Glass Material Oxidation And Dissolution System: Converting Miscellaneous Fissile Materials to Glass

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ABSTRACT

The cold war and the development of nuclear energy have resulted in significant inventories of miscellaneous fissile materials (MFMs). MFMs include (1) plutonium scrap and residue, (2) miscellaneous spent nuclear fuel (SNF), (3) certain hot cell wastes, and (4) many one-of-a-kind materials. Major concerns associated with the long-term management of these materials include: safeguards and nonproliferation issues; health, environment, and safety concerns; waste management requirements; and high storage costs. These issues can be addressed by converting the MFMs to glass for secure, long-term storage or repository disposal; however, conventional glass-making processes require oxide-like feed materials. Converting MFMs to oxide-like materials with subsequent vitrification is a complex and expensive process.

A new vitrification process has been invented, the Glass Material Oxidation and Dissolution System (GMODS), which directly converts metals, ceramics, and amorphous solids to glass; oxidizes organics with the residue converted to glass; and converts chlorides to borosilicate glass and a secondary sodium chloride (NaCl) stream. Laboratory work has demonstrated the conversion of cerium (a plutonium surrogate), uranium, Zircaloy, stainless steel, multiple oxides, and other materials to glass. However, significant work is required to develop GMODS further for applications at an industrial scale. If implemented, GMODS will provide a new approach to manage these materials.

I. INTRODUCTION

Defense and civilian nuclear activities have generated MFMs containing $^{239}$Pu and $^{235}$U as byproducts of other activities such as (1) research and (2) production of clean fissile materials. The fissile content of the MFMs was sufficiently high that these materials were not considered waste. However, in most cases these MFMs also contained other materials that made recovery of clean fissile materials for reuse difficult and/or expensive. There are major concerns in the safe storage of many MFMs. The value of the fissile materials in the MFMs is clearly less than the costs of recovery. There is now a need to convert many of these MFMs to acceptable forms for safe, long-term storage and, in many cases, for ultimate disposal.

GMODS is a new process with the unique capability to directly convert these diverse MFMs into homogeneous glass to solve the current safety, storage, disposal, and economic problems associated with them. Conventional glass-making processes accept only oxide-like feeds; thus, conversion of MFMs to glass using conventional technologies requires that the MFMs first be converted to oxides. This is a complex task with existing technologies. This paper describes MFMs, the potential requirements for their disposal, the GMODS process, the status of GMODS development, and modeling results.

II. MFM CHARACTERISTICS

Plutonium scrap and residue are by-products from the processing of plutonium. A dozen categories of plutonium scrap and residue contain several tons of plutonium in 100+ t of material. Within each category, chemical and physical forms vary widely. During the cold war, most of the easily processed scrap and residue was processed to recover the plutonium leaving problem materials. The total inventory of separated plutonium in the U.S. is about 100 tons. Scrap and residue contains a small fraction of the total plutonium inventory but the total mass and volume is much larger than the inventory of pure plutonium because of the other elements in this stream.
Some of this material is moderately radioactive. When plutonium was recovered from old weapons to build new weapons, the plutonium was often purified with extraction of the radioactive daughter product $^{241}\text{Am}$ from the plutonium. Much of the americium is in the scrap and residue.

There are 55 different categories of miscellaneous SNF with a total fissile content of 51 t in 2,646 t of heavy metal. This includes about 200,000 items with a gross weight of 4,681 t. About half is low-enriched Hanford-N SNF. The remainder of the categories have fissile enrichments from natural to high-enriched uranium (HEU) with $>90\%$ $^{235}\text{U}$. Examples include research reactor fuel, irradiated targets, Three Mile Island (TMI) core debris, and navy SNF. Burnup varies from near zero to in excess of 200,000 MWD/t. Significant quantities of this material are poorly characterized. For example, TMI canisters contain core debris (fuel debris, control rod debris, structural materials) and cleanup debris (filters, filter aids, equipment) unsorted in canisters. The quantity of material is small compared to the 100,000 t of low burnup SNF reprocessed for defense needs, the 84,000 t of SNF expected from commercial reactors, and the 1000 t of HEU in the defense complex.

This MFM inventory that built up over five decades requires processing to a stable storage form and ultimate disposal. For the few categories that contain significant quantities of SNF with relatively uniform compositions (i.e., Hanford-N SNF, navy SNF), custom-designed treatment processes are feasible; but for much of this inventory, general purpose treatment processes are needed to minimize treatment costs.

III. REQUIREMENTS FOR DISPOSAL

If SNF is to be disposed of, it must meet repository waste acceptance criteria (WAC). Any MFM should be acceptable if it meets SNF WAC. If such criteria are met, the MFM should also be acceptable for long-term storage. There are four classes of WAC: mechanical, thermal, nuclear, and chemical.

A. Mechanical and Thermal WAC

Two of the four WAC are easily achieved if MFM are converted to glass. Converting MFM to glass and pouring the molten glass into high level waste (HLW) canisters meet the mechanical WAC for a standard waste package. The thermal WAC limits the heat load in any package to avoid excessive package temperatures. This WAC can be met by mixing high-heat MFM with low-heat MFM in the conversion process.

B. Nuclear WAC

Nuclear criticality must be prevented in a repository to effect safe disposal and to meet regulatory requirements. A repository is designed to contain radioactivity; thus, the generation of added radioactivity from a nuclear criticality event is not the major concern. The concern is that the generation of heat will cause waste form degradation and will accelerate the movement of groundwater and result in the transport of radioactivity to the environment.

MFMs contain plutonium and/or uranium. Plutonium decays to HEU; thus, the repository long-term criticality issue is enriched uranium. Uranium in geological environments migrates and reconcentrates into uranium deposits. Geological history shows that nuclear criticality has occurred in uranium ore deposits in which the initial uranium enrichment was $3.6%$ $^{235}\text{U}$. Studies$^1$ of these natural nuclear reactors have documented conditions under which nuclear criticality may occur.

A way to prevent nuclear criticality in a repository$^2$ from MFMs is to add $^{238}\text{U}$ to the MFMs. The $^{238}\text{U}$ is not fissile and acts as a neutron poison; thus, it eliminates nuclear criticality concerns in the repository environment. Because the different isotopes of uranium have the same chemical behavior, there is no possibility of the fissile material ($^{235}\text{U}$) separating from the neutron poison ($^{238}\text{U}$). It is the mechanism that prevents nuclear criticality from $^{235}\text{U}$ in natural uranium ore deposits today. For plutonium in the repository, when the plutonium decays to $^{235}\text{U}$, that $^{235}\text{U}$ is born into a world of $^{238}\text{U}$ and is isotopically diluted to low enrichment levels.

The National Academy of Sciences has recommended$^3$ that a "spent fuel standard" be met when disposing of HEU and plutonium. This standard states that potential weapons useable materials should be disposed of in such a manner that recovery of these materials for use in nuclear weapons would be as difficult as recovery of plutonium in SNF. This recommendation is intended to address national security and arms control issues. Addition of depleted uranium for criticality control reduces uranium enrichment levels far below the uranium enrichment levels required for nuclear weapons. Simultaneous
conversion of MFMs with appropriate mixing of materials would reduce concerns associated with these limited amounts of plutonium. 4, 5

C. Chemical WAC

The preferred chemical form for MFM in a repository is borosilicate glass. Billions of dollars invested in three decades of research in multiple countries resulted in a good understanding of borosilicate glass in the repository environment. Other chemical forms can be accepted by a geological repository; however, there must be very large incentives in order to consider alternative chemical forms given the resources required to demonstrate performance of any new waste form.

Borosilicate glass is accepted worldwide because it is a good waste form and can accept almost any element within its chemical structure. However, there are limits on the quantities of any specific element that can be incorporated into the glass and still produce a high-quality glass. This creates incentives for simultaneous processing of different MFMs. One MFM may contain too much of element X while a second MFM may contain too much of element Y. If each is processed separately, the glass may have a low MFM loading to avoid concentration limits of specific elements. If the MFMs are processed together, the total glass volume may be substantially reduced because each MFM dilutes the limiting element in the other MFM.

IV. GMODS

A. Process Description

GMODS converts MFMs directly to borosilicate glass. GMODS may be operated as a batch (Fig. 1), semibatch, or continuous process. 6 The process described herein is a batch process during which sequential process steps convert feeds to glass. The initial condition for the process is a melter filled with a molten oxidation-dissolution (lead borate) glass, which has a composition of two or more moles of lead oxide (PbO) per mole of boron oxide (B₂O₃). The PbO is a component of the glass and an oxidizing oxide. The process consists of the following steps:

1. Addition of feed material to the molten dissolution glass (Fig. 1b). The ceramic and amorphous components in the feed dissolve into the glass. While metals and organics do not dissolve into conventional molten glasses, the GMODS dissolution glass has special properties to process these materials in situ. The inclusion of the sacrificial oxide—PbO—in the molten glass provides a method to oxidize in situ (a) metals to metal oxides and (b) organics to carbon dioxide (CO₂) gas and steam. When uranium, plutonium, or another metal is fed to the melter, it is converted to a metal oxide. These metal oxides dissolve into the glass; carbon oxides (gaseous form) and steam exit the melter. The reaction product, molten lead, separates from the glass and sinks to the bottom of the melter to form a separate layer,

\[ Pu + 2PbO \rightarrow PuO_2 + 2Pb \] (1)

\[ C + 2PbO \rightarrow CO_2 + 2Pb \] (2)

2. Addition of glass additives [silicon dioxide (SiO₂) etc.] to improve product quality (Fig. 1c). The optimum compositions of glasses for rapid oxidation-dissolution of materials in molten glass are different from those for long-term durability. Consequently, additives that create a more durable glass are introduced after feed oxidation-dissolution takes place.

3. Addition of carbon to remove excess PbO (Fig. 1c). Carbon reduces the PbO to lead metal while producing gaseous CO₂. Excess PbO is removed from the dissolution glass for multiple reasons: (l) more durable glass, (2) reduction of the volume of glass, and (3) avoidance of the costs to provide added sacrificial PbO. The final glass may contain some or no lead, depending on the desired glass composition.

4. Pouring glass from the furnace followed by solidification (Fig. 1d). The product glass is poured into the waste container.

5. Addition of B₂O₃ and PbO, as needed, to the melter for processing the next batch of materials (Fig. 1e). Boron oxide and PbO that left with the product glass are replaced with new feed materials. Note that lead oxide is only added if the product glass contains lead oxide.
6. Reoxidation of the lead at the bottom of the melter to PbO by addition of oxygen (Fig. 1f). Oxygen is injected into the molten lead. This oxidation step creates the new dissolution glass for the next batch of feed to be processed. Lead is an oxygen carrier that does not leave the system. The oxidation reaction is

$$2\text{Pb} + \text{O}_2 \rightarrow 2\text{PbO} \quad (3)$$

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

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

For the processing of MFM, the option exists to produce marbles rather than logs. If there is a wide variation in feed materials, (1) different batches of MFM can be converted to glass marbles; (2) marbles can be mixed to produce a consolidated batch of marbles with the desired average chemical, nuclear, and thermal characteristics; and (3) the marbles can be melted to produce the final glass log.

B. Equipment Description

The primary GMODS equipment is an induction-heated, cold-wall melter (Fig. 2), which is required because of the corrosive characteristics of the initial dissolution glass. Cold-wall melters have cooling jackets in their walls to produce a “skull” of solidified material that protects the wall from the melter’s contents. They are used to melt high-temperature materials (e.g., titanium and superalloys) and to produce ultra-pure materials (e.g., glass for fiber optics). Russia, France, and the U.S. are modifying such equipment for processing various radioactive wastes. In Europe, cold-wall melters are currently being developed for throughputs of up to 800 kg/h.

C. Status of Laboratory Work

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

Tests demonstrated the dissolution of $\text{UO}_2$, $\text{ZrO}_2$, $\text{Al}_2\text{O}_3$, $\text{Ce}_2\text{O}_3$, $\text{MgO}$, and other oxides. Oxidation-dissolution tests demonstrated the oxidation of the following metals and alloys (followed by the dissolution of their oxides into the melt): U, Ce, Zircaloy-2, Al, stainless steel, and other metals. Oxidation-dissolution tests also demonstrated the oxidation of carbon and graphite, with production of $\text{CO}_2$.

The other process steps (addition of glass frit, removal of lead from the glass, and oxidation of lead back to lead oxide) have been investigated in the laboratory. They are also used in the glass, lead smelting, and lead-battery industries on very large scales and are well understood.

V. MODELING

GMODS performance was modeled using FLOW $^7$ to better understand the process and allow predictions of final glass volumes and compositions for different MFM feed streams. FLOW provides a tool to determine when mixing different MFM feeds during processing can reduce final glass volumes.

FLOW is an advanced simulation tool developed at ORNL that is designed to simulate new processes when only limited data is available. Although commercial software is available that simulates chemical processes (e.g., ASPEN$^\text{TM}$ and CHEMCAD$^\text{TM}$), these packages tend to emphasize the unit operations and material properties that are most common in the conventional chemical industry. Unit operations used in advanced or new process technologies, mostly for waste treatment processes, are generally not available.

Cost, risk, and uncertainty models are built into and can be integrated directly into performance simulations. Heuristic handling of component properties and behavior permits streamline specification of separations and realistic results even when data are missing. Decision modules permit integration of WAC, operating constraints, blending of recipes, and regulatory and other requirements in the flowsheet.

A. GMODS Flow Model Assumptions

GMODS process simulation was performed by integrating the GMODS process and chemistry, the requirements for production of glass, and the application of the FLOW modeling tools. This simulation modelled the time-averaged material flows, compositions, conformance to specifications, and product quality of GMODS for a variety of feed materials. A number of simplifications and assumptions were incorporated into the model that do not mirror the GMODS process exactly, but these simplifications and assumptions are made so that the essential behavior of GMODS, with respect to the purpose of the study, is captured and to facilitate the calculations. Some of the more important assumptions are as follows:

1. Steady state. GMODS is a multistep, batch, dynamic process. FLOW treats it as a steady-state, continuous process. This is a good approximation because time-averaged flows from the
process are of principle interest than instantaneous conditions. A dynamic simulation would have only complicated reaching this simulation's objectives.

2. Single process vessel. Most of the various steps of the GMODS process take place in a single vessel in an induction furnace. The FLOW model of GMODS sequences through a flowsheet of unit operations connected by streams. For this simulation, the FLOW unit operation models can be thought of as process steps taking place within the same vessel, and the connecting streams can be considered as the materials added or removed from that vessel at different times.

3. Phase equilibria. Solubilities and distribution of constituents between phases are estimated based on experimental data and then entered by the analyst, approximated by FLOW's group or phase separator modules, or assumed based on engineering judgement.

4. Chemical kinetics and equilibrium. Reaction equilibria are assigned by the analyst, and the residence-time in the vessel is assumed to be long enough to achieve an assumed extent of reaction.

5. Glass optimization model. The glass formulation model calculates the amount of SiO₂ that must be added to the melt to maximize the glass loading. A companion FLOW module brings the melt viscosity into an acceptable range by adding other constituents and adjusting the temperature. The glass formulation model calculations are based on the ternary-phase diagram for SiO₂-B₂O₃-other oxides (R₂O) glass (shown in Fig. 3). The ternary-phase diagram shows an elliptical region (known homogeneous waste glass region) having acceptable performance characteristics. The FLOW model uses the information of this ternary diagram to produce an acceptable glass composition. Beginning with a starting composition somewhere in the ternary-phase diagram, FLOW draws a line from the starting point to the A and B vertices. The algorithm searches for the point on the surface of the ellipse that results in the maximum waste loading in the glass.

Parameters supplied by the user include the "minimum design temperature" of the melter, the Gibbs free energy of hydration (ΔG), and the compound check which is constrained on the maximum wt % of TiO₂, Cr₂O₃, P₂O₅, and Fe²⁺. Adjusting the ΔG is more difficult than adjusting the viscosity, although the free energy rarely needs to be adjusted.

When an adjustment is required, other components are added to the glass. Viscosity is calculated by the program as well.

B. Production of Acceptable Glass

The methodology to formulate and predict the glass quality was based on work performed at Clemson University in conjunction with the Savannah River Laboratory for development of HLW glasses for the Defense Waste Processing Facility (DWPF). In this initial analysis, it is assumed that the performance of the plutonium glass should be equivalent to a HLW glass. Glass formulations must be chosen on the basis of two key factors in the vitrification processes: product quality and processability. Glass-forming compounds are added to the melt to obtain the desired glass properties. Sometimes trade-offs must be made between product quality attributes and processability properties when glass compositions are formulated.

The high-quality glass compositions can be mapped as a region in the glass-phase diagram. The most important factors for determining processability are the viscosity and liquidus temperatures of the melt.

1. Glass quality. The term quality refers to the long-term performance and durability of the glass in performing its role as a matrix for immobilizing radionuclides. The durability of a glass, measured by silicon release rates and constituent leach rates in groundwater, is a key factor in determining glass quality. Product durability is associated with the chemical and physical properties of waste glasses including chemical immobilization, physical durability, and devitrification. These properties are closely interrelated to and result from the structural characteristics of glass. Among these properties, the single most important characteristic of waste glass is chemical immobilization, or the ability to resist leaching of the immobilized contaminants when contacted by water or other liquids. In this study only the chemical immobilization was considered.

2. Processability. The most important factors for determining processability are the viscosity and liquidus temperatures of the melt. Viscosity is a function of temperature and determines the rate of melting of the raw feed, the rate of gas-bubble release, and the rate of homogenization. If the viscosity is too high, the melt does not readily pour out; consequently, the product quality is reduced by causing voids in the final glass.
FIG. 3. The ternary phase diagram for SiO$_2$-B$_2$O$_3$-R$_2$O.

The liquidus defines the highest temperature at which spinel (MgAl$_2$O$_4$ having octahedral crystals), with or without nepheline (feldspathoid mineral), crystallizes. The glass formulations must have a liquidus below the minimum design temperature of the melter (i.e., 1050°C for a DWPF glass melter; the minimum design temperature is the temperature that gives acceptable viscosity). The liquidus temperature is determined based on the free energy of formation of the liquidus phases, spinel, and nepheline. The Gibbs free energy of hydration is used as a measure of glass durability and the release rates of silicon and boron.

The GMODS process acceptance criteria are not yet available experimentally. Consequently, the acceptance criteria to be used by the GMODS process may vary from the values that have been determined for HLW glasses in conventional furnaces. The following values are acceptable for HLW glass:

- **Processability:** Liquidus temperature ≤ 1050°C. 20 smelt viscosity ≤ 100 poise.
- **Acceptability:** Leach rate ≤ 1 g/m$^2$/d.
- **Durability:** $\Delta G$ of hydration ≥ -7.5 kcal/mol.

C. Results and Incentives for Mixing Feeds

The initial analysis$^9$ examined processing of plutonium scrap and residue with GMODS for long-term storage or as an intermediate step toward disposal. Both initial and final plutonium content were determined to ensure that nuclear criticality would not occur in the glass. Ratios of glass to feed were determined in order to analyze the volume increase. Silicon dioxide (SiO$_2$), B$_2$O$_3$, and Na$_2$O concentrations were determined to establish the need for vitrification material compatible with an acceptable glass formation region of the phase diagram. Melting temperature was determined in order to analyze the potential mechanical difficulties within the GMODS furnace. Viscosity and $\Delta G$ were determined in order to analyze the processability and durability of the glass. Table 1 shows the results of the simulation for rich and lean scrap.
Two of the rich scrap sub-streams, ash and chlorides salts, were blended together in different combinations in order to assess the effects of blending various waste streams on final glass mass. In the first simulated run, both of the waste streams were treated separately. This produced a total final glass mass of 217,500 kg (77.5 m³), 28,500 kg from treating the ash stream and 189,000 kg from treating the chloride salt stream. Then various mixtures of the waste streams were created by combining all of the chloride salts stream and an increasing amount of ash ranging from 10 wt % of the ash stream up to 100 wt % of the ash stream. This blend was then fed to GMODS models to produce the final glass product. The remaining ash, that was not used in the mixture, was fed as a separate stream into the GMODS process and also produced a final glass product. The total mass of glass produced by blending the two waste streams was ~70,000 kg—a two thirds reduction in glass mass. This reduction in final glass mass and volume shows the incentives to look for appropriate blends within the different subcategories of plutonium scrap.

For furnaces in which the temperature is a limitation, the preferred option for a viscosity reduction is an increase of the amount of Na₂O, thus increasing the final volume of glass. The GMODS process does not have such a limiting parameter. For example, if the process starts with 1 kg of chlorides scrap, the melting point reaches 1103°C, and the corresponding Na₂O concentration is about 20 wt%; the resulting final glass mass is about 6.5 kg. If the temperature is allowed to increase to about 1167°C, the final glass mass is about 3 kg. By changing the temperature 64°C, there is a reduction of about 50 wt % in the final glass mass. This is a key consideration when selecting GMODS operating parameters.

VI. CONCLUSIONS

New technologies are required to convert MFMs into stable forms for long-term storage or disposal. The key characteristics of MFMs are the highly variable physical, nuclear, and chemical properties. Because the quantity of any specific MFM is small, development of specific processes for each MFM may become very expensive. GMODS is a new process with the unique capability to convert complex mixtures of metals, ceramics, organics and halogens into a high quality borosilicate glass. It represents a promising new approach to solve the problems of MFMs.

REFERENCES


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