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# Conversion of Ion-Exchange Resins, Catalysts and Sludges To Glass With Optional Noble Metal Recovery Using The GMODS Process

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## ABSTRACT

*Chemical processing and cleanup of waste streams (air and water) typically result in products, clean air, clean water, and concentrated hazardous residues. These residues include ion-exchange resins, catalysts, sludges, and other materials. Typically, these streams contain significant quantities of complex organics. For disposal, it is desirable to destroy the organics and immobilize any heavy metals or radioactive components into stable waste forms. If there are noble metals in the residues, it is desirable to recover these for reuse.*

*The Glass Material Oxidation and Dissolution System (GMODS) is a new process that directly converts radioactive and hazardous chemical wastes to borosilicate glass. GMODS oxidizes organics with the residue converted to glass; converts metals, ceramics, and amorphous solids to glass; converts halides (such as chlorides) to borosilicate glass and a secondary sodium halide stream; and recovers noble metals. GMODS has been demonstrated on a small laboratory scale (hundreds of grams), and the equipment necessary for application to larger masses has been identified.*

## INTRODUCTION

Chemical processing and cleanup of waste streams (air and water) typically result in products, clean air, clean water, and concentrated hazardous residues. When the residues contain organic solids and heavy metals or radionuclides, there are two process requirements: (1) destroy the organics to reduce volumes, eliminate hazardous chemical components, and avoid difficulties in processing the residual materials and (2) immobilize the residual heavy metals or radionuclides. If the heavy metals are immobilized, the final material may be considered nonhazardous. If the feed contains radionuclides, immobilization is required before the waste is disposed. A generally preferred immobilization form is borosilicate glass.

The Glass Material Oxidation and Dissolution System (GMODS) is a recently invented vitrification process [*1*] to convert complex waste streams to borosilicate glass [*2*] while destroying organics. It is a new glass-making process in that glass is made from unusual materials (organics, metals, ceramics, chlorides, etc.), whereas conventional vitrification processes can convert only oxides and oxide-like materials to glass. GMODS also recovers noble metals.

## THE PROCESS

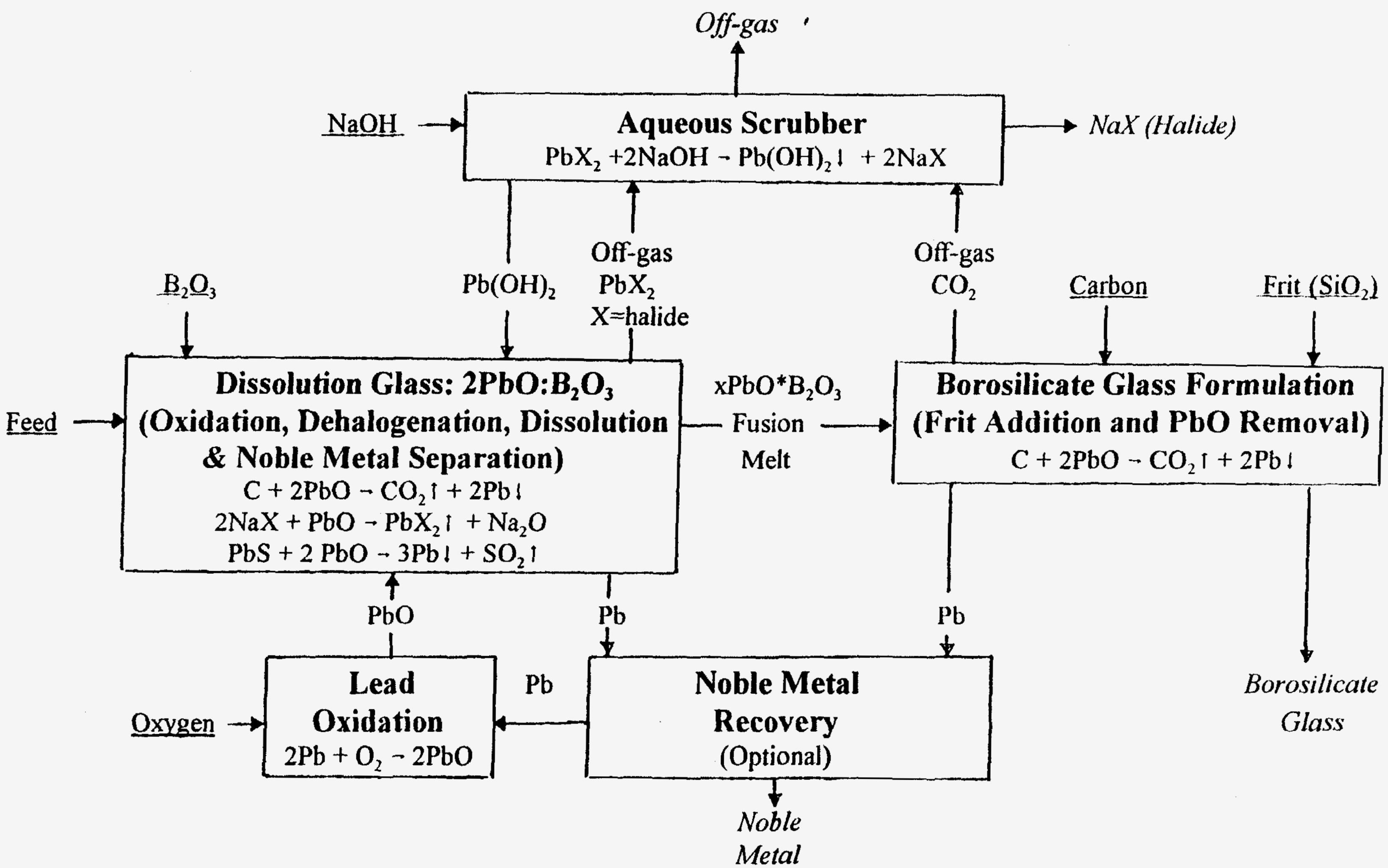
GMODS may be operated as a batch, semibatch, or continuous process (Figure 1). The process described herein is a continuous process. The initial condition for the process is a melter filled with a molten oxidation–dissolution (lead borate) glass, which has a composition of 2 or more moles of lead oxide (PbO) per mole of boron oxide ($B_2O_3$). This composition maximizes dissolution rates and solubilities of complex feeds in the dissolution glass. The PbO is both a component of the glass and a sacrificial oxide. The process consists of the following steps:

### Addition of Feed Material to the Molten Dissolution Glass

The feed materials are directly placed into the melter. The ceramic and amorphous components in the feed that are exposed to the molten glass rapidly dissolve into the glass. Molten glasses dissolve most oxides, but they do not dissolve organics or metals. To dissolve these latter components into the glass, the metals and organics must first be oxidized. In GMODS, oxidation occurs in situ within the glass melter. The PbO in the glass is the oxidizing agent. If the feed contains organics, the organics are oxidized to carbon dioxide ($CO_2$) and water ($H_2O$), and the by-product lead metal sinks to the bottom of the melter. The $CO_2$ and $H_2O$ gases exit the melter via the off-gas system. Metals (excluding the noble metals) are oxidized by the PbO in the glass to metal oxides and, subsequently, dissolve into the glass. The lead by-product then sinks to the bottom of the melter. Typical chemical reactions are:

$$2\,Al + 3\,PbO \rightarrow Al_2O_3 + 3\,Pb\downarrow$$

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




Underline = Input to Process
**Bold** = Process
*Italic* = Process Output

**FIGURE 1** GMODS conversion of wastes to borosilicate glass.

Rapid oxidation and dissolution are the results of the special characteristics of the $B_2O_3$-PbO dissolution glass. At operating temperatures (700 - 900° C), the PbO is a powerful oxidizer. However, some metals and other materials form protective oxide coatings. Boron oxide is a powerful dissolution agent for oxides; it is used in many welding fluxes and analytical procedures for rapid dissolution of oxides. The combination of $B_2O_3$ and PbO create the unique oxidation-dissolution capabilities of this molten glass.

**Separation of Halogens from Feed Materials in the Molten Dissolution Glass**

GMODS is designed to convert halogen-containing wastes to glass and to create a separate, clean, sodium halide waste stream. Halogens, such as chlorides, make poor-quality waste forms; hence, they must be separated from other components in the wastes. The process separates halogens within the feed during feed dissolution. For example, let us consider a feed containing chlorides. In the dissolution glass, chlorides in the feed form lead chloride ($PbCl_2$), which is volatile at glass-melter temperatures and exits to the aqueous sodium hydroxide (NaOH) scrubber. In the scrubber, the $PbCl_2$ reacts with the NaOH to yield insoluble lead hydroxide [$Pb(OH)_2$] and soluble NaCl salt. The insoluble $Pb(OH)_2$ is recycled back to the melter, in which it decomposes to PbO and steam. The aqueous NaCl stream is cleaned and discharged as a chemical waste. Other halogen-containing feeds behave similarly.

**Separation of Sulfides and Sulfates from Feed Materials in the Molten Dissolution Glass**

GMODS oxidizes sulfur-containing components in the feed to sulfur oxides that exit via the off-gas. Sulfur compounds make poor-quality glass. GMODS processing of high sulfur feeds (such as sulfur-cross-linked ion-exchange resins) is very similar to standard lead-smelter processes [*3*]. Lead smelters convert lead ores (primarily sulfides) and recycle materials into lead metal and lead oxide. The same processes are used within GMODS to remove sulfides and other sulfur compounds from the feed materials Typical reactions include:

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

$$PbS + O_2 \rightarrow Pb + SO_2\uparrow$$

$$PbS + 2\,PbO \rightarrow 3\,Pb + SO_2\uparrow$$

**Removal of Noble Metals from the Molten Dissolution Glass**

The noble metals are not oxidized by the PbO and are not soluble in glass, but they are highly soluble in molten lead [*4*]. During feed dissolution, the noble metals separate from the glass, dissolve into the lead metal, and sink with the molten lead to the bottom of the melter.

The noble metals can be separated from the lead by vacuum distillation of the lead or by several other industrial processes on a continuous or batch basis. Significant quantities of noble metals are found in some lead ores. These noble metals remain with the lead metal during smelting operations. Consequently, multiple processes for noble metal separation from lead have been developed and deployed [*5*].

**Conversion of Molten Dissolution Glass to a Borosilicate Glass**

The optimum compositions of glasses for rapid oxidation-dissolution of materials in molten glass are different from those compositions that are optimum for long-term durability. Consequently, additives (silicon dioxide [$SiO_2$] etc.) that create a more durable glass are introduced after feed oxidation-dissolution takes place. The addition of such materials to molten glass is a process that is used in the production of many specialty glasses [*6*].

Excess PbO is removed from the dissolution glass by reducing the PbO with carbon to lead metal, thus producing gaseous $CO_2$. Excess PbO is removed from the dissolution glass for multiple reasons: (1) to obtain a more durable glass, (2) to reduce the volume of glass, and (3) to avoid the cost of added sacrificial PbO (see below). The final glass may contain some or no lead, depending on the final desired glass composition. The use of carbon to reduce PbO to lead metal in glassy slags is used in many lead-smelter processes [*5,7*]. The glass product is poured from the furnace and solidified.

**Reoxidation of the Lead to PbO by Adding Oxygen**

Oxygen is injected into the molten lead recovered from (1) the lead-borate dissolution step and (2) the conversion of the dissolution glass to the final borosilicate glass. Lead, an oxygen carrier in the dissolution process, is oxidized to PbO. The oxidation reaction is:

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

The lead oxide is recycled to make the next batch of lead-borate dissolution glass. This process step is currently used to make PbO for lead-acid batteries and other purposes [*5,8*].

## PROCESSING OPTIONS

As a continuous process, GMODS has similarities to several state-of-the-art lead-smelter processes such as the Queneau-Schuhmann-Lurgi (QSL) continuous lead-smelting process [*3,7,9*]. An understanding of the QSL process and its industrial operations provides some perspectives on how a continuous GMODS process could operate on a large scale (>1000 t/year).

Figure 2 shows the QSL process. The lead ore is fed continuously into the right side of the reactor and melted to produce a slag. The feed includes lead sulfides and may include carbon, an auxiliary fuel needed for some feeds. The reactor has a layer of molten slag floating on a layer of

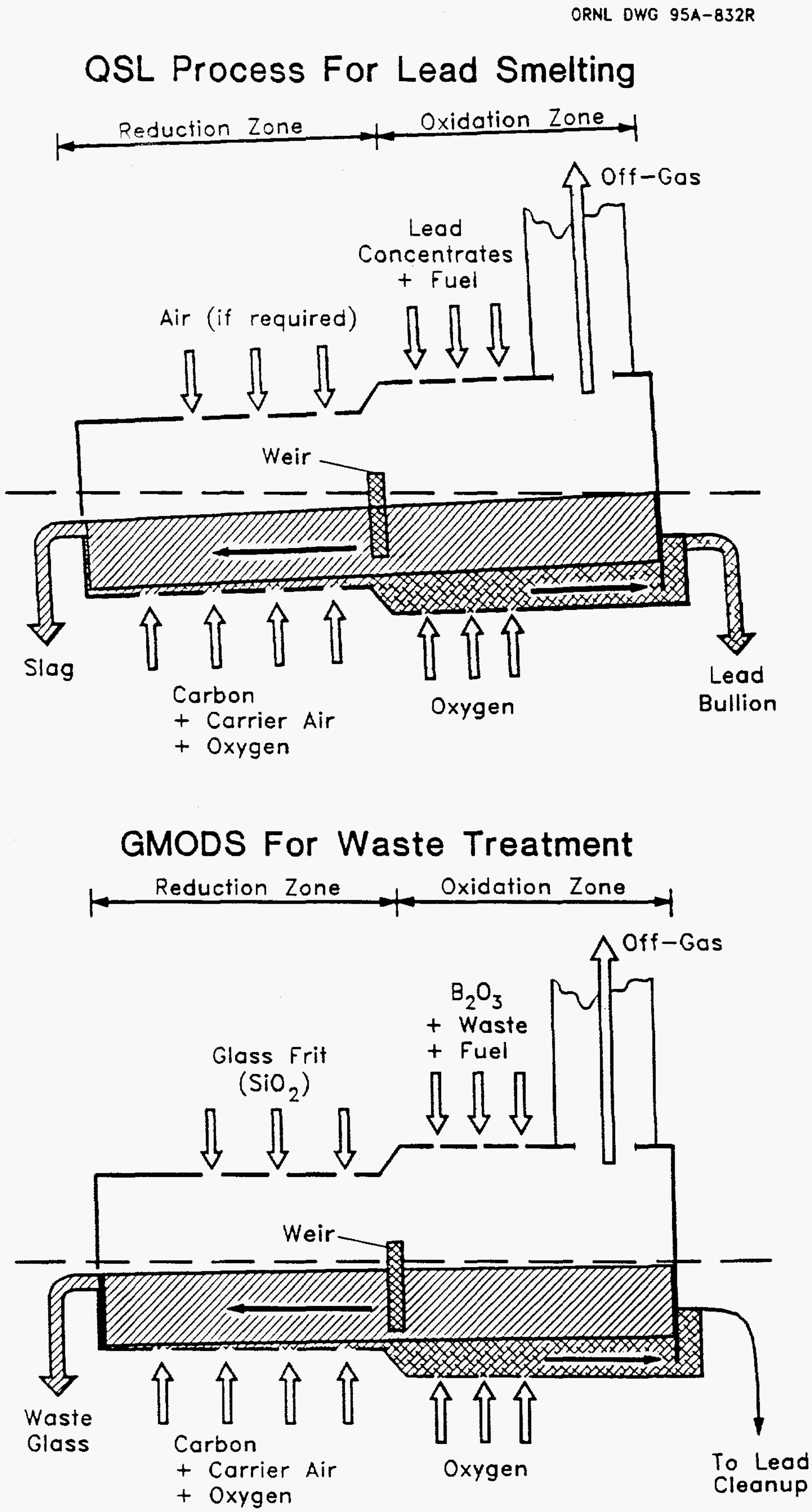



**Figure 2** QSL and GMODS continuous processes.

molten lead. Oxygen is injected into the molten lead to create oxidizing conditions and burn out the sulfides. Some of the key reactions are:

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

$$PbS + O_2 \rightarrow Pb\downarrow + SO_2\uparrow$$

$$PbS + 2\ PbO \rightarrow 3\ Pb\downarrow + SO_2\uparrow$$

The net result of these chemical reactions is oxidation of the lead sulfide, thus producing lead metal and a slag rich in lead oxide. The slag flows through a submerged weir to a second zone operated under chemically reducing conditions. Coal-oxygen submerged combustors produce a reducing gas that, in turn, reduces the lead oxide in the slag to lead metal that sinks into the lead pool. The slag exits as waste. Typically the slag has a high silica content.

The QSL process is chemically similar to that of GMODS. If GMODS is used to process large quantities of material, a similar chemical reactor design may be appropriate (Figure 2). The main differences between the two processes are:

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

*Product* The GMODS product is waste glass, not lead. The production of glass requires high oxygen-injection rates into the oxidizing part of the lead bath to fully convert lead metal to PbO. The PbO then reenters the glass.

*Dissolution glass composition.* The glass in the GMODS process contains carefully controlled quantities of $B_2O_3$ to assist dissolution of metal oxides - particularly protective metal oxides that form on some metals.

*Product composition* The final glass composition in the GMODS process is adjusted by addition of glass frit to produce a high-quality waste glass.

## EQUIPMENT

The GMODS equipment configuration depends upon the scale of operation. For large-scale processing (>10,000 t/year), large-scale chemical reactors similar to the QSL reactor (Figure 3) are a potential option. QSL lead smelters have typical capacities of 60,000 to 75,000 t/year. The lead industry has developed chemical reactors potentially applicable to GMODS for sizes from tens of tons per year up to the scale of the QSL reactors.

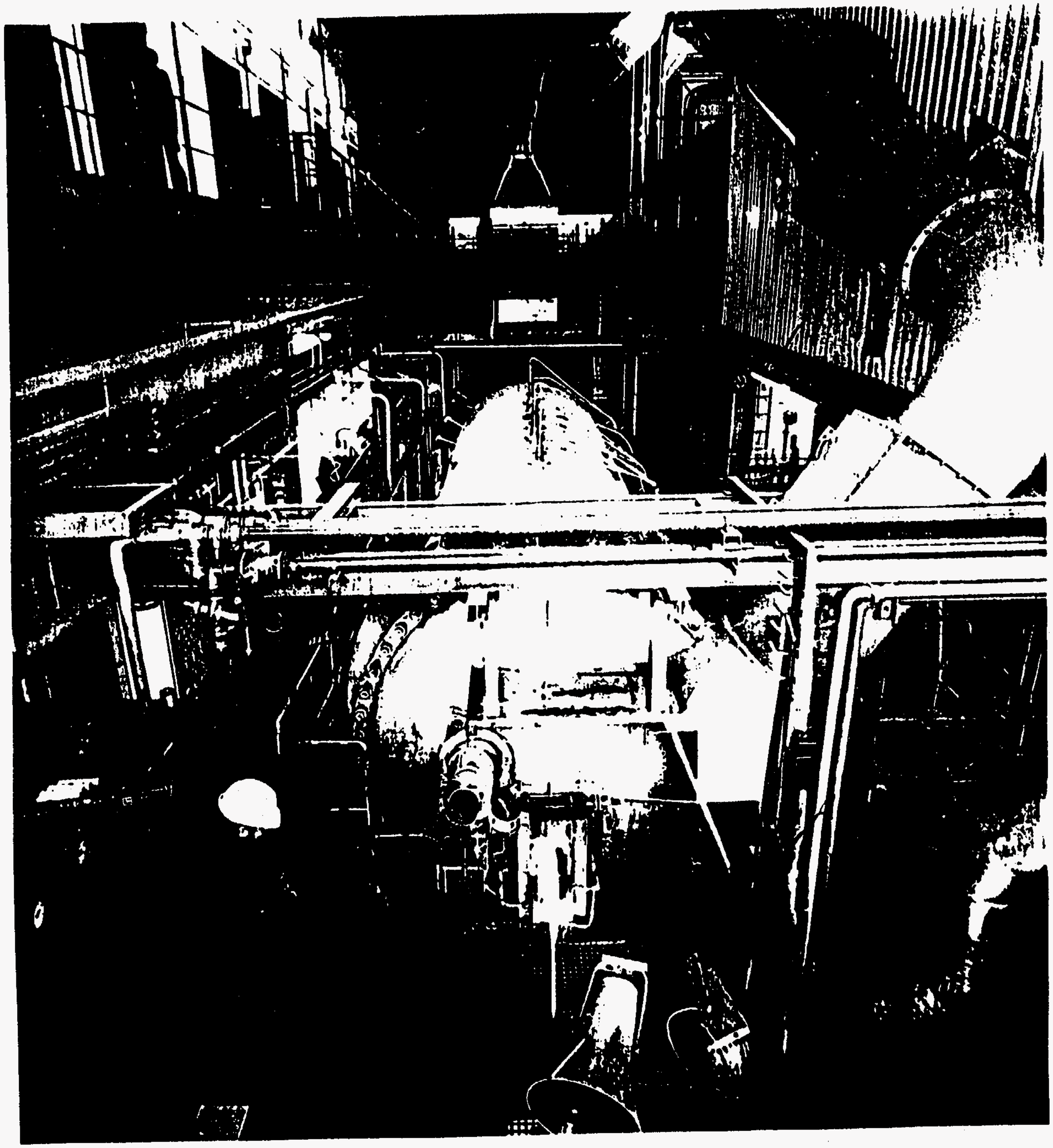


**Figure 3** Interior of QSL plant (courtesy of Lurgi Corp.).

## STATUS OF DEVELOPMENT

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.

The addition of feed materials involves oxidation, dissolution, and mixing of the feeds with the molten dissolution glass. Each of these steps has been investigated, and tests have demonstrated the dissolution of $Al_2O_3$, $Ce_2O_3$, MgO, $UO_2$, $ZrO_2$, and other oxides. The glasses were examined by a variety of methods to ensure complete dissolution. As expected, the glass melt with high concentrations of boron oxide had good dissolution capabilities for oxides.

Oxidation-dissolution tests demonstrated the oxidation of the following metals and alloys (followed by the dissolution of their oxides into the melt): Al, stainless steel, U, Ce, Zircaloy-2, and other metals. Oxidation-dissolution tests also demonstrated the oxidation of carbon and graphite, with production of $CO_2$. For centuries, organics have been used to convert PbO to lead metal. This conversion process is a part of many lead-smelting processes. It is also the basis for the fire assay method [*10*] for recovering noble metals (primarily gold) from silicate rock. Lead oxide, various organics, and silicate rocks are mixed together and heated. As the mixture melts, the PbO is reduced to metal by the organics. The noble metals in the molten mass then dissolve into the lead and the lead with dissolved noble metals sinks and forms a separate layer at the bottom of the vessel. This lead is processed to separate the noble metal from the lead.

Limited chloride dissolution tests with NaCl demonstrated that lead exits the dissolution glass as $PbCl_2$, thus providing a separation of the chloride from other materials. This is a major mechanism for lead to escape from processes in which lead and chlorides coexist at high temperatures [*11*]. The basic chemistry has been studied extensively.

## SUMMARY

GMODS is a new process designed to (1) convert metals, ceramics, and amorphous solids to glass; (2) oxidize organics with conversion of residues to glass; and (3) convert halides into a halide-free borosilicate glass and a secondary clean sodium halide stream. The process allows recovery of noble metals. As a new technology, however, there are significant technical uncertainties associated with scale-up and equipment that must be resolved.

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