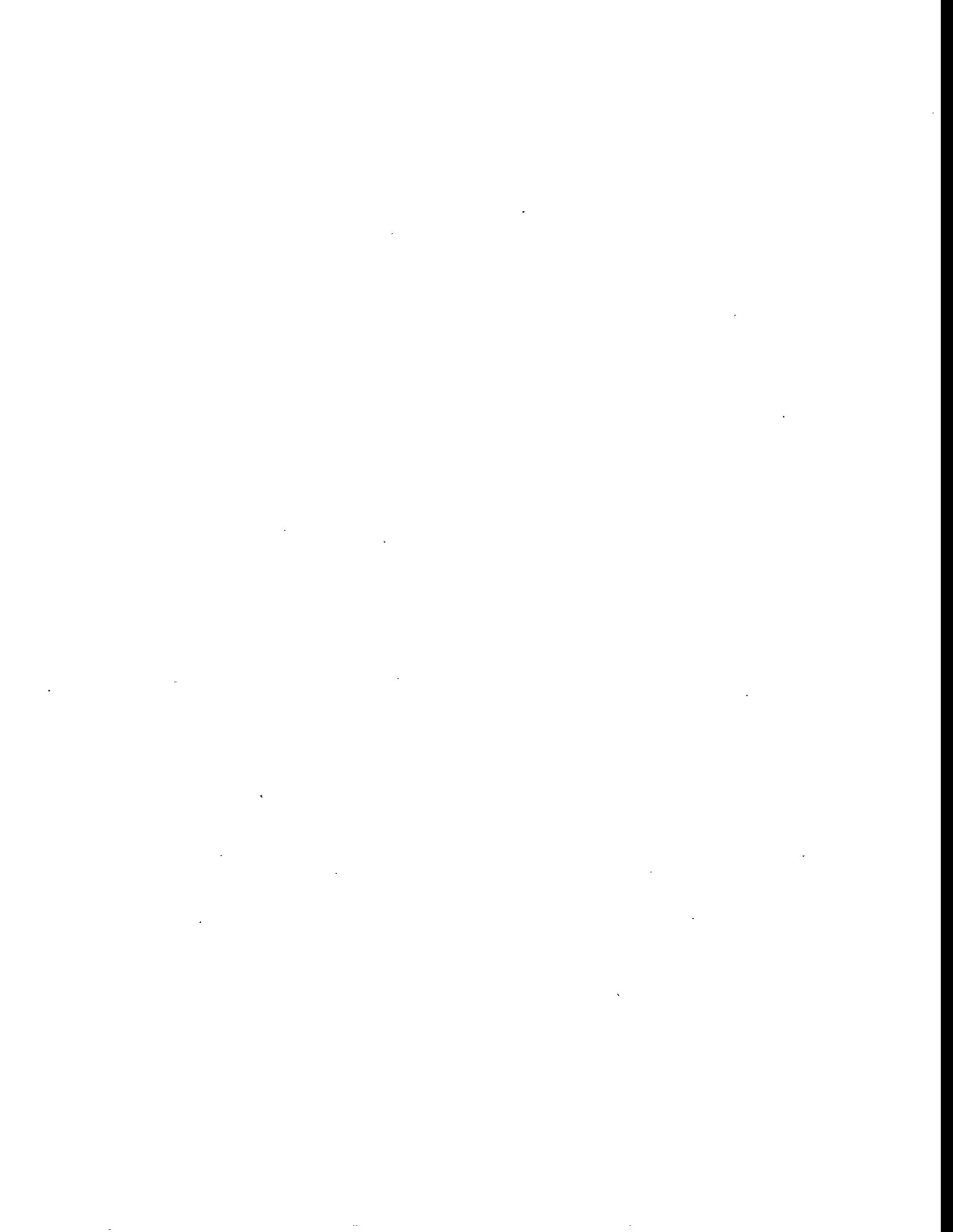
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Appendix F:

CHOICE OF COLD-WALL, INDUCTION-HEATED MELTER



APPENDIX F: CHOICE OF COLD-WALL, INDUCTION-HEATED MELTER

The preferred melter for large-scale GMODS systems is the cold-wall, induction-heated melter. For smaller systems with uniform feed materials, there are multiple options including ceramic crucibles with external heaters. The bases for these conclusions and background information on these melters are presented in this appendix.

F.1 INDUCTION HEATING

F.1.1 Industrial Applications

Induction furnaces are transformers in which the electrically conducting furnace charge constitutes the secondary and load resistance. They are suitable for heating and melting all metals; their principal industrial uses are for iron, copper, aluminum, zinc, and the alloys of these metals. Furnace capacities range from a few kilograms to several hundred metric tons, and power ratings range from 20 to 20,000 kW. There are three basic types: channel induction-melting furnaces, coreless induction-melting furnaces, and induction-heating furnaces.

In general, these furnaces are not cooled externally, and operations are designed to minimize thermal cycling to prolong the life expectancy of the furnace refractory crucible. The lining or crucible life is normally in the range of 50–200 cycles, depending on temperature and application.

F.1.2 Glass Industry Melters

The glass industry uses a variety of melters: joule heating, induction heating, gas-fired heating, microwave heating, and external heating. External heating of glass baths is practical only with (1) very small systems because of limited rates of heat transfer through the walls of the container or (2) glass baths with large, flat surface areas (gas-heated melters).

F.1.3 Radioactive Waste Management Glass Production

The first-generation Russian vitrification facilities at Chelyabinsk-65 (Weber, 1991) are induction furnaces with refractory lining. The first melter operated ~1 year (it was decommissioned in 1987), and was shut down because of accelerated refractory corrosion and electrode failure. A new melter was developed and placed into operation. After modifications, this melter has been reliable. This melter processes molten phosphate glass, which is more corrosive than borosilicate glasses and thus requires special features to handle the more corrosive materials.

In industrial applications, erosion/corrosion of the induction furnace refractory lining is expected and accepted; when the lining fails, the process is shut down, the refractory lining is replaced, and the process is restarted. However, in a radioactive vitrification process, with remote maintenance requirements, periodic replacement of a melter liner is not desirable.

The French (Alexandre, Chotin, and LeBlay 1987) have developed and deployed large-scale, metal, induction-heated HLW borosilicate glass melters at Marcoule and La Hague. The R7 and T7 facilities handle, respectively, the HLW solutions from the UP-2 and UP-3 reprocessing plants at La Hague. Each of these reprocessing plants has a rated capacity of 800 t/year of LWR SNF with average SNF burnups of 3.3×10^4 (MWd/t). Each vitrification facility has three vitrification lines, and each line has a capacity of 600-L/h feed, resulting in 2.5 kg/h HLW glass.

F.1.4 GMODS Melter Selection

GMODS contains both metal and glass that disqualify many types of melters. Metals will short out or damage both joule-heated and microwave-heated glass melters. High, localized current flows damage electrodes in joule-heated melters. HLW glass melters, such as those at Savannah River, have a number of special design features to avoid metals in the melters because of the incompatibility of joule-heated melters with metals. Local microwave heating can damage melter walls.

Gas-fired heaters are technically compatible with GMODS operations, but they create large off-gas streams that must be treated when radioactive material is processed. Thus, they are generally avoided in radioactive waste processing.

These considerations suggest that induction-heated melters would be preferred. The use of induction-heated melters in most of the world for processing HLW provides a substantial experience base for this technology. Induction-heated melters can obtain temperatures higher than those of any other type of melter, allow precise control of heat input, and minimize process time with faster heatup rates. The rapid heating rates and the options for very high temperatures are possible because induction heating allows bulk heating vs other heating methods that are limited directly or indirectly by the surface area of the melter.

F.2 COLD-WALL MELTERS

In the last 25 years, French, Russian, and American research has led to the development of "cold-wall," "cold-crucible," "skull" induction-heated melters. In this melter design, a sectionalized, externally cooled metal crucible contains the melt. The crucible is typically made of copper or stainless steel. The water-cooled walls provide a frozen layer of material of whatever is in the pot to ensure that there is no vessel corrosion. Figure F.1 shows a schematic of such a melter.

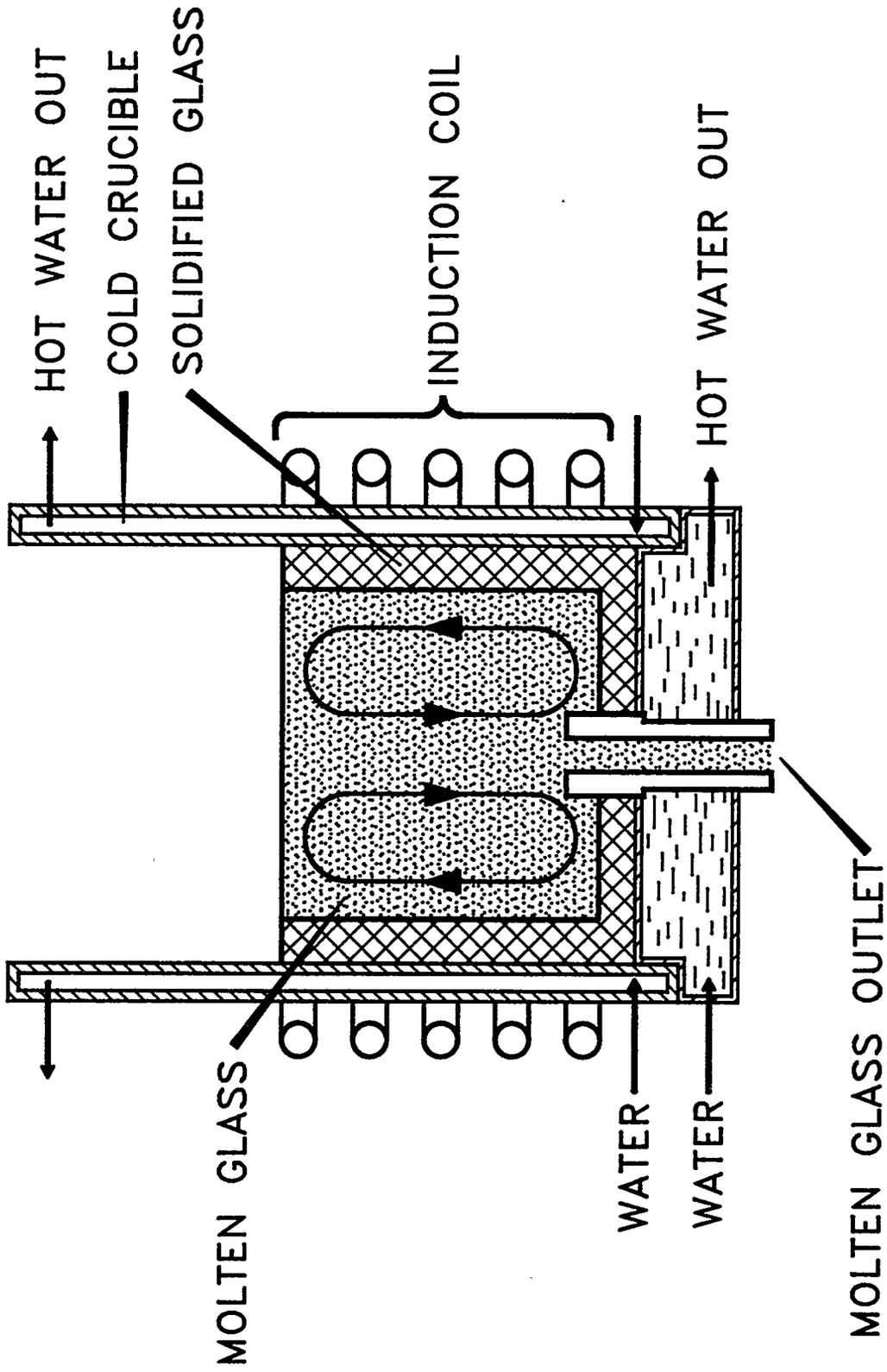


Fig. F.1.1. Schematic of cold-wall, induction-heated melter.

There are multiple industrial users of cold-wall induction-heated melters. In each case, the melters have been chosen because they eliminate problems with selection of materials.

- High-temperature melting and casting. This is the technology of choice for melting very high temperature materials such as titanium and super alloys (Reed and Jones 1993; Gubchenko and Brutskus, 1990). By definition, there can not be solid materials of construction when the highest-melting point materials are being melted.
- Ultrapure materials processing. Glass for fiber optics and certain electronic materials must be ultrapure. The cold-wall melter with a frozen wall of the same material that is being processed avoids potential product contamination (Reed and Jones 1993; Gubchenko and Brutskus, 1990).
- Corrosive molten materials. Some molten materials are highly corrosive to known materials of melter construction. The second generation Russian HLW glass melters are cold-wall, induction-heated melters that can process highly corrosive phosphate HLW glasses (Weber 1991; Elliott 1994).
- Corrosive high-temperature material processing. Such melters are used to purify high-melting point refractory metals by contact of molten metal with molten slag with extraction of impurities from the molten metal into the molten slag. This technology was primarily developed in Russia. The functional requirements of these systems are nearly identical to those required for GMODS.

In addition to the above production operations, cold-wall, induction-heated melter technology is being further developed to process a variety of other radioactive materials. The primary additional complication in processing radioactive materials is the need to maintain equipment in radioactive environments. Some of the ongoing activities include:

- The French have developed cold-wall melters to convert radioactive Zircaloy hulls and hardware to ingots (Berthier et al., 1993; Jonan, 1987) and to produce borosilicate glasses from radioactive wastes (Jonan et al., 1991). The Russians have a parallel program (Weber, 1991). In both cases, the variability of waste materials with variability in molten waste corrosivity have created strong incentives to develop melters whose glass chemical composition do not control design or materials of construction of the melters.
- The La Hague, France, vitrification plant (R7 and T7) is planning to use a cold-crucible melter (Elliott, 1994; Jonan et al., 1991) when the current La Hague vitrification plants are upgraded. Major advantages of this melter are (1) very high operating temperatures can be achieved, (2) no erosion of the crucible occurs, (3) precise formulation and control of the melt composition can be maintained, (4) uniform composition in the cast product is produced, and (5) thousands of cycles (heats) are possible without melter-liner replacement.
- Russia and the United States are developing cold-wall, induction-heated melters to process mixed waste (low-level or transuranic waste that is chemically hazardous) into a metallic waste stream and a slag stream. Oxygen may be injected into the melter to oxidize organics.

The known disadvantages of cold-wall, induction-heated melters are lower electrical efficiency and higher capital costs because of the need for large power supplies. Their unique capabilities and higher productivity compensate for these disadvantages in many applications.

F.3 THROUGHPUT

Induction-heated melters are available in capacities from kilograms to hundreds of metric tons. They are widely used in the electronics industry for special materials, in the metallurgical industry for high-temperature materials, and in the steel industry for specialty steel production.

Cold-wall melters for high temperature metal melting have been designed to melt up to 100 kg of titanium alloys or 200 kg of super alloys (per batch) (Reed and Jones, 1993). The French radioactive glass melter production rates for a 0.55-m-diam melter is ~50 kg/h (Elliott, 1994). The current French development program is testing a low level waste (LLW) melter with a glass throughput in excess of 200 kg/h. The Russians give a production capacity of ~100 kg/h in their Mayak HLW glass plant (Elliott, 1994). Celes (France) is developing a cold-wall, induction-heated melter to process 800 kg/hr of hazardous flyash to glass. These production rates exceed that needed for GMODS applications.

F.4 MELTER SHAPE

Induction-heated melters come in many shapes. The geometry of the melter will depend upon design-specific issues. For steel making, the melters are usually cylinders with height-to-diameter ratios of 2 to 1. This allows a cold scrap metal charge to fill the melter and generate a molten bath in a cylinder with the diameter approximately equal to the height. This minimizes heat loss and is the traditional design. The Russians, however, use a rectangular cross-section in their melter design.

The geometry of the GMODS melter will depend upon feed and product characteristics. Large height-to-diameter melters may be chosen for criticality control. Alternatively, small height-to-diameter melters may be chosen in specific applications for the following reasons:

- Criticality control can be ensured by a pancake melter with short height.
- If the chemical reactions generate significant gases, pancake melters allow more surface area for the escape of gas without generating aerosols, which can result from high gas flows.
- If the lead contains significant quantities of dissolved plutonium and other metals to be oxidized and extracted into the glass at the glass interface, pancake designs maximize mass transfer area.

F.5 COLD-WALL, INDUCTION-HEATED MELTER VENDORS

F.5.1 France

SGN markets the French CEA (French Atomic Energy Agency)-designed, cold-wall, induction melter (Fig. F.2) for radioactive operations. French-designed induction-heated melters are currently in operation at La Hague in France and at Sellafield in the United Kingdom. Cold-wall, induction-heated melters are in operation at the Marcoule site.

The Celes company of France (Celes 1995a; Celes 1995b) develops, designs, and builds cold-wall, induction-heated melters for a variety of industrial applications. The company is currently developing such a melter to convert hazardous flyash to glass at a rate of 800 kg/hr. A pilot plant melter with a throughput of tons per day is shown in Fig. F.3.

F.5.2 Russia

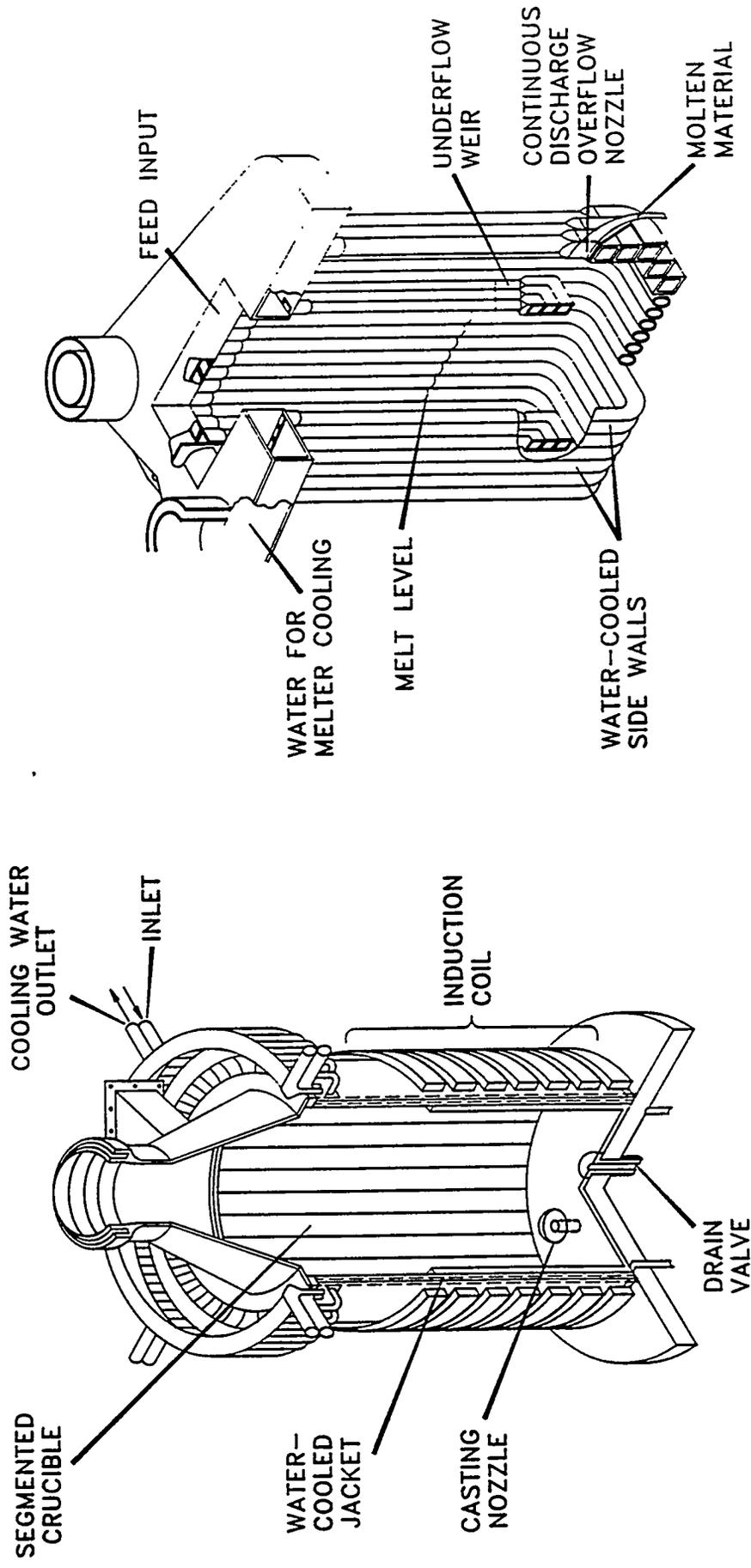
Waste vitrification in Russia is coordinated by the All-Union Scientific Research Institute of Inorganic Materials (VNINM). The development of the double-stage process (which includes a cold-wall melter) for high-active waste solidification was performed by VNINM (Nikiforov, 1991). One Russian cold-wall melter is illustrated in Figs. F.2 and F.4.

The All-Russian Research Institute of Chemical Technology (Forsberg, 1995; Schumacher, 1995) has developed cold-wall, induction-heated melters for materials processing. Materials that have been processed include zirconium, uranium alloys, plutonium, hafnium, titanium, rare earths, fluorides, and other materials. Melters have been built in sizes from 90 to 650 mm diam with power supplies up to 2000 kw. In many of these applications, metals are purified by extraction of impurities from the molten metal into a molten slag. The physical characteristics of a molten metal–molten slag system are very similar to the GMODS system of molten lead–molten glass. The melters have almost identical functional requirements.

Some of the cold-wall, induction-heated melters have auxiliary plasma torches (Fig. F.5) to boost heating rates and, hence, product output. DOE is acquiring a pilot plant unit (200 mm inside diam, 600 kw induction-heated power supply, 100 kw plasma torch) as a method to convert mixed waste to a metal waste stream and a slag waste stream.

F.5.3 United States

The Duriron Company developed an induction skull melting (ISM) process based on earlier work of the United States Bureau of Mines (Reed and Jones, 1993). In September 1987, Duriron signed an agreement with Consarc Corporation, an equipment manufacturer headquartered in Rancocas, New Jersey, under which Consarc would design and manufacture ISM equipment for other metals producers using Duriron-developed technology and patent rights. The Consarc ISM is illustrated in Fig. F.6.



RUSSIAN COLD-WALL, INDUCTION-HEATED MELTER

FRENCH COLD-WATER, INDUCTION-HEATED MELTER

Fig. F.2. Cold-wall, induction-heated melter.

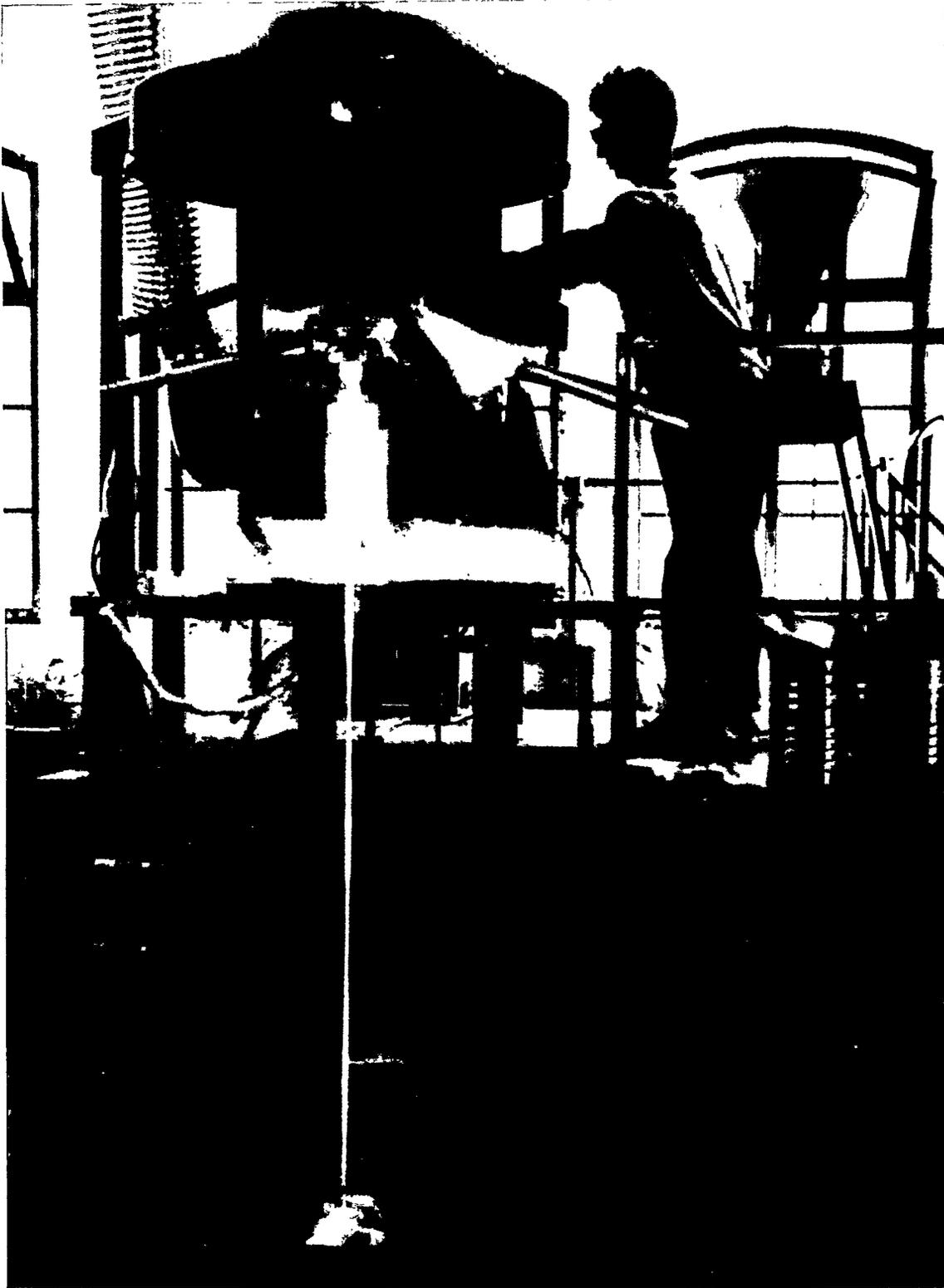


Fig. F.3. Cold-skull, induction-heat melter: Celes experimental plant. (Courtesy of Prométhée, Group Schneider and Celes, Group Fives-Lille, Paris-France.)

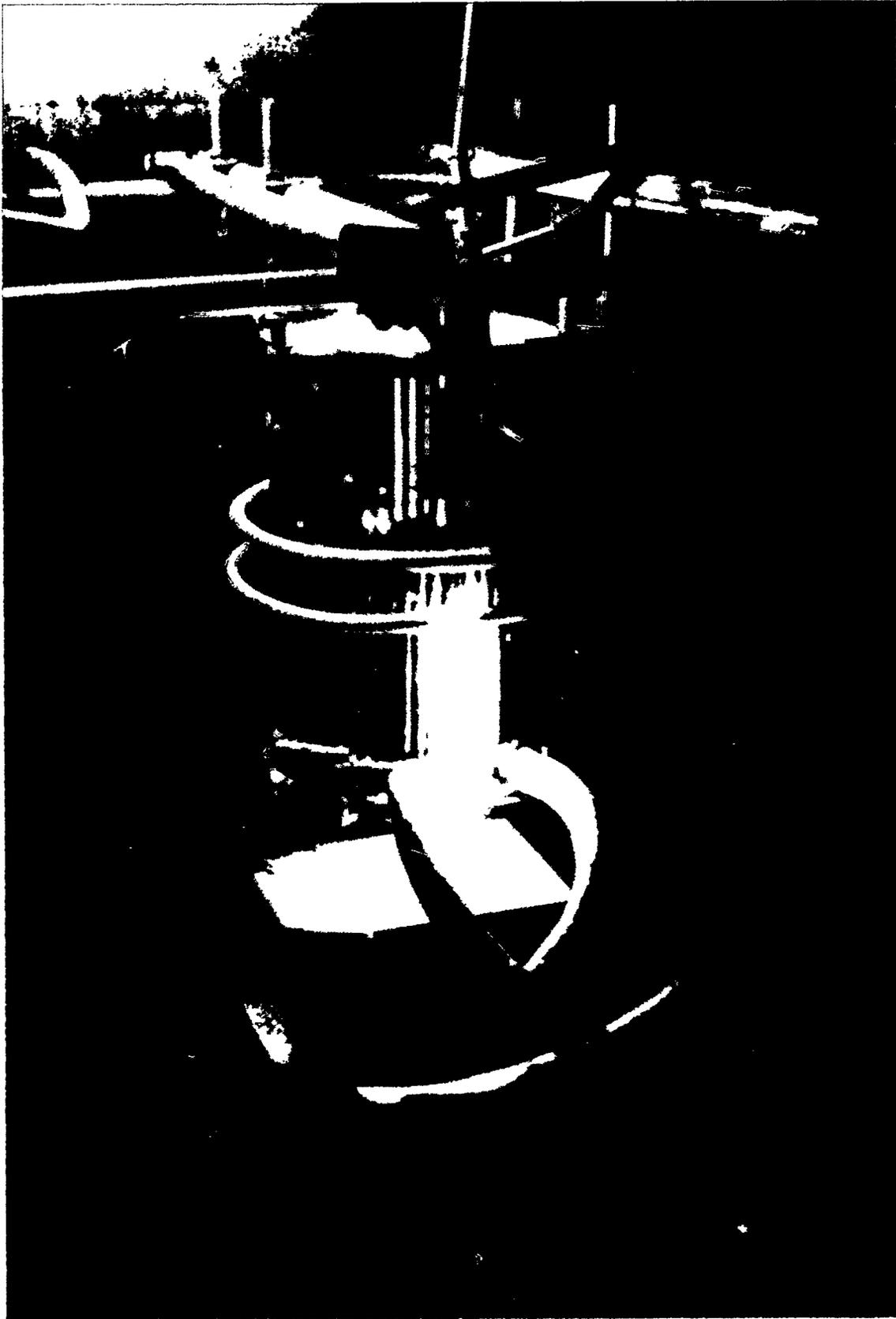


Fig. F.4. Developmental unit pouring glass at Radon Institute, Zagorsk, Russia (*photo taken during U.S.-DOE Vitrification Team visit, October 25, 1991*).

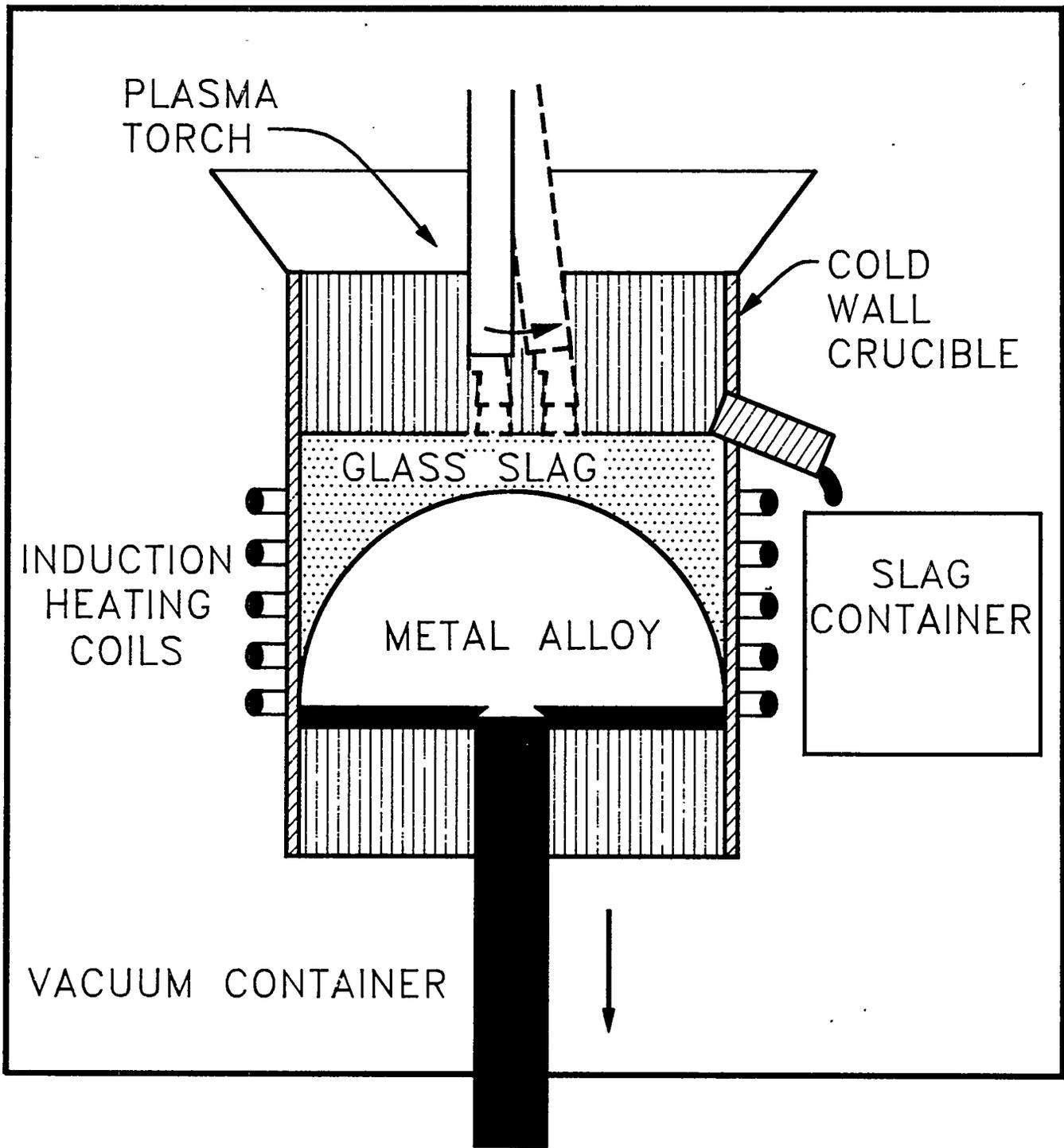


Fig. F.5. Russian plasma induction cold crucible melter.

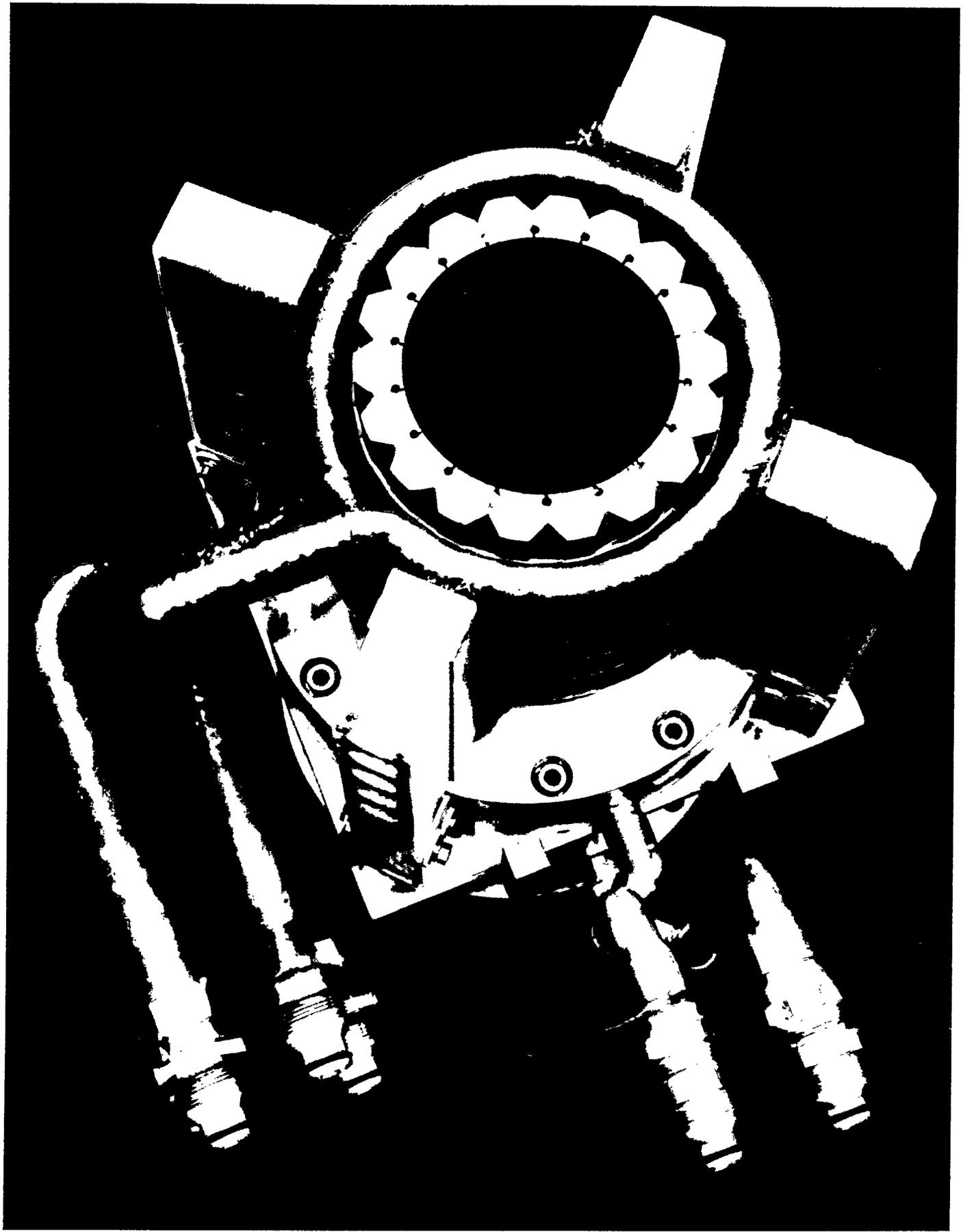


Fig. F.6. Commercial cold-wall, induction-heated melter (*photo courtesy of Consarc—Rancocas, New Jersey*).

F.5.4 Leybold AG, Hanau, Germany

Leybold AG has developed a vacuum-induction, cold-crucible furnace that can be used for casting or, together with inert gas atomization, for production of metallic powders. This is a commercial process for the production of ultrapure titanium or titanium alloy ingots and powder (Hohmann and Jonsson, 1990).

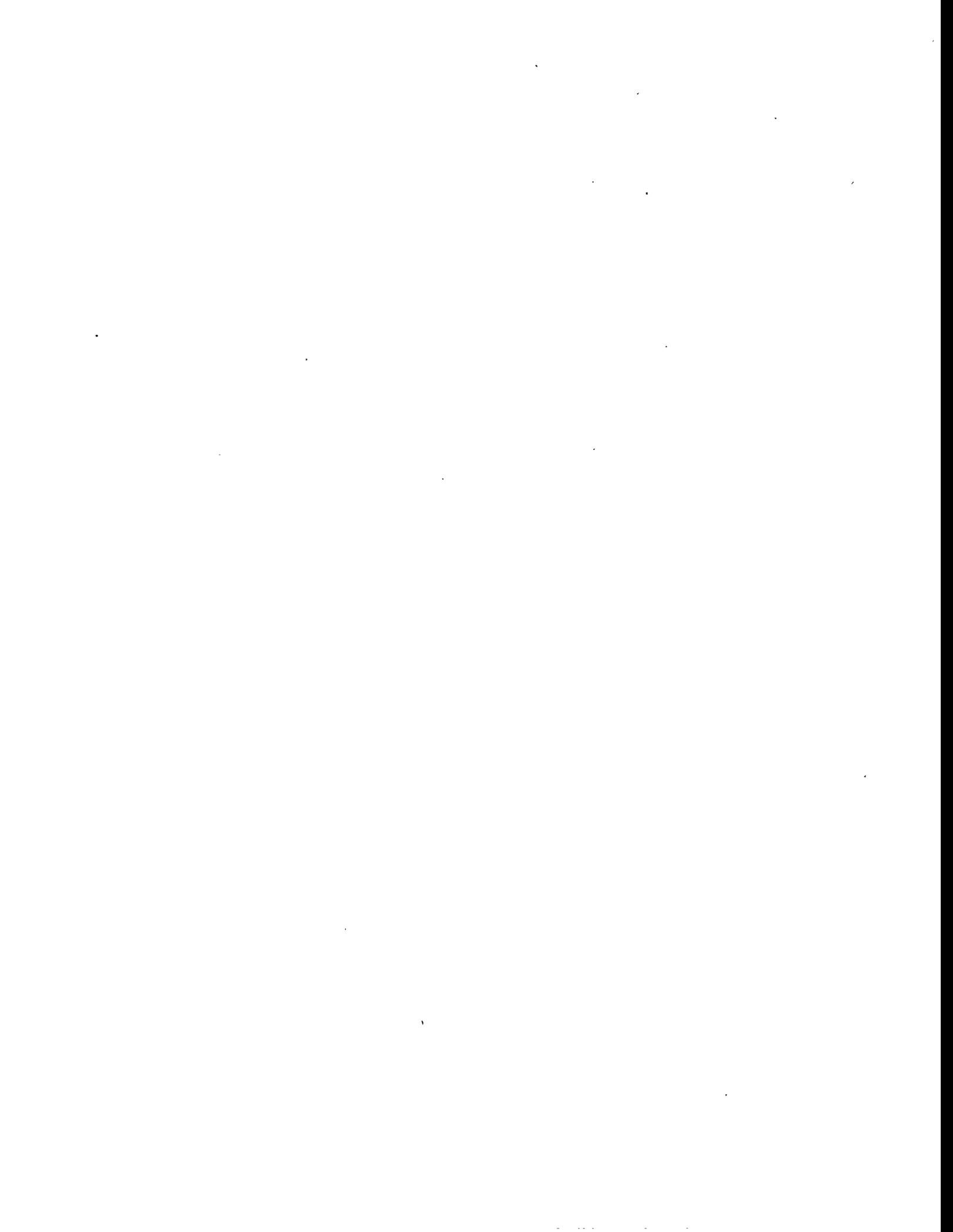
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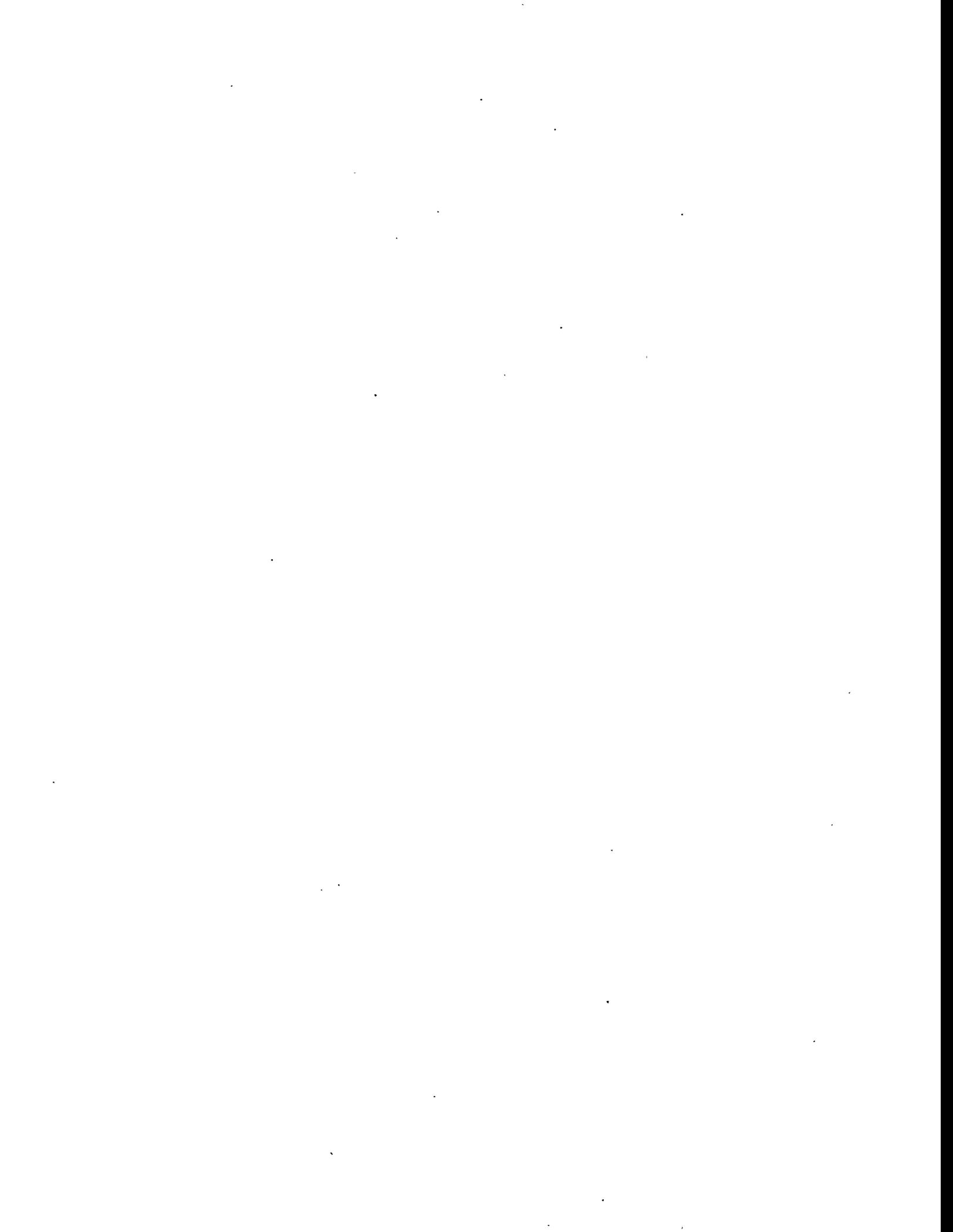
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Appendix G:

DIRECT CONVERSION OF SNF AND PLUTONIUM TO GLASS



APPENDIX G: DIRECT CONVERSION OF SNF AND PLUTONIUM TO GLASS

G.1 INTRODUCTION

One option for the disposition of PCM is the conversion of PCM and SNF together into HLW glass (Fig. G.1). There are three classes of SNF with important proliferation, storage, and/or disposal concerns. These SNFs would be used in such a process to address multiple national issues. The SNFs include:

- Degraded SNF that must be converted into a more stable waste form for disposal.
- SNFs that contain HEU that may not be acceptable as a waste form (Appendix B) and are a potential proliferation concern.
- SNFs containing high concentrations of plutonium that may not be acceptable as a waste form (Appendix B) and are a potential proliferation concern.

A combined GMODS conversion of PCMs and some of the above SNFs would have advantages compared to separate treatment of the SNFs and PCMs. With appropriate mixing of SNF and PCMs, the chemical and radiological characteristics of the HLW product glass can (1) meet waste and nonproliferation goals not easily achievable by separate treatment of these materials and (2) reduce the volume of final waste compared to separate treatment of the two wastes. This appendix will describe these advantages of the combined conversions, describe an example flowsheet, and estimate waste quantities (Forsberg, 1995).

This option is also one of the more complex applications of GMODS and has been used to better understand GMODS systems issues. It is complex in two dimensions:

- The feed material is highly variable.
- The product HLW glass must meet multiple, strict product specifications.

G.2 INCENTIVES

There are five incentives for this SNF-plutonium disposal option.

G.2.1 Meets NAS Spent Fuel Standard

The final HLW glass meets the NAS spent fuel standard for disposition of PCMs. The plutonium is (a) within a matrix of highly radioactive materials, (b) mixed with large quantities of LEU as in commercial SNF (low concentration of plutonium), (c) isotopically diluted with other plutonium isotopes, and (4) in a chemically resistant waste form.

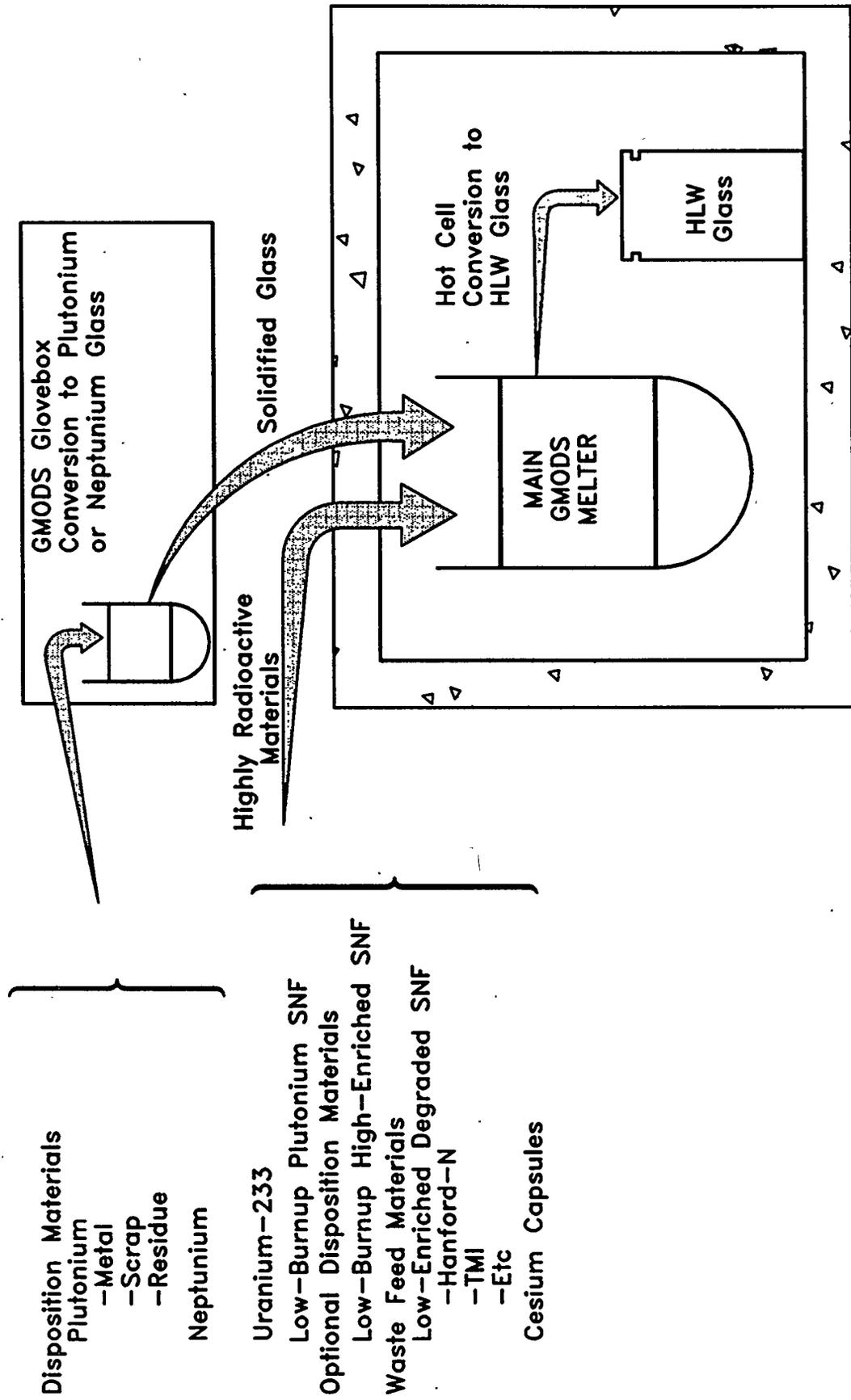


Fig. G.1. Direct conversion of PCMs, SNF, and other materials to HLW glass.

G.2.2 Provides Unlimited Supply of SNF

Three sources of radioactivity can be used to spike plutonium in glass as a barrier to its extraction for use in nuclear weapons. The sources are (a) SNF, (b) cesium capsules, and (c) HLW in tanks. The SNF is the only material in effectively unlimited supply. Furthermore, the radioactivity of any batch of glass can be boosted to very high levels by adding appropriate quantities of high-burnup SNF.

G.2.3 Addresses Other Plutonium and Nonproliferation Concerns

Three classes of SNF are potential proliferation concerns: (a) unirradiated or low-burnup plutonium containing SNF; (b) HEU, low-burnup SNF; and (c) degraded SNF. Conversion of these SNFs by themselves or in combination with other SNFs, as appropriate to HLW glass, would eliminate the concerns.

Significant quantities of SNF were designed to be reprocessed for recovery of plutonium and uranium. Examples include the British Magnox SNF (and the North Korean copies), the production reactor SNF at Hanford, and similar fuels in other nuclear weapons states. The long-term management options (Bendixsen, 1994) for these SNFs are (a) chemical reprocessing with recovery of plutonium and uranium and conversion of wastes to HLW glass, (b) direct disposal in a geological repository, and (c) conversion to HLW glass by GMODS or an equivalent process.

With excess plutonium and the objective of reducing the risk of proliferation, there are incentives not to reprocess. Simultaneously, some of these SNFs may not be acceptable for repository disposal in their current forms. These SNFs were designed to be quickly reprocessed after reactor discharge and not designed for long-term storage or disposal. An alternative approach may be required to convert such materials to an acceptable waste form without reprocessing.

Significant quantities of HEU, low burnup SNF exist. The concern is that the HEU could be recovered from these SNFs. HEU can be used to manufacture nuclear weapons. The concerns about HEU SNF can be avoided by conversion of the SNF and depleted uranium simultaneously to a LEU HLW glass.

G.2.4 Assures Repository Acceptance

Conversion of PCMs and SNF to HLW glass allows acceptance of the plutonium-loaded, LEU HLW glass within the current envelope for repository licensing and design. The repository is to be designed and licensed to accept HLW glass and LEU SNF. A plutonium-loaded, LEU glass fits within this repository licensing and design envelope.

There are four types of repository WAC (U.S. DOE, 1993): mechanical (container size, etc.); chemical (waste form performance, etc); thermal (maximum decay heat load); and nuclear (criticality). An HLW glass

meets the mechanical, chemical, and thermal criteria. An HLW glass made from PCMs and LEU SNF meets the long-term repository nuclear criticality criteria the same way that commercial SNF meets the criteria. Both use isotopic dilution for criticality control over geological time frames (Appendix B).

In a repository, selective dissolution and precipitation of uranium in groundwater over geological time may concentrate uranium. This concentration may initiate nuclear criticality events if the original uranium is highly enriched in ^{235}U . The same concern exists with plutonium because it decays to ^{235}U . Geological evidence shows that naturally occurring nuclear reactors have been created in the past by these mechanisms when the uranium enrichment exceeds several weight percent ^{235}U . LWR SNF with its LEU concentration is acceptable for direct repository disposal. Plutonium in LWR SNF is acceptable because it decays to ^{235}U , which is born into a matrix of ^{238}U , thus assuring criticality control by isotopic dilution with ^{238}U . The repository as a whole is saturated in ^{238}U . Repository nuclear criticality control for HEU SNF and PCMs can be met by combining the PCMs with LEU SNF to create LEU HLW glass with actinide isotopics similar to LWR SNF. There are large quantities (see the following) of low-enriched SNF that can be combined with PCMs for repository criticality control.

Other approaches to criticality control in repositories exist [see Appendix B or Sandia repository performance assessment by Rechard et al. (1993) or Westinghouse Savannah River new production reactor spent fuel direct disposal studies by Patrick and McDonell (1992)], but they may require alternative repository design and licensing philosophies and present additional uncertainties.

G.2.5 Improves Waste Management

DOE has about 2800 t (U.S. DOE, 1994) of miscellaneous SNF, some of which is badly degraded and is considered an unresolved safety issue. Much of the SNF must be processed to an acceptable form for disposal. Use of this material would address major safety and environmental issues associated with SNF management while disposing of excess plutonium.

The primary inventory of miscellaneous SNF is the 2100 t of Hanford-N-reactor SNF. This fuel is part of an unresolved safety issue, and much of it is degraded. This SNF has very low uranium enrichments (0.95 and 1.08% before irradiation). There are also 82 t of Three Mile Island (TMI) core debris. In addition to DOE miscellaneous SNF, DOE will accept commercial SNF for disposal. Most of this spent fuel is in good condition and is acceptable for direct disposal. There is, however, a small fraction that may have to be processed to meet repository acceptance criteria.

It is noted that significant quantities of miscellaneous SNF exist in many countries. Much of it has not been reprocessed because reprocessing has been viewed as uneconomic. Some of this fuel will have to be either (a) reprocessed with uranium and plutonium recovery and solidification into glass or (b) new processes must be developed to convert it to a form suitable for disposal.

G.3 EXAMPLE OF A SPECIFIC CASE

For an example plutonium disposition flowsheet with conversion of plutonium and SNF to HLW glass, it was assumed that the SNF was from the Hanford-N reactor. Currently, there are 2100 t of this SNF with initial uranium enrichments of 0.95 and 1.08%. This is an uranium metal fuel with Zircaloy clad. Much of this fuel is degraded. It is part of an unresolved safety question at the DOE Hanford site.

In actual practice, a facility to convert PCMs and SNF to glass would mix various feed materials. Appropriate mixing would minimize the total quantities of HLW produced. The feed materials may also include adding cesium capsules to particular batches of SNF that have insufficient radioactivity to meet product requirements.

The PCMs would first be converted to glass. This plutonium glass and the SNF would then be fed to a larger melter to produce a plutonium-loaded, LEU glass. The plutonium conversion requires small batch sizes and careful measurements of plutonium concentrations to provide control of nuclear criticality. Once a plutonium containing glass is produced, criticality control during further production operations is ensured by the boron in the glass. The SNF conversions require large batch sizes and shielded, remote operation as a result of fission product radioactivity. Criticality is not a major concern. Adding plutonium glass is easier than the simultaneous conversion of both uranium metal and plutonium metal to oxides in the same operation. This combination of process steps is shown as a block diagram (Fig. G.2).

For the combined disposal of plutonium and SNF, the glass compositions must meet three different requirements.

- One melt must effectively dissolve the plutonium metal (oxidize it to PuO_2 and be a good solvent for PuO_2).
- One melt must effectively dissolve the SNF (the zirconium-uranium, metal, or oxide fuel for an example flowsheet).
- The final mixture after composition adjustments must be an acceptable composition for the product glass requirements.

The two dissolver melts do not each have to meet the product requirements. The amount of melt from the SNF dissolution will be much larger than the amount from the plutonium dissolution. Therefore, this SNF dissolution product must be near the final product glass composition, while the plutonium dissolution glass could be much different.

The borosilicate glass compositions (Ramsey, 1994) for storage (Table G.1) would also apply for a combined disposal of plutonium and SNF. The UO_2 content would be the maximum (20 wt. % UO_2) listed in order to maximize the content of SNF. Long-term nuclear criticality is controlled by dilution with ^{238}U (low enrichment of U). A high B_2O_3 content is not necessary for repository criticality control. There has been only limited work on uranium glasses; hence, the maximum waste loading is not well defined.

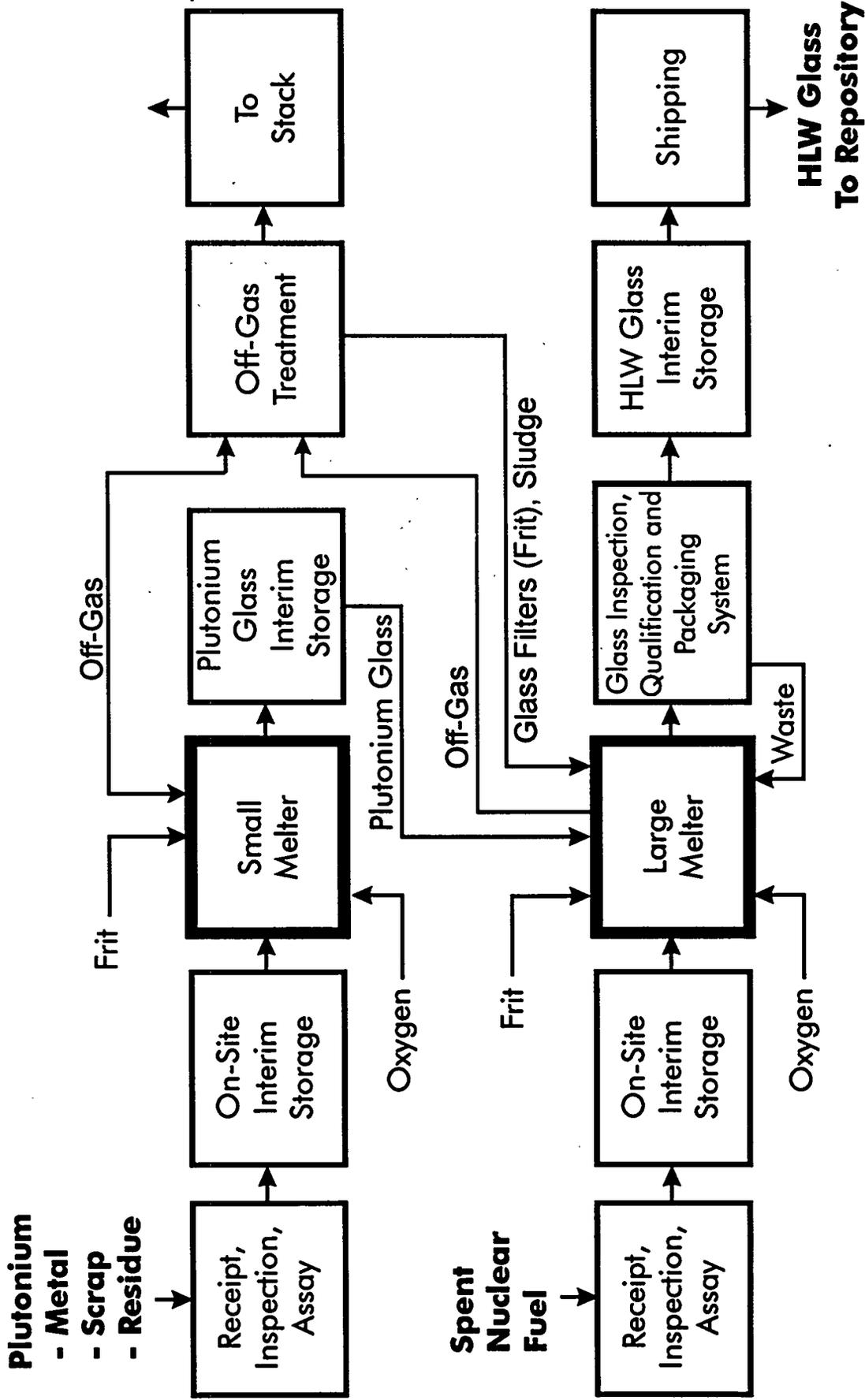


Fig. G.2. Block flow diagram: Direct conversion of PCMs and SNF to HLW glass.

Table G.1. Nominal actinide borosilicate glass compositions tested at Savannah River

Component^a	Range tested (wt. %)
<i>SiO₂</i>	21-30
<i>B₂O₃</i>	5-8
<i>BaO</i>	2-4
<i>Al₂O₃</i>	3-13
<i>PbO</i>	8-14
<i>PuO₂</i>	<i>a</i>
<i>UO₂</i>	0-20
<i>Am₂O₃</i>	<i>b</i>
<i>Cm₂O₃</i>	<i>b</i>
<i>La₂O₃</i>	0-55
<i>Nd₂O₃</i>	0-55
<i>CeO₂</i>	0-18

^aCeO₂ and ThO₂ used as surrogates for plutonium in glass when conducting glass formulation tests.

^bNd₂O₃, Eu₂O₃, and La₂O₃ tested as surrogates.

Note: Typical densities for 10 wt. % plutonium glass are 4.8 g/cm³.

A material balance, shown as Fig. G.3, can be calculated using the following assumptions:

1. Composition limits as listed for a borosilicate glass (Table G.2).
2. An N-reactor spent fuel of 92.6 wt. % uranium metal and 7.4 wt. % zirconium cladding.
3. Each batch contains 1 kg of Pu.
4. Mixing of the two product glasses gives a final waste glass composition of 20 wt. % of U₃O₈ and 0.4 wt. % of Pu.

The glass product composition that results from these assumptions is listed as Table G.2. One set of corresponding flows, including recycling lead and some excess of PbO with product adjustments are shown as Fig. G.3.

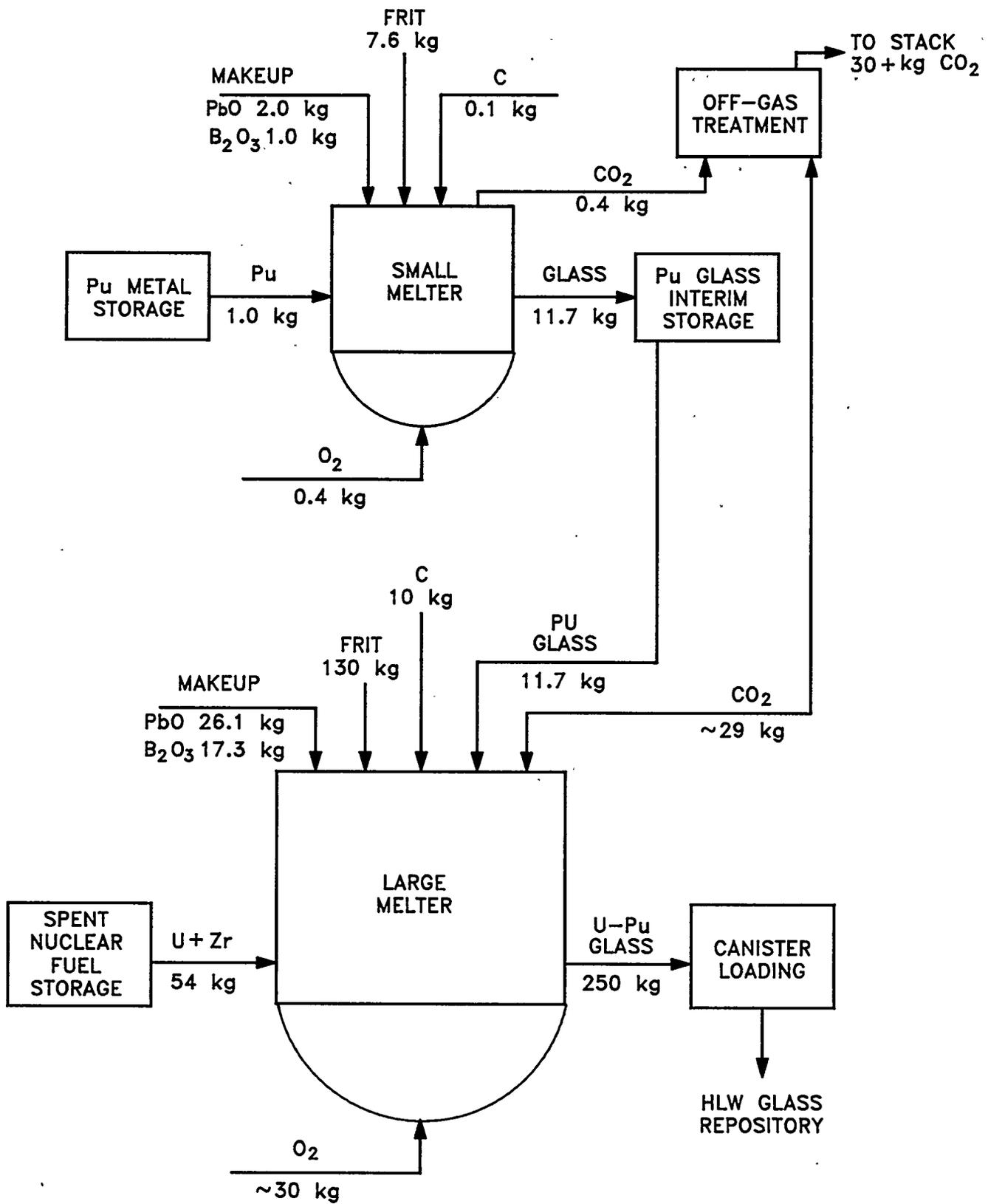


Fig. G.3. Material balances for a combined GMODS processing of plutonium and Hanford-N reactor.

Table G.2. Product glass compositions for a combined conversion of plutonium metal and Hanford-N reactor fuel

Metal	Final product				
	<u>Moles metal</u> Mole uranium	Oxide weight (kg)	Oxide (wt. %)	In Pu waste glass (kg oxides)	In spent fuel waste glass (kg oxides)
U	1.00	58.95	23.6	0.0	58.95
Pu	0.02	1.146 ^a	0.46 ^a	1.146	<i>a</i>
Zr	0.21	5.42	2.2	0.0	5.42
Si	5.2	65.5	26.2	3.2	62.3
Pb	0.6	28.12	11.2	2.0	26.1
Al	1.0	10.17	4.3	≥1.0	≥9.7
B	2.5	18.28	7.3	1.0	17.3
Ba	0.3	9.66	3.9	0.4	9.3
Other (Na, Ca, ?)		52.21	20.8	~3.0	49.2
Total		250.0	100.0	11.7	238.0

^aThe spent fuel will contain plutonium, which is not included in this table.

G.4 FINAL WASTE QUANTITIES

The waste quantity is determined by the SNF. For the previous example, a single waste package filled with HLW glass contains the glass product from 720 kg of SNF and 14.4 kg of plutonium. This assumes a standard SRS HLW package (height = 120 in.; diameter = 24 in.) with an effective waste volume of 0.75 m³/package and a glass density of 4.8 g/cm³.

For 50 t of plutonium and the associated SNF, about 3500 waste canisters are required. The number of added canisters required for disposal of plutonium and SNF vs only the SNF is about 70.

The quantities of SNF that may ultimately require treatment (such as conversion to glass) before geological disposal are not well known. A reasonable estimate is between 3000 and 5000 t. With the above waste loadings, this implies 4000 to 7000 waste canisters. If this SNF is converted to glass, there will be more than sufficient glass to incorporate all excess PCMs to HLW glass. It is noted that there will be another ~100,000 t of commercial SNF that is acceptable for repository disposal but that could be used to dispose of added excess plutonium in glass if required.

Most of the SNF for PCM disposition is from government operations, but some of it is commercial, degraded SNF (TMI core debris, etc.). It is noteworthy that the U.S. government has reprocessed ~100,000 t of SNF and that the commercial nuclear power industry is expected to generate ~100,000 t of SNF. The SNF discussed herein (about 2% of the cumulative total produced) are the “cats and dogs” of SNF.

G.5 OTHER CONSIDERATIONS

Many types of PCMs and SNFs may be converted to HLW glass. When there are large quantities of homogenous PCM and SNF feeds, the previous flowsheets can be used. If small lots of PCMs and SNFs are to be processed, economics may require an added processing step.

For heterogenous feeds (Fig. G.4), the main glass melter produces marbles. The marbles from particular production campaigns are inspected and stored in bins. Marbles not meeting intermediate product requirements are recycled to the main melter. The final glass logs are produced by mixing different marbles from different campaigns to produce a homogeneous, high-quality HLW glass. Strong incentives exist to produce a single homogeneous HLW glass from a multitude of different PCMs and SNFs using marbles as an intermediate product:

- *Container heat limit criteria.* Glass from high-heat SNF is blended with glass from low-heat SNF to meet waste package thermal limits.
- *Quality assurance criteria.* Glasses from different batches of SNF are blended to meet all quality assurance criteria.
- *Economics.* Glasses are blended to reduce disposal costs. There are concentration limits for specific elements in glass if durable glasses are to be made. If a particular SNF is high in an element *E* and a second SNF is low in element *E*, blending of glass from these SNFs can be used to maximize waste loading in the glass.
- *Criticality criteria.* Mixing different wastes ensures nuclear criticality control by mixing depleted uranium from SNF with (a) HEU from SNF or (b) plutonium from PCMs.
- *Characterization avoidance.* It minimizes the need to fully characterize certain PCMs and SNFs before processing. Some PCMs and SNFs (such as TMI core debris) are poorly characterized. It would be difficult and expensive to characterize these materials. The option exists to convert them to homogeneous glasses, analyze the homogeneous glasses, and mix with other glasses to produce an acceptable waste form.

It is important to recognize the characteristics of miscellaneous SNF and the implications for waste management. The miscellaneous SNF is highly variable in composition, and much of it is poorly characterized. The requirements for an acceptable HLW product is that it is homogeneous, meet tight WACs,

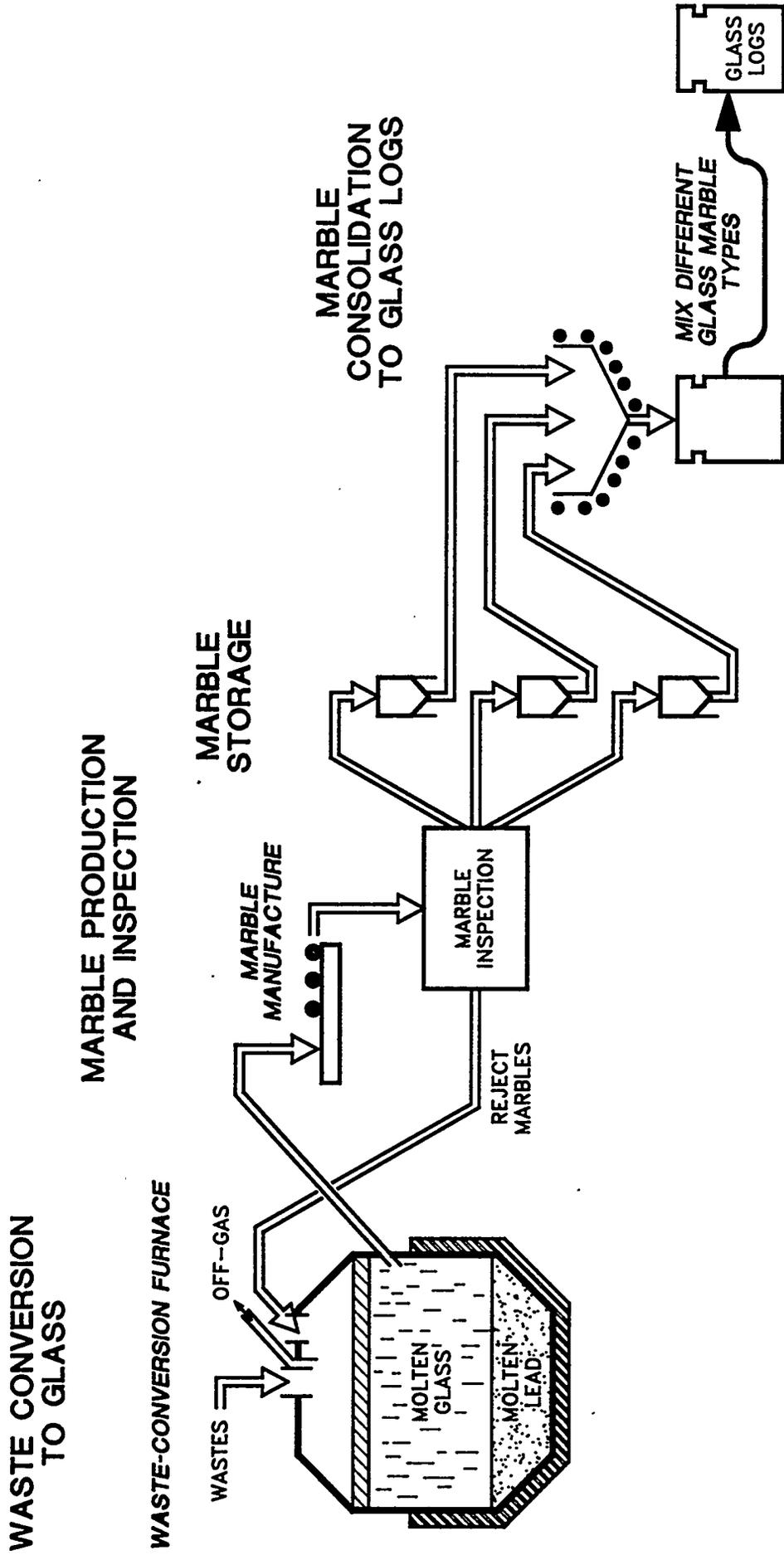


Fig. G-4. Conversion of miscellaneous SNF and other wastes to HLW glass.

and be well characterized. These contradictory requirements can be met only if somewhere in the process there is a mixing process that mixes waste from different batches of SNF. There are, in practice, two ways to accomplish this. At facilities such as the Defense Waste Processing Facility at the SRS, homogeneous feed to the glass plant is achieved by mixing HLW from different reprocessing campaigns in million-gallon tanks and feeding a uniform, characterized material to the glass plant. The alternative is an internal mixing process such as glass marbles in GMODS.

The remelting of marbles to glass logs is a relatively simple, small operation and requires only small equipment. A simple, consolidation melter (0.5 m³ internal volume for a 250 MT/year plant) melts the glass marbles into glass logs. It is simpler because, unlike the GMODS melter, there is (1) minimal off-gas, (2) no large-scale inhomogeneous mixtures, (3) no chemical reactions that must go to completion, and (4) no lead cycle. The option does exist to use the mainline GMODS melter for remelting glass marbles.

The actual implementation of GMODS would be highly dependent upon the quantities of miscellaneous SNF to be processed. If relatively small quantities of miscellaneous SNF were to be processed, the option may exist to use GMODS to make glass marbles and feed the glass marbles as an auxiliary feed material to a large vitrification plant processing HLW from tanks. This option is shown in Fig. G.5. In effect, GMODS becomes a special front-end processing system for a special waste. This option avoids the need to build a separate consolidation melter and the HLW canister-handling equipment. With such an option, one or more existing facilities might be backfitted with the GMODS process. The intermediate marble form would be shippable; thus, facilities need not be collocated.

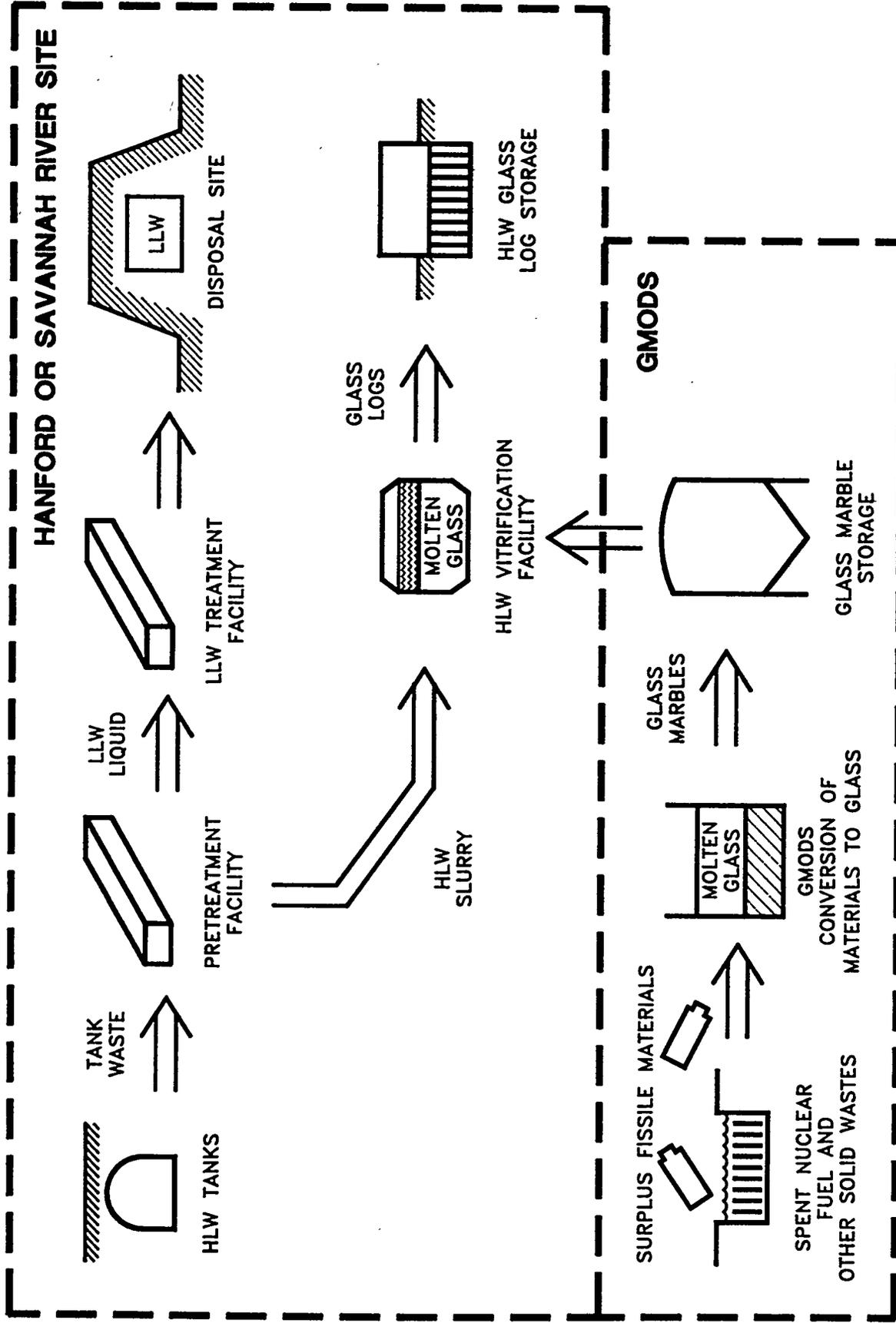


Fig. G.5. Combined tank HLW vitrification and GMODS system for all wastes requiring treatment before geological disposal.

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Appendix H:

CHOICE OF GLASS FORM GEOMETRY



APPENDIX H: CHOICE OF GLASS FORM GEOMETRY

Two possible glass forms can be readily produced: the glass log and the glass marble. The choice depends on both feed characteristics and product requirements. The dominant glass form worldwide in waste management is the glass log, which is used for the production of HLW glass; however, marbles are often the preferred product (Mason, 1994) when producing LLW glass. The glass marble can exist as an intermediate product form or a final product form.

Glass marbles can be incorporated into a secondary matrix or formed into glass logs by adding marbles to a container, creating vacuum conditions, warming the glass marbles to the softening temperature, and compressing them into the final desired form. This process is relatively simple and clean because full glass melting is not required and the glass marbles are inert.

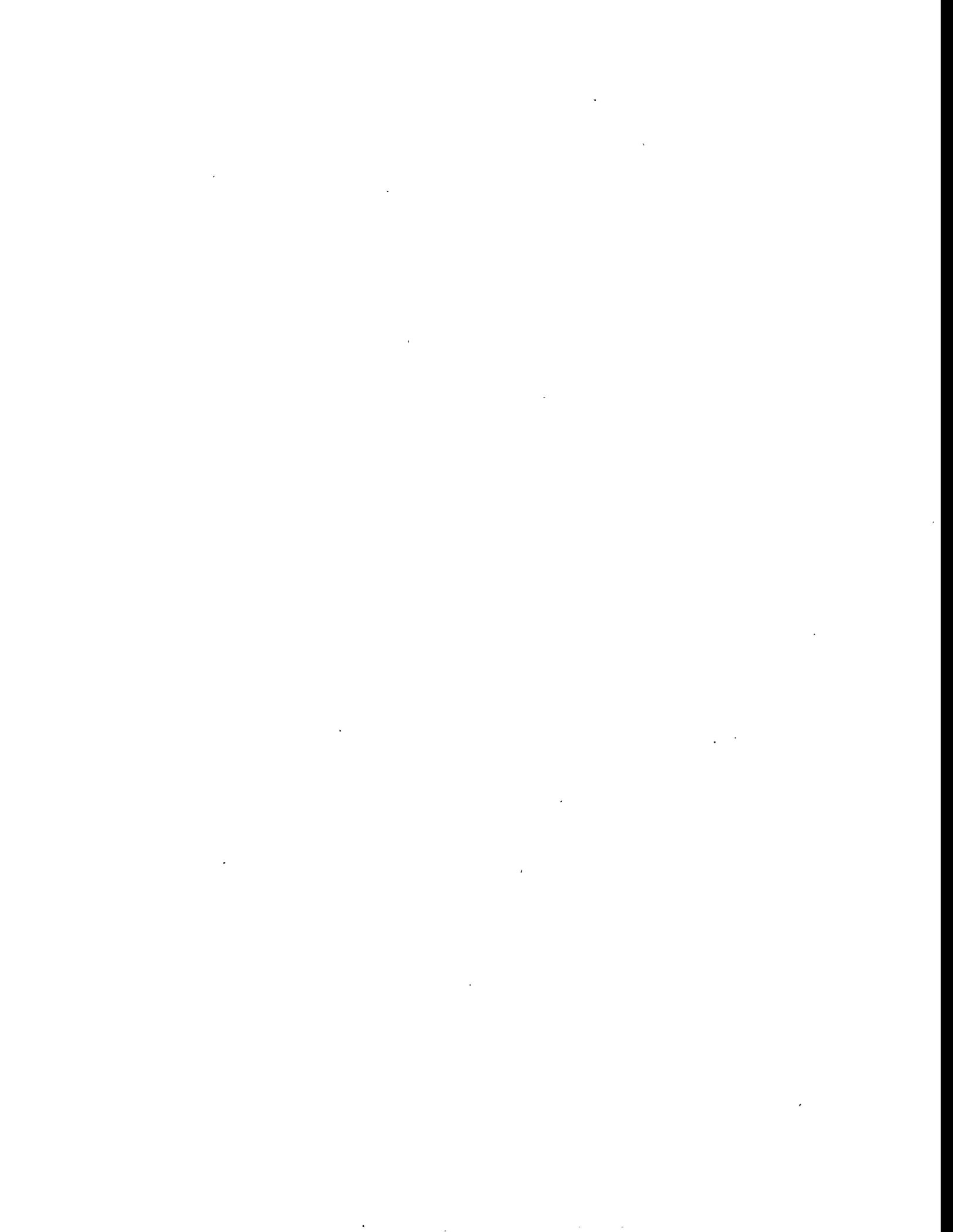
There are two important advantages to using glass logs: a final monolithic form is directly produced, and handling is minimized. The disadvantages are difficult product quality control, the large equipment size, and a need for minimum glass pours from the melter. Logs are likely to be preferred if there is a uniform feed to the glass process that results in reasonable assurance of a uniform product.

There are two important advantages to producing a glass-marble product form: the equipment is small, and the product can be easily sampled to be sure of product quality. For highly heterogeneous feed material, the latter provides an independent confirmation that the process did create a uniform glass. The more variable the feed, the greater incentive to use marbles as an intermediate or a final product to confirm product specifications have been met. Off-specification products can be easily recycled back to the melter. The disadvantage for plutonium-containing glass marbles is that an added process will likely be required to create a monolithic form for storage and disposal.

The option exists to create glass marbles of different materials (plutonium glass and SNF glass), combine them in a cylinder, heat the cylinder, and produce a uniform glass log. The marbles are mixed in the cylinder by using two sizes of marbles so that the smaller marbles fill the space between the larger marbles. The process is conceptually similar to certain fuel fabrication technologies that produce small spheres converted then into fuel matrixes.

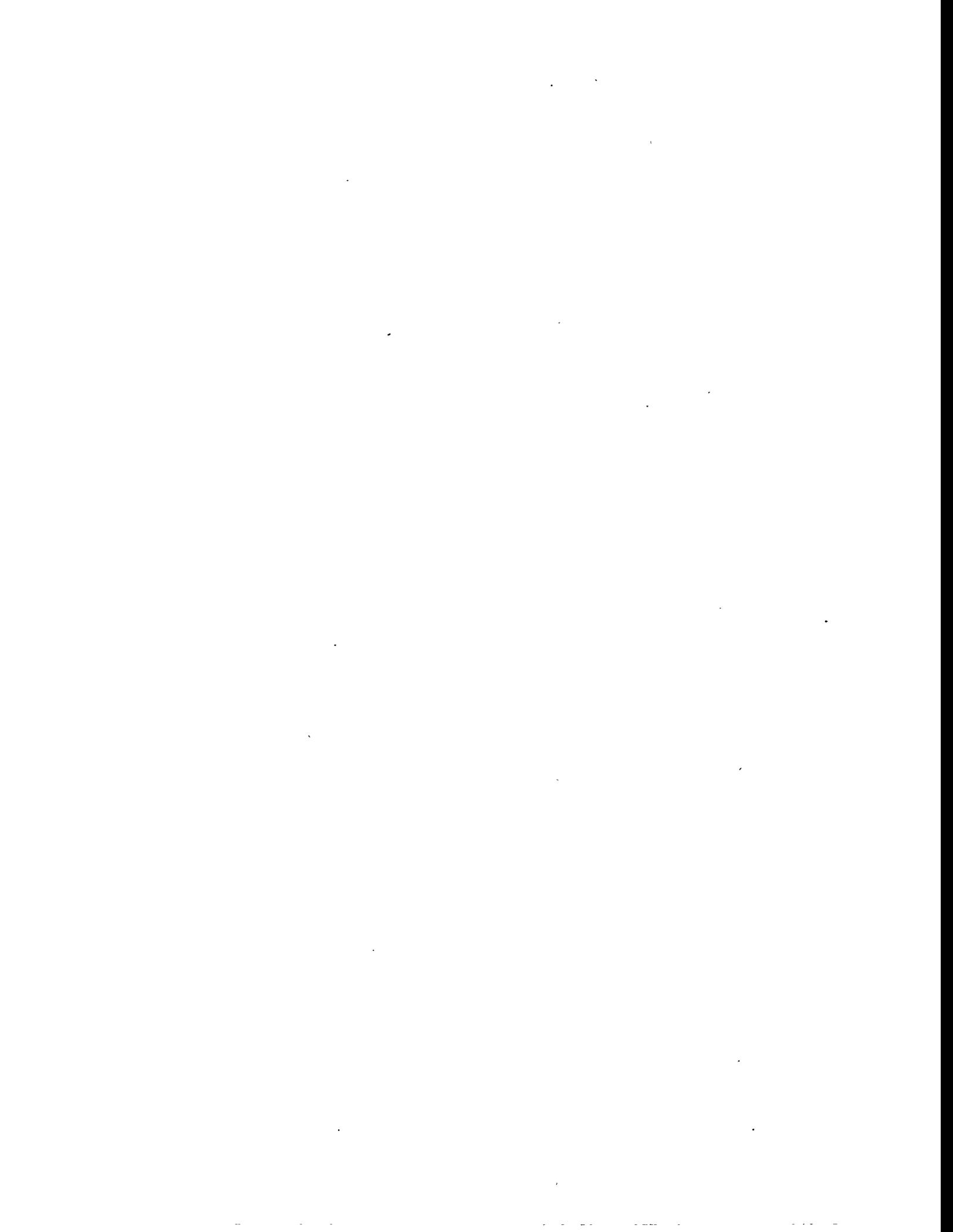
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Appendix I:

GMODS INSTRUMENTATION



APPENDIX I: GMODS INSTRUMENTATION

I.1 REQUIREMENTS

GMODS requires the usual instrumentation of any glass melter. In addition, GMODS requires instrumentation for process control specific to the GMODS process and specific to the processing of plutonium and other fissile materials.

It is required to determine when a homogeneous molten glass mixture exists within the melter. In each process step, GMODS starts with a highly heterogeneous mixture. The process step is finished when the glass becomes uniform in chemical composition. In principle, one can assure GMODS operation by simply providing sufficient melter time to assure the existence of a homogeneous molten glass mixture at the end of each step. In practice, this is an expensive option since the time to create a homogeneous molten glass mixture will vary with feed type. Providing sufficient time for creation of a homogeneous glass in the worst case implies that during normal operation, the melter will be doing nothing much of the time when homogeneous molten glass mixtures form faster than in the worst case.

A plutonium waste form is being produced; thus, there are safeguard requirements that the quantity of plutonium in the glass be accurately known. Plutonium concentrations in the glass can be measured to high precision if the glass is homogeneous so that a small sample is representative of the entire batch of glass. It is also desirable to determine plutonium concentrations on a real-time basis to assure appropriate plutonium concentrations in the glass.

Last, fissile materials create the potential for nuclear criticality. To assure nuclear criticality does not occur, on-line determination of fissile material concentrations is desirable. Total fissile mass in the melter is most easily determined when the glass is homogeneous.

I.2 INSTRUMENT APPROACHES

In a typical glass melter, it is difficult to determine when a molten glass mixture is homogeneous. As a consequence, homogeneous glass mixtures in many industrial glass melters are assured by use of uniform feeds and sufficient melter time. Two characteristics of GMODS allow on-line measurement of glass homogeneity:

- GMODS is processing radioactive materials. When the radioactive materials are homogeneously distributed within the molten glass, they create a homogenous radiation source. Therefore, radiation detectors outside the melter can determine when the glass mixture is homogenous.

- GMODS uses a cold-wall, induction-heated glass melter. These are high power, high throughput, well stirred glass melters. Their smaller size for any given throughput, high stirring rates and relatively thin walls provide a good environment to monitor radioactivity within the melter.

Radiation detectors can detect gamma rays or neutrons from the molten glass. Nuclear materials safeguards technologies (Eccleston 1995) and waste management technologies (Davidson, 1995) are directly applicable for process homogeneity molten glass measurements within the GMODS melter. Many of these same measurements can also determine plutonium concentrations. Development work will be required for this process application. Four techniques have been identified for measuring glass homogeneity:

- *Passive neutron coincidence counting.* This technique (Eccleston 1992, Menlove 1992) is based on the observation that plutonium undergoes spontaneous fission with the release of fast neutrons. These neutrons can be detected and the sources of neutrons located. By using coincidence neutron measurements, the plutonium distribution in the melter can be determined separately from neutrons produced by alpha particles interacting with light elements in the glass. This allows determination of plutonium concentrations.
- *Active neutron counting.* With this technique (Eccleston 1993; Eccleston 1990, Menlove 1992) pulse or steady-state neutron sources scan the melter with the fission neutrons detected by multiple detectors.
- *Random neutron emission.* This technique (Russo 1993a; Russo 1993b) depends upon the alpha-neutron reactions between alpha decay sources in the glass and light elements create a background neutron source. Plutonium and other actinides emit alpha particles. The distribution of the neutrons provides a measure of glass homogeneity.
- *Tomographic gamma-ray scanning.* This technique (Prettyman 1994; Eccleston 1991) determines a three dimensional source map of gamma ray sources and, hence, how homogeneous it is. It also includes the option of a strong gamma-ray source on one side of the meter with measurement of attenuation through the melter at different locations.

I.3 OBSERVATIONS

In practical systems, multiple instrument techniques will be used to assure glass homogeneity. These are likely to include one technique measuring neutrons and one technique using gamma rays. The neutron counting techniques provide a basis for absolute measurements of plutonium concentrations. The different techniques compliment each other and each have their own strengths and weaknesses.

The characteristics of GMODS in some ways simplify the design of such instrumentation and in other ways complicate accurate measurements. GMODS characteristics assisting measurements include: (1) fixed geometry, (2) uniform compositions at the end of each process step, and (3) analytical analysis of glass after each batch that provides highly accurate compositional measurements of the glass composition. These

characteristics allow accurate calibration of instrumentation on-line. GMODS characteristics complicating measurements include: (1) a dense glass, (2) inhomogeneous feed materials, and (3) process requirements for fast analysis.

It is noted that many of the instrument requirements will be controlled by the need for process control rather than by nuclear criticality and safeguards requirements. This implies highly automated systems with self calibration.

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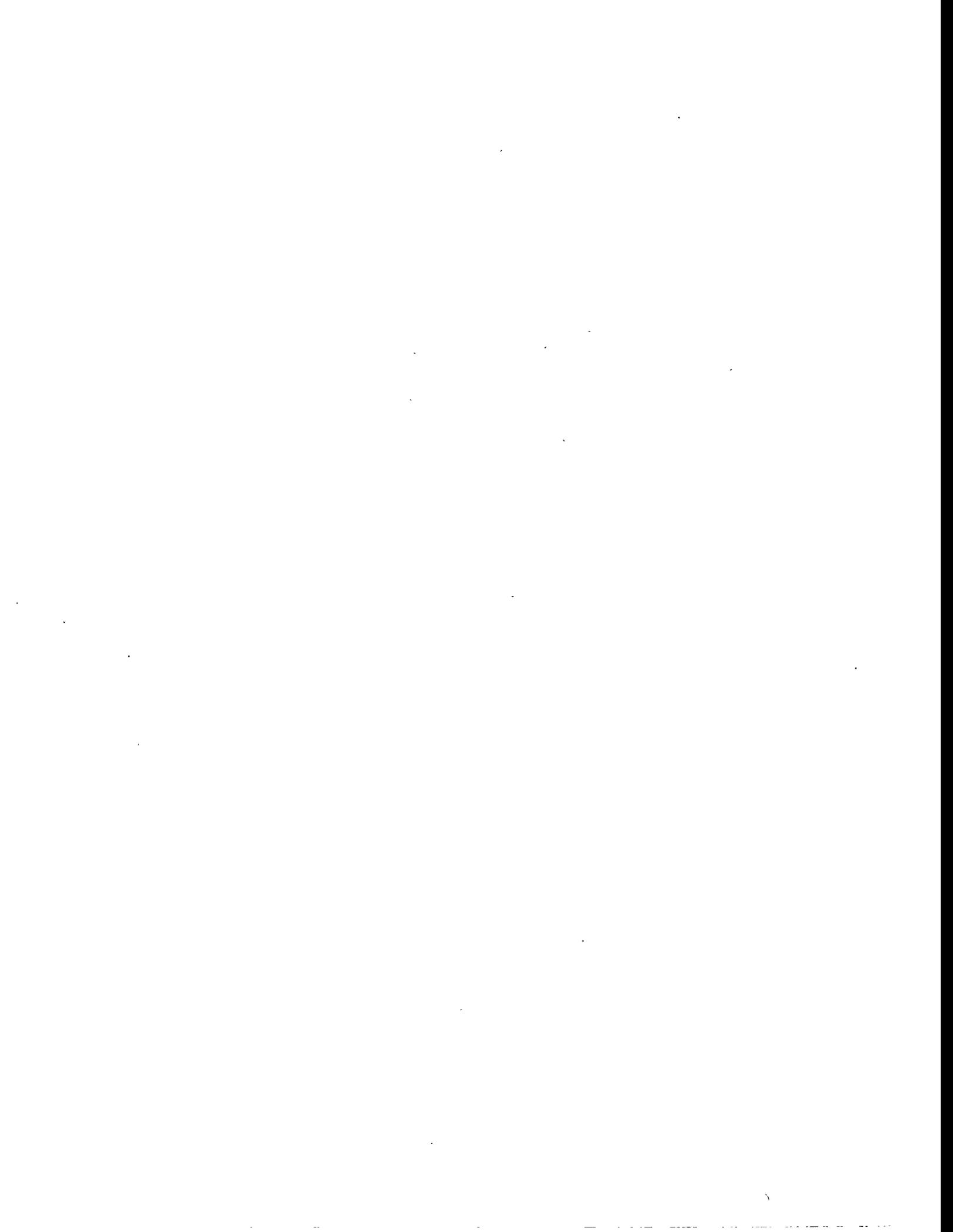
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Appendix J:

PROCESSING PCMs WITH CHLORIDES



APPENDIX J: PROCESSING PCMs WITH CHLORIDES

Many types of PCMs contain chlorides in various chemical forms (salt, plastic, etc.) as a result of metal production and fabrication operations. Many glasses can not accept significant chlorides within their chemical structure. Furthermore, chloride-containing materials generally have poor performance as a storage or waste form. The analogy used in waste management is that good storage forms for radioactive materials can be found at any beach. Materials that make good beach sand (silica in glass, etc.) make good storage forms. Materials that dissolve in sea water (chlorides, etc.) make poor storage forms. These considerations necessitate removal of chlorides before a final plutonium glass form is produced.

GMODS (Forsberg, 1995) converts PCMs with chlorides into glass and a secondary nonradioactive sodium chloride salt stream (Fig. J.1). This separation process avoids chlorides in the glass and their negative impact on product quality. When GMODS processes PCMs with chlorides, the chlorides react with the lead-borate glass to produce lead chloride. Lead chloride ($PbCl_2$) is volatile and exits the melter as a vapor.

The melter off-gas can be sent through an aqueous sodium hydroxide scrubber that removes lead particles, glass aerosols, and the lead chloride. The lead chloride dissolves into the scrub solution. After entering the scrubber solution, the lead ions in solution react with the hydroxide ions and are precipitated from the aqueous scrubber solution as lead hydroxide. The chemical reaction is:



The sodium chloride that remains after lead hydroxide has precipitated is highly soluble in water. This salt solution is either filtered to remove the lead hydroxide, or the lead hydroxide precipitate is allowed to settle from the solution. This solids-liquids separation also separates and removes aerosols scrubbed by the aqueous solution. The lead hydroxide is recycled back to the melter where it thermally decomposes into lead oxide (PbO) and water (H_2O).

The aqueous solution of sodium chloride is filtered and sent through a charcoal or an ion-exchange system to remove residual dissolved lead and other ions, and the clean salt is disposed of as nonradioactive waste. Filter material, ion-exchange resin, and charcoal are fed back to the melter for disposal. The removal of low concentrations of lead compounds in aqueous solutions is an industrial process used in both water treatment plants and lead recycle plants. The chloride exits the system separately from the PCMs with which it entered.

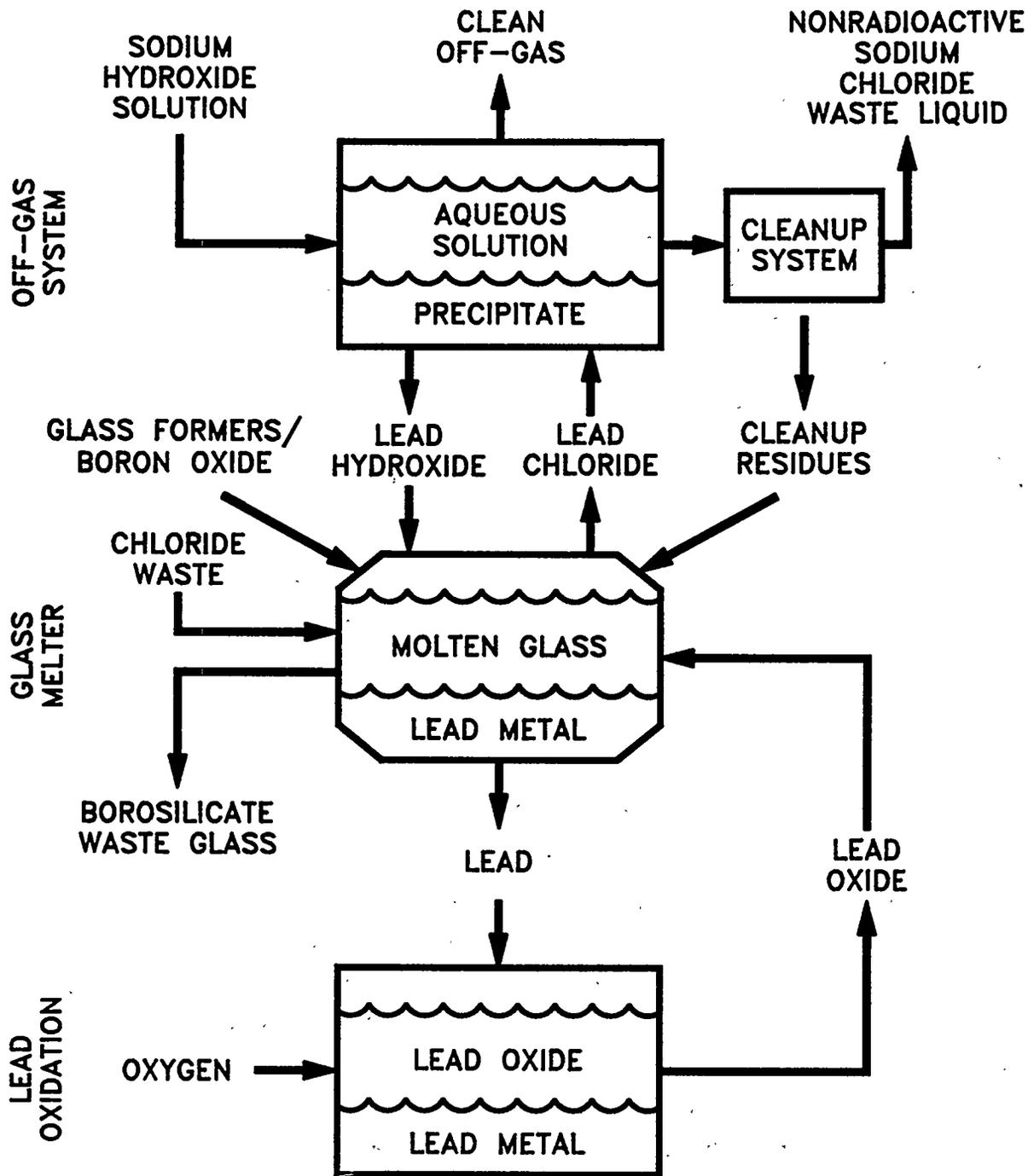


Fig. J.1. Separation of chlorides from wastes while converting other waste compounds to glass using GMODS.

Table J.1 shows the key physical and chemical parameters for the operation of this system (Dean, 1973).

Table J.1 Properties of key compounds when processing halogen wastes with GMODS.¹

Compound	Boiling Point °C	Solubility ² g/100 g water
PbF ₂	1290	0.064
PbCl ₂	950	0.99
PbBr ₂	918	0.84
PbI ₂	954	0.063
Pb	1751	Insoluble
Pb (OH) ₂	³	0.0155
NaF	1704	4.0
NaCl	1473	35.7
NaBr	1390	90.0
NaI	1300	158.7
NaOH	1390	108.0

¹Lange's Handbook of Chemistry, Eleventh Edition.

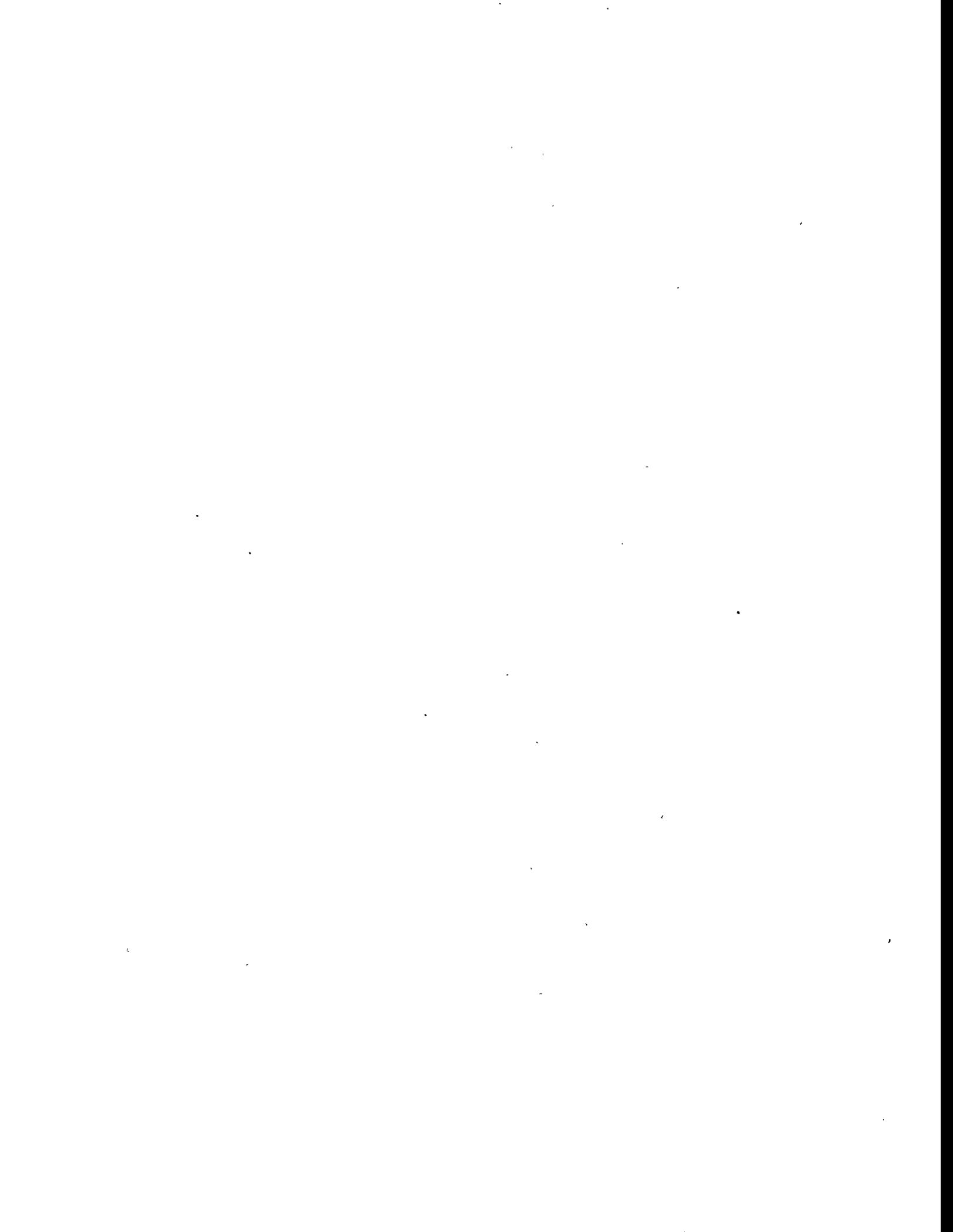
²Solubility at 20° C.

³Decompose to PbO and H₂O at 145° C.

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