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# Preliminary Investigation of a Technique to Separate Fission Noble Metals from Fission Product Mixtures

G. B. Mellinger  
G. A. Jensen

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August 1982

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PRELIMINARY INVESTIGATION OF A TECHNIQUE  
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## SUMMARY

The purpose of this work is to examine a variation of the gold-ore fire assay technique as a method for recovering palladium, rhodium and ruthenium from fission product mixtures. The fission noble metals are created during the fissioning of nuclear fuel. During reprocessing, they and the other fission products are separated from the fuel. The work reported in this document was performed using a nonradioactive oxide simulation of such a fission product mixture. In this method, the mixture of fission product oxides is combined with glass-forming chemicals, a metal oxide such as PbO (called a scavenging agent), and a reducing agent such as charcoal. When this mixture is melted, a metal button is formed which extracts the noble metals. The remainder of the melt cools to form a glass that may be suitable for nuclear waste storage. Further laboratory, bench-scale and developmental effort will be performed to verify that this process is suitable for recovery of the noble metals found in nuclear waste.

Recovery was found to depend only on reduction of the scavenger oxide to metal. When such reduction was achieved, no significant difference in noble metal recovery efficiency was found among the scavengers studied (PbO, SnO, CuO, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>). Not all reducing agents studied (graphite, charcoal, silicon, flour, cornstarch and sugar), however, were able to reduce all scavenger oxides to metal. Only graphite would reduce SnO and CuO and allow noble metal recovery. The scavenger oxides Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and PbO, however, were reduced by all of the reducing agents tested. Similar noble metal recovery was found with each.

Lead oxide was found to be the most promising of the potential scavengers. It was reduced by all of the reducing agents tested, and lead's higher density may facilitate the separation of the metal from the glass. Use of lead oxide also appeared to have no detrimental effect on the glass quality. Charcoal was identified as the preferred reducing agent for technical and economic reasons and will be used in future experiments.

The scavenger and reducing agent additions to the batch were varied to determine the minimum amounts required for successful recovery. As long as a

separable metal phase was formed in the melt, noble metal recovery was not dependent on the amount of reducing agent and scavenger oxide used in these experiments.

The effect of glass viscosity on recovery was tested. High viscosities were found to inhibit separation of the molten scavenger, while low viscosities apparently allowed volatile loss of  $\text{RuO}_4$  from the melt. A viscosity of  $\sim 20$  poise at the processing temperature was found to offer a good compromise between scavenger separation and Ru recovery.

Although detailed evaluation of the waste storage-related properties of the glass was beyond the scope of this work, the glass was briefly investigated. Glasses in which  $\text{PbO}$  was used as the scavenging agent were found to be homogeneous in appearance. In addition, the resistance to leaching of the glass tested was found to be close to that of certain waste glasses reported in the literature. Environmental risks from the lead in the waste glass were not evaluated.

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## INTRODUCTION

This document reports the results of a study of fission product noble metal recovery from fission product mixtures. The technique examined would, using a single process, separate the noble metals from the remaining nuclear waste and produce a waste disposal glass.

The work reported herein summarizes the first-year laboratory bench-scale studies of this recovery technique. The primary emphasis during this period has been in determining those aspects of the technique which most affect noble metal recovery and optimizing that recovery. Enhancement of the waste disposal related qualities of the resulting glass has been secondary. This will receive greater emphasis in future work, however.

The platinum-group metals (platinum, palladium, osmium, iridium, rhodium and ruthenium) are valuable strategic materials and interest in these metals stems from their great usefulness (Hampel 1954; Dix 1978; Jensen, Rohrmann and Perrigo 1980). The metals are essential in the petroleum and chemical industry as catalysts and find application in electronic components because of their corrosion and oxidation resistance. They are also used in laser mirrors, infrared lenses, and aircraft engines, and in the automotive industry in catalytic converters.

An unexploited source of these metals is the Pd, Rh and Ru created as fission products during the burnup of nuclear fuel. The potential supply of these elements from both plutonium-production reactors and commercial power reactors is great (Rohrmann 1968; Jensen, Rohrmann, and Perrigo 1980). The primary reason for exploring the use of this source is that natural occurrences of the noble metals are scarce and not widely distributed. Over 90% of the naturally occurring world supply of these metals is found in the Soviet Union and the Union of South Africa (National Research Council 1980). Less than 1% of this supply is available from United States sources. It may be to our advantage to develop the domestic resource of these materials contained in nuclear wastes. One obstacle in this development to date has been that the cost of recovering these materials has exceeded that of the natural metals.

The separation method examined in this report may allow economical recovery of the fission noble metals if glass proves to be an acceptable disposal form for fission product waste. The separation technique is based on a gold-ore fire assay method (Naish et al. 1953). Figure 1 compares the fire assay method and its proposed modification for use in recovering the noble metals.

In fire assay, the ore is mixed with lead oxide, a fluxing agent such as  $\text{Na}_2\text{CO}_3$  or  $\text{Na}_2\text{B}_4\text{O}_7$ , and a reducing agent (e.g., charcoal). When this mixture is melted, the lead oxide is reduced to metallic lead which separates from the melt and alloys with the gold present in the ore. The remainder of the melt forms a glass slag upon cooling.

In applying this technique to fission-product noble metal recovery, the process stream that contains the noble metals would be mixed with a glass-forming material, a metal oxide (called a scavenger oxide) such as  $\text{PbO}$ , and a

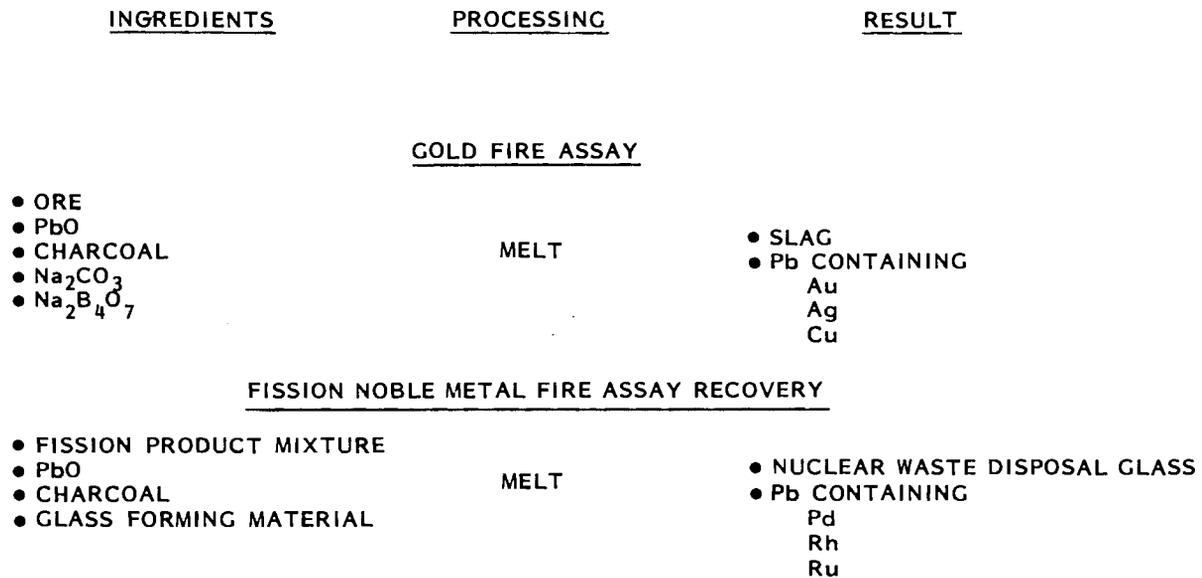


FIGURE 1. Comparison of Gold Fire Assay with Fission Noble Metal Fire Assay Recovery

reducing agent. Figure 2 shows how fire assay recovery of noble metals might be integrated into a nuclear-waste vitrification system. The mixture would be melted in a nuclear-waste glass melter. During melting, the PbO and reducing agent react to form molten lead. The molten lead scavenger alloys with the noble metals in the batch and sinks to the melter bottom as a separate phase where it can be collected. This alloy would be processed by conventional methods to separate the noble metals from the lead scavenger and recover the lead for reuse. The glass could be cast into cylinders or marbles, or undergo further processing developed or proposed for nuclear waste glasses (Mendel 1978; Rusin et al. 1978).

There will be radioactivity associated with the fission product noble metals. Most will be due to the noble metals themselves. Before use, a storage period may be needed to allow decay of the short-lived fission noble

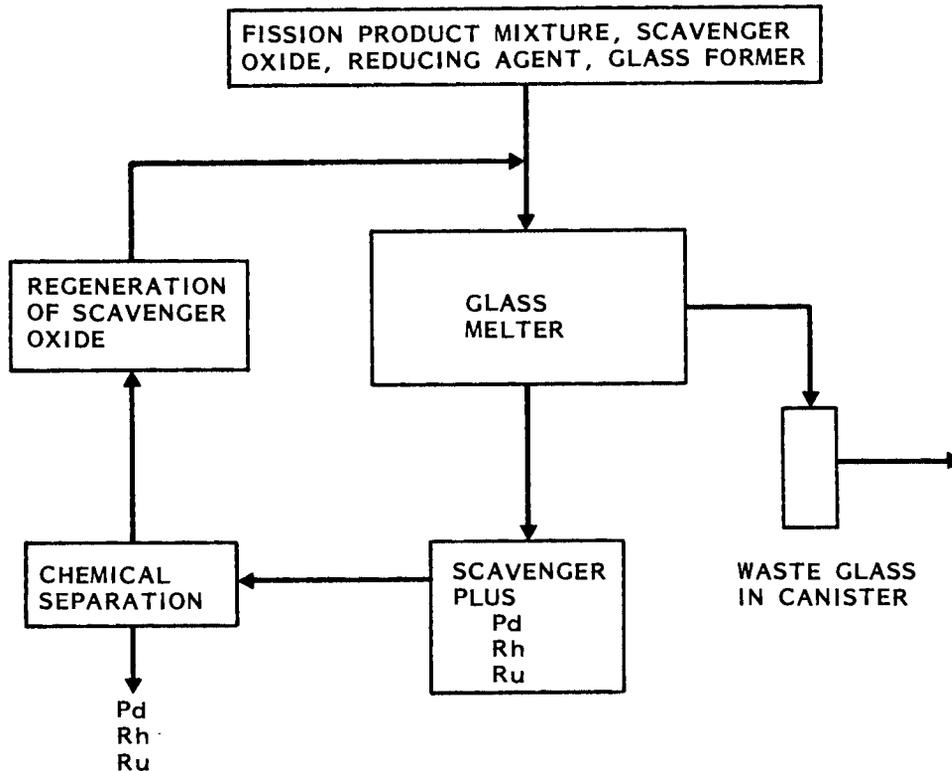


FIGURE 2. Schematic of Fire Assay Recovery of Noble Metals Incorporated into Nuclear Waste Glass Production

metal isotopes and so reduce the potential for radiation exposure. Ruthenium-106 and  $^{107}\text{Pd}$  dominate the longer-term radioactivity of the noble metals. Use of these materials will require applications in which this radioactivity will not result in significant population exposure.

Radioactivity may also be present from contamination of the extracted material by other radionuclides from the batch. Present indications are that this contamination will be very low. The scavenger extracts very little in addition to the noble metals. The degree of contamination will be determined from tests performed using actual fission product mixtures. If significant, separation of the non-noble-metal radionuclides may be accomplished using standard chemical processing techniques.

## CONCLUSIONS

Several conclusions were reached during the course of this work. The most noteworthy are summarized below.

- The fire assay technique appears to offer promise as a means of recovering strategic noble metals and producing a nuclear waste glass in a single process.
- Recovery was found to depend only on reduction of the scavenger oxide to metal. When such reduction was achieved, no significant difference in noble metal recovery efficiency was found among the scavengers studied. These included PbO, SnO, CuO, Bi<sub>2</sub>O<sub>3</sub>, and Sb<sub>2</sub>O<sub>3</sub>.
- Not all reducing agents studied (flour, cornstarch, sugar, graphite, charcoal and silicon) were able to reduce all scavenger oxides to metal. Only graphite would reduce SnO and CuO. However, Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and PbO were reduced by all of the reducing agents tested.
- Palladium, Rh, and Ru recoveries of ~90% were achieved in "crucible-scale" tests with lead used as a scavenger.
- Lead appears to exhibit the best scavenger characteristics. It extracts the noble metals and does not appear to have a detrimental effect on the quality of the glass produced.
- Viscosity is an important property of the melt. An excessively high viscosity hampers separation of the scavenger metal, whereas a low viscosity may lead to increased volatile loss of RuO<sub>4</sub>.
- Glasses were produced that appeared homogeneous and exhibited leach behavior in a 24-hour test of crushed glass in 99°C distilled water comparable to that of nuclear waste glasses reported in the literature. These glasses were produced from batches containing PbO as a scavenger and charcoal as a reducing agent.



## SAMPLE PREPARATION AND ANALYSIS

The fire assay recovery technique was tested using mixtures of a fission product oxide simulation, various scavenger oxides and reducing agents, and glass forming materials. These mixtures were melted and the scavenger metal was separated from the glass. Noble metal recovery was determined from analyses of the scavenger metal and glass. It is not anticipated that use of a liquid slurry feed instead of a mixture containing a fission product calcine will adversely affect noble metal recovery. Liquid feeding may actually be helpful as it will ensure the thorough mixing of the components which may be necessary for good extraction.

### SAMPLE PREPARATION

The ingredients used in tests of the fire assay recovery technique are shown in Table 1. The simulated fission product, Pw-4b-6+7, is a nonradioactive mixture. Its composition is based on a fuel burnup of 33,000 MWd/MTU (Mendel et al. 1977). The frit, 76-101, is a premelted and crushed glass developed for nuclear waste vitrification (Mendel et al. 1977). Lead oxide was chosen for testing as scavenger because it is used in the gold ore fire assay technique upon which the noble metal recovery is based. Each of the remaining oxides was investigated because of its proximity to PbO on the periodic table or, in the case of CuO, because of its chemical similarity to PbO. All of the metal oxides, graphite, and silicon metal used were reagent-grade materials. Briquets, crushed to -200 mesh, were used as the charcoal source. The flour, cornstarch, and sugar were ordinary kitchen materials. All combinations of scavenger oxide and reducing agent were tested and evaluated for their efficiency for recovering noble metals from the mixture.

The required amounts of each material were mixed with an automatic mortar and pestle. Batch size was ~100 g. Each batch was poured into a porcelain crucible that was then placed in a preheated furnace. The same processing temperature, 1100°C, was used for all melts except for the first two screening test experiments. These were melted at 1050°C. All batches were melted in air. After 30 minutes, each melt was removed from the furnace and poured onto

TABLE 1. Materials Used in Fire Assay Recovery Tests

Simulated nonradioactive fission product (F.P.) mixture<sup>(a)</sup>

Glass additive<sup>(b)</sup>

Na<sub>2</sub>CO<sub>3</sub>

Scavenger oxide:

- SnO
- Bi<sub>2</sub>O<sub>3</sub>
- Sb<sub>2</sub>O<sub>3</sub>
- CuO
- PbO

Reducing agent:

- Graphite
- Flour
- Sugar
- Cornstarch
- Silicon
- Charcoal

---

(a) Contained 5.50 wt% RuO<sub>2</sub>, 3.10 wt% PdO, and 1.23 wt% Rh<sub>2</sub>O<sub>3</sub>.

(b) 76-101 frit: 59.7 wt% SiO<sub>2</sub>, 14.2 wt% B<sub>2</sub>O<sub>3</sub>, 4.2 wt% Na<sub>2</sub>O, 7.45 wt% ZnO, 3.0 wt% CaO, 4.45 wt% TiO<sub>2</sub>.

a steel plate where the scavenger metal, if it had reduced, separated from the glass. The degree to which the metal coalesced into an easily separated button was evaluated. The appearance of the glass was also evaluated for gross phase separation and crystallinity.

#### ANALYTICAL METHODS

The chemical compositions of the simulated fission product mixture, metal buttons, and glass samples were determined with Induction-Coupled Plasma Spectrophotometry (ICP). Samples of each material were analyzed for their Pd, Ru and Rh contents. With this information, the efficiency of recovery of noble metals from each batch was calculated. Details of the analysis of the noble metals are found elsewhere (Lautensleger and Hara 1982).

In addition, the noble metal distribution in certain lead and bismuth recovery samples was determined using the microprobe capability of a Scanning Electron Microscope (SEM).

The reaction sequences in a number of batches were studied in order to provide information about the reaction temperatures, reaction rates and other

conditions necessary for successful recovery. Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) measurements were used in this investigation. The unit used for these measurements was a duPont Model 990 thermal analyzer.<sup>(a)</sup> A heating rate of 10°C/min was used for all measurements. A number of batches were analyzed, both those from which metal was recovered and those in which scavenger metal did not reduce. It was hoped that characteristic differences between these two types of batches would be observed.

The viscosity of the glass was known to be a factor that affected scavenger metal recovery. If the glass were too viscous, it would be more difficult for the metal to separate. The viscosity of the glass was measured using a Brookfield Model RVT rotating spindle viscometer<sup>(b)</sup> with a platinum spindle. This instrument was calibrated using a standard viscosity glass obtained from the National Bureau of Standards (NBS). Measurements were made in air in a resistance-heated furnace.

The leaching resistance of the glass portion of the melt was not of primary importance in this investigation. However, leach resistance is an important storage-related property of a waste glass, and it would be advantageous to know what approximate durabilities might be expected. Thus, the chemical durability of one glass was measured by using a Soxhlet extraction technique. A 1-g sample of glass ground to -40 +60 U.S. standard mesh size was placed in a 200-mesh stainless steel envelope and subjected to 99°C distilled water for 24 hours. The weight loss of the glass was determined.

---

(a) E. I. duPont de Nemours, Inc., Wilmington, Delaware.

(b) Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts.



## EXPERIMENTAL RESULTS

Various aspects of the fire assay technique were investigated. A number of different scavengers and reducing agents were tested, and the effect that each had on noble metal recovery was evaluated. The effect of varying the amount of scavenger, reducing agent, and flux in the batch was also explored. This was done to determine the minimum amounts of these materials needed for successful recovery. Information needs specifically related to process design such as scavenger recovery and recycling procedures or reaction times were not addressed in this study.

### SCREENING TESTS

The composition of the initial batch used for determining whether fire assay extraction of noble metals might be possible is shown in Table 2. A 2:1 weight ratio of glass additive (76-101) to fission-product mixture was chosen. This ratio was the proportion for which this glass additive was designed (Mendel et al. 1977), and was maintained throughout the course of the work. Low levels of PbO and graphite were added in order to cause as little change in glass composition as possible. For this same reason, no Na<sub>2</sub>CO<sub>3</sub> was added; the addition of sodium would reduce the resulting glass' resistance to leaching.

No metal button was produced after heating the mixture for 2 hours at 1050°C in air. The melt might have been too viscous to permit the lead, if it had been reduced to metal, to easily separate from the glass.

TABLE 2. Batches Used During Initial Fire Assay Recovery Testing

<u>Component</u>	<u>First Experiment, wt%</u>	<u>Second Experiment, wt%</u>
Simulated FP mixture	28.4	12.8
Glass additive	57.6	25.6
PbO	12.9	34.2
Graphite	1.1	1.7
Na <sub>2</sub> CO <sub>3</sub>	--	25.6

A second experiment was performed with a batch designed to ensure that lead metal would be produced. This batch is shown in Table 2. Greater proportions of lead oxide and graphite were present than in the first experiment. Sodium carbonate was added to reduce the glass' viscosity. The desired result was achieved; lead metal formed and was easily separated from the remainder of the melt. This button was found to contain most of the Pd and Rh present in the fission-product mixture. Testing of the leachability of the glass from which the lead was removed was beyond the scope of this preliminary work. However, large sodium additions to glass are known to degrade its resistance to leaching (Mellinger 1979). Because of the large quantity of  $\text{Na}_2\text{CO}_3$  added to the batch, the glass undoubtedly had a high leachability. In later work, the amount of flux addition was varied to determine the minimum that could be added while still assuring adequate recovery. This minimum addition would result in glass with higher leach resistance. During full-scale noble metal recovery no flux such as  $\text{Na}_2\text{CO}_3$  would be added. The pre-melted glass additive would be formulated to have the correct viscosity without sodium or other addition.

#### EFFECTS OF SCAVENGER AND REDUCING AGENT TYPES

A number of materials were chosen for evaluation as potential scavengers and reducing agents. Each scavenger was tested in combination with each reducing agent. The batches used for this work are shown in Table 3. These were the same as the second of the two screening batches, except that the proportion of reducing agent was doubled. This was done in order to insure that an adequate amount of reducing agent was present to reduce the scavenger oxide.

The amount of scavenger metal recovered from each melt was determined. These values are shown in Figure 3. Multiple values for a single pair indicate the recovery from replicate experiments. Because of the difficulty in separating all of the metal from the glass, the error band on each of these values is fairly large. They do, however, give a relative indication of how recovery was affected by differences in reducing agent and scavenger.

SCAVENGER	REDUCING AGENT					
	FLOUR	GRAPHITE	SILICON	CORNSTARCH	SUGAR	CHARCOAL
Sb	13	61	29	21	20	44
Pb	(a)	61	23	9 0	14	33
Bi	7	86	22	4 31 22	19	78
Sn	(a)	48	(a)	(a)	(a)	(a)
Cu	(a)	77	(a)	(a)	(a)	(a)

(a) NO METAL PRODUCED

FIGURE 3. Scavenger Metal Recovery with Various Reducing Agents and Scavenger Metals (wt%)

TABLE 3. Batches Used to Test Scavengers and Reducing Agents

<u>Component</u>	<u>wt%</u>
Simulated F.P. mixture	12.6
Glass additive	25.2
Na <sub>2</sub> CO <sub>3</sub>	25.2
Scavenger oxide <sup>(a)</sup>	33.6
Reducing agent <sup>(b)</sup>	3.4
	<u>100.0</u>

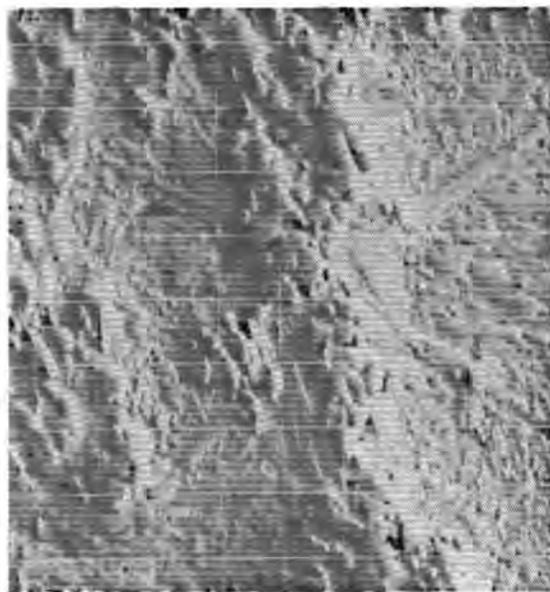
(a) SnO, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, CuO, or PbO

(b) Carbon, flour, sugar, cornstarch, silicon, or charcoal

It can be seen that graphite was the only reducing agent capable of reducing significant quantities of all scavenger metals tested. Charcoal was only slightly less effective than graphite. Sugar, cornstarch, and silicon had a much lower degree of effectiveness. Flour was the least effective of the reducing agents investigated.

Bismuth and antimony oxides were the most easily reduced scavengers. PbO was close to these oxides in this respect. SnO and CuO were the most difficult to reduce.

An SEM examination of bismuth and lead recovery samples showed that on a microscopic scale the noble metals are not homogeneous in these scavengers after cooling. Figure 4 is a scanning electromicrograph which shows the noble



10 $\mu$

A) PHOTOMICROGRAPH OF SAMPLE

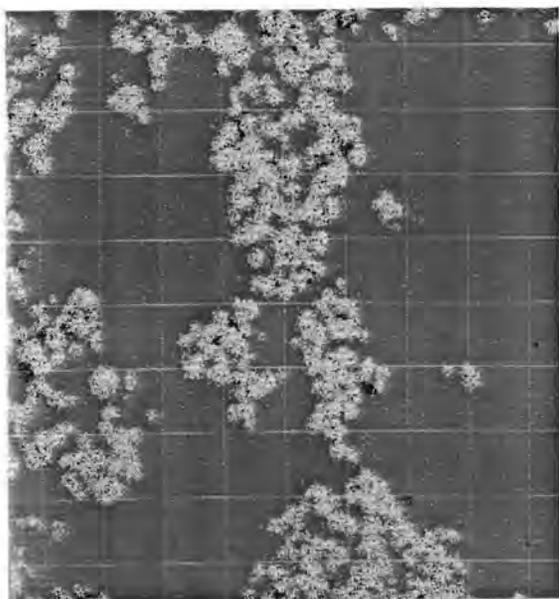


10 $\mu$

B) MICROPROBE ANALYSIS FOR Pb

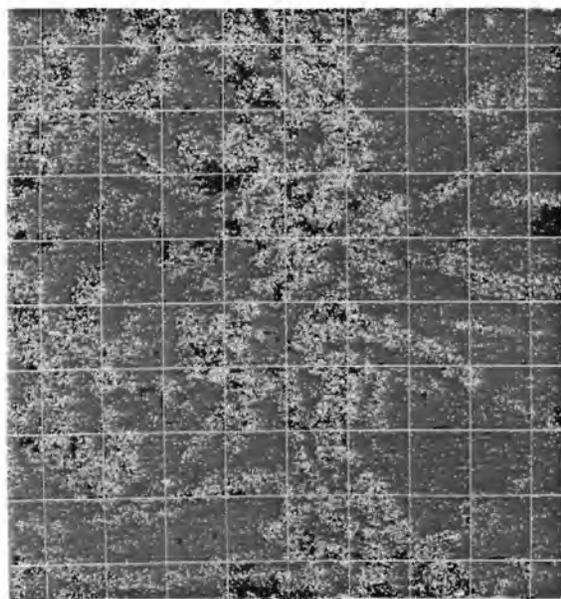
FIGURE 4. Lead Metal-Scavenger Sample

Figure 4. (cont)



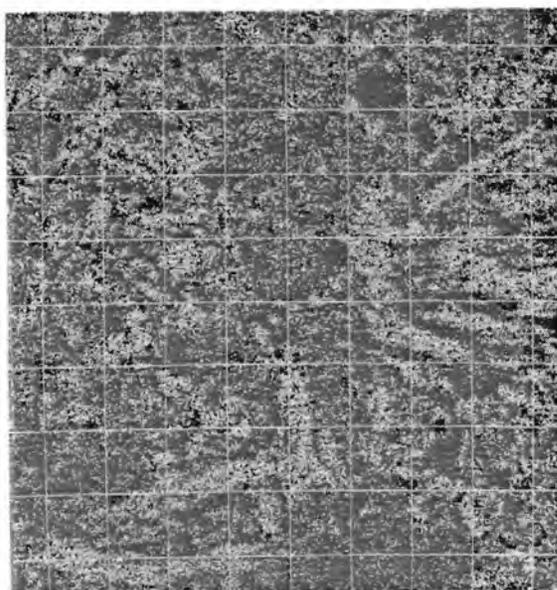
10 $\mu$

C) MICROPROBE ANALYSIS FOR Ru



10 $\mu$

D) MICROPROBE ANALYSIS FOR Pd



10 $\mu$

E) MICROPROBE ANALYSIS FOR Rh

metal distribution in a recovered lead-button sample. The Ru in the button is seen to be segregated in a separate phase. This phase also contains some Rh and an insignificant amount of Pd, but does not contain Pb. A second phase is present that contains Rh, Pd, and Pb. The remainder of the sample contains Pb and Pd, which appear to be fairly uniformly distributed. The bismuth sample is shown in Figure 5. Noble metal distributions are similar to those in the Pb sample. The Ru and Rh are present in a phase from which Pd and Pb are excluded. Rhodium and Pd are found in a second phase. In the bismuth button, however, the remainder of the Pd is not uniformly distributed, but is present in two additional types of inclusions. The bismuth in this sample appears to be uniformly distributed, except where the Ru-Rh phase is present.

The microscopic heterogeneity of the noble metals in the lead and bismuth scavengers indicates that macroscopic nonuniform distribution of these elements could be expected in products of the recovery process. The noble metal phases might be expected to precipitate from the molten metal prior to its solidification. In addition, all of the noble metals have densities greater than the densities of any of the molten scavengers. Thus the precipitated phase would be expected to sink in the molten metal and result in a nonuniform distribution.

The recovery efficiency of each scavenger-reducing agent pair was determined. The scavenger metal reduced from a mixture was analyzed for Pd, Ru and Rh content. The following equation was then used to calculate the percentage of each noble metal recovered from the batch:

$$\frac{R \times S}{B} \times 100 = N$$

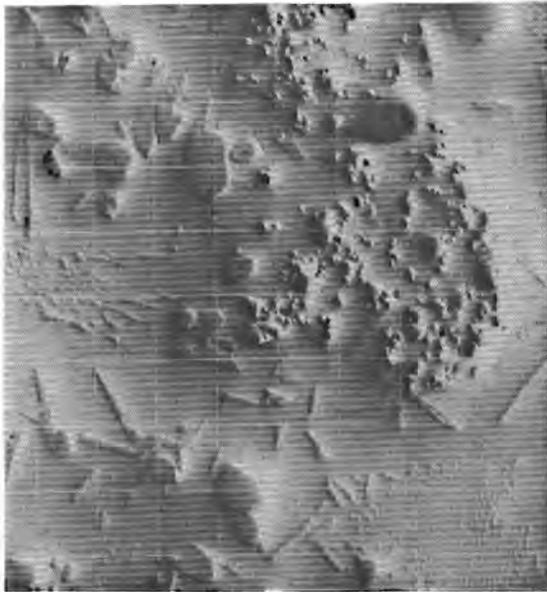
where

R = weight fraction of Pd, Rh, or Ru in recovered scavenger metal

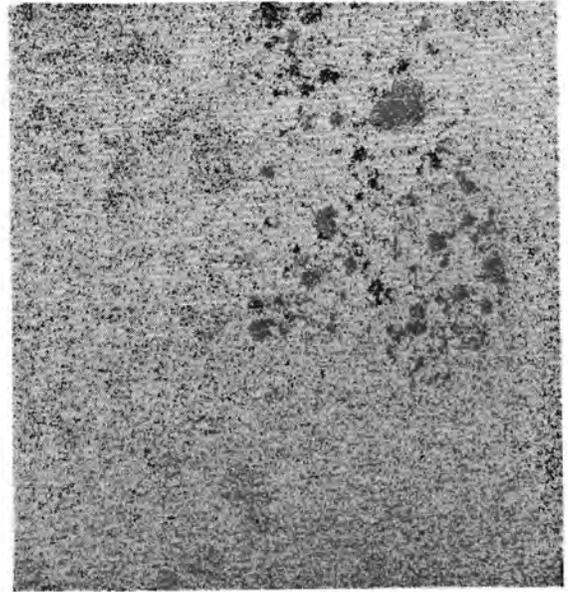
S = weight of scavenger metal recovered

B = weight of Pd, Rh, or Ru in batch

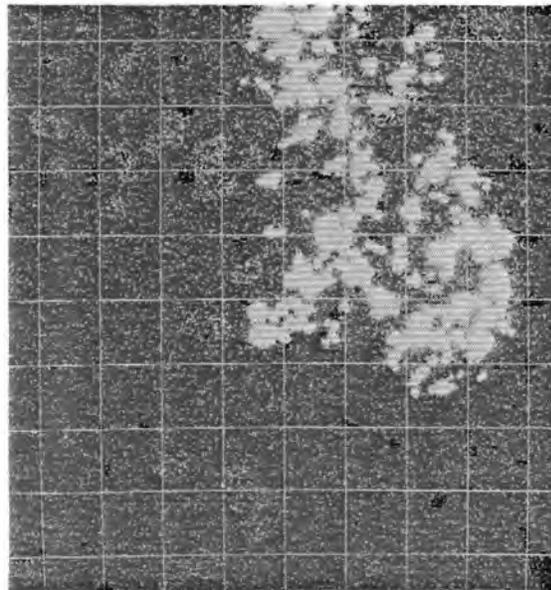
N = percentage of Pd, Rh or Ru recovered in scavenger metal.



A) PHOTOMICROGRAPH OF SAMPLE

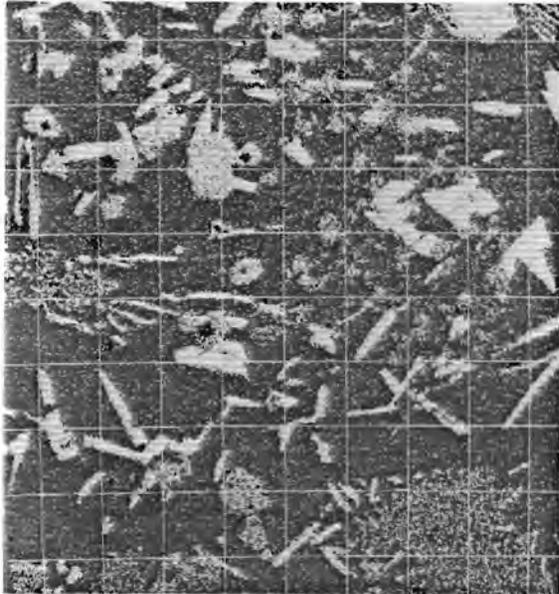


B) MICROPROBE ANALYSIS FOR BI



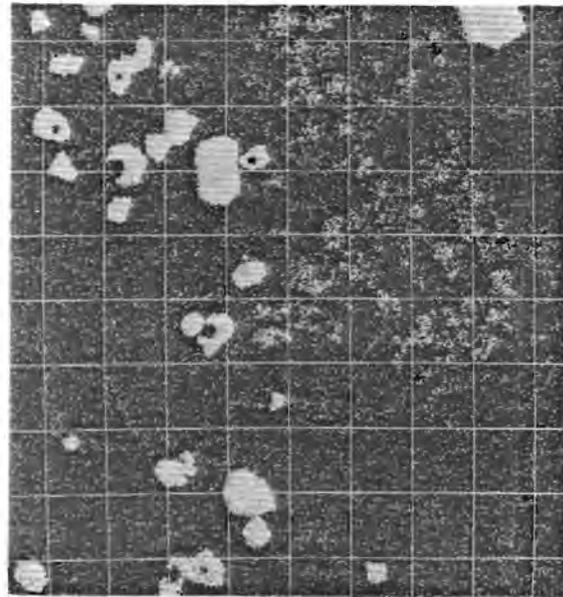
C) MICROPROBE ANALYSIS FOR Ru

FIGURE 5. Bismuth Metal-Scavenger Sample



10 $\mu$

D) MICROPROBE ANALYSIS FOR Pd



10 $\mu$

E) MICROPROBE ANALYSIS FOR Rh

FIGURE 5. (Cont.)

The validity of two assumptions affected the accuracy of the above equation. The first assumption was that each noble metal is uniformly distributed throughout each scavenger reduced from a melt. This assumption was made because only a portion of a scavenger sample was analyzed. It was later found that the previously discussed nonuniform distribution occurs. This contributed significant uncertainty to the results. Higher or lower recovery efficiency might be calculated depending upon whether the portion of scavenger chosen for analysis was enriched or depleted in a noble metal. The second assumption was that all scavenger metal reduced from the melt could be separated from the glass, allowing the metal to be weighed. In some melts this was difficult. An error in the determination of this quantity would cause the

calculated recovery efficiency to be low. The estimated uncertainty resulting from the homogeneity and scavenger weight assumptions is  $\pm 30\%$ , based on multiple experiments.

The calculated recovery efficiencies for each scavenger-reducing agent combination are shown in Figures 6 through 8. Recovery efficiency was found to be solely dependent on reduction to metal of a portion of the scavenger oxide. When noble metal recoveries are compared to the scavenger recoveries shown in Figure 3 it can be seen that within the bounds of our data, noble metal recovery did not correlate with the amount of scavenger reduced from a melt. Also, none of the scavengers or reducing agents were found to contribute to consistently better noble metal recovery.

Both Pd and Rh were more effectively recovered than Ru. Palladium and Rh recoveries ranged from  $\sim 70$  to 100%. Ruthenium recovery was lower, ranging from  $\sim 30$  to 70%. The lower Ru recovery was probably due to loss of volatile  $\text{RuO}_4$  from the melt; this oxide is known to be a volatile Ru species (Christian 1976). Volatile loss is suspected because of the low mass balances for this element. The mass balances

$$\frac{(\text{Noble metal in scavenger} + \text{amount of glass})}{(\text{amount in batch})} \times 100$$

for Ru were  $\sim 60$  to 80%. Those for Rh and Pd were higher,  $\sim 75$  to 113%. Most if not all of the Pd and Rh could be accounted for, while much of the Ru could not. Variation in the mass balance is probably due to the previously discussed uncertainties in noble metals distribution and scavenger weight.

One aspect of the use of different scavenger/reducing agent pairs is their effect on the quality of the glass that remains after the noble metals have been separated. A phase-separated, heterogeneous, highly crystalline material is almost certain to be found unacceptable as a glass for waste disposal. Figure 9 shows the effects of the various reducing agents and scavengers on the observed homogeneity of the glass produced from each batch. When Pb or Bi were used as scavengers, the glasses produced were observed to be homogeneous single phase materials, although minor crystallinity could be seen in batches containing Bi. Use of any other scavenger resulted in a

REDUCING AGENT

	FLOUR	GRAPHITE	SILICON	CORNSTARCH	SUGAR	CHARCOAL
Sb	100	100	97	100	84	90
Pb	(a)	72	75	66	75	73
Bi	94	34	120	63	113	82
Sn	(a)	69	(a)	(a)	(a)	(a)
Cu	(a)	100	(a)	(a)	(a)	(a)

(a) NO SCAVENGER PRODUCED

FIGURE 6. Palladium Recovery When Using Various Reducing Agents and Scavenger Metals (wt%)

	<u>REDUCING AGENT</u>					
	FLOUR	GRAPHITE	SILICON	CORNSTARCH	SUGAR	CHARCOAL
Sb	88	100	113	113	25	52
Pb	(a)	(b)	88	(b)	75	90
Bi	100	50	100	56	88	77
Sn	(a)	100	(a)	(a)	(a)	(a)
Cu	(a)	50	(a)	(a)	(a)	(a)

(a) NO SCAVENGER PRODUCED

(b) NOT ANALYZED

FIGURE 7. Rhodium Recovery When Using Various Reducing Agents and Scavenger Metals (wt%)

		<u>REDUCING AGENT</u>					
		FLOUR	GRAPHITE	SILICON	CORNSTARCH	SUGAR	CHARCOAL
SCAVENGER	Sb	62	67	76	73	19	71
	Pb	(a)	(b)	57	(b)	62	58
	Bi	44	19	89	27	63	45
	Sn	(a)	55	(a)	(a)	(a)	(a)
	Cu	(a)	100	(a)	(a)	(a)	(a)

(a) NO SCAVENGER PRODUCED  
 (b) NOT ANALYZED

FIGURE 8. Ruthenium Recovery When Using Various Reducing Agents and Scavenger Metals (wt%)

		REDUCING AGENT					
		FLOUR	GRAPHITE	SILICON	CORNSTARCH	SUGAR	CHARCOAL
SCAVENGER	Sb	●	●	●	●	●	●
	Pb	▲	▲	◆	▲	◆	◆
	Bi	▲	●	◆	▲	▲	▲
	Sn	■	●	■	■	■	●
	Cu	●	●	●	●	●	●

■ VERY POOR  
 ● POOR  
 ▲ GOOD  
 ◆ VERY GOOD

**FIGURE 9.** Glass Homogeneity When Various Reducing Agents and Scavenger Metals Were Used

material which was a very heterogeneous, crystalline glass. Batches containing SnO produced a non-glass assemblage of materials. When the glass was made up without scavenger or reducing agent addition, a very good homogeneous melt resulted.

A 24-hour Soxhlet leach test was performed on the glass that was made from an extraction batch containing 40 wt% PbO and 15 wt% Na<sub>2</sub>CO<sub>3</sub>. Other waste glasses which have been tested using this technique have shown values of ~0.5 to 1.5 wt% (Mendel et al. 1977). A weight loss of 2.4% was found for the extraction glass. Improvements in the leachability can be expected with further development aimed at enhancing glass quality. It should be possible to design a batch from which extraction can be accomplished and an acceptable waste glass produced.

Based on the comparison of recovery efficiencies, effect on glass quality, and anticipated materials costs, PbO and charcoal were chosen as the materials with which further testing would be carried out.

#### EFFECTS OF REDUCING AGENT LEVEL ON SCAVENGER REDUCTION

Varying the amount of reducing agent in the batch will vary the amount of scavenger oxide which is reduced to metal. A series of tests was performed to determine the relationship between reducing agent level and scavenger metal recovery. The stoichiometric relationship between scavenger and reducing agent was not taken into consideration in this work. This was primarily because these crucible scale tests were performed in air, and a portion of the reducing agent reacted with the oxygen in air rather than the scavenger oxide.

A linear relationship between reducing agent addition and scavenger metal recovery was found with scavenger recovery below 85 to 95%. Once this recovery was achieved, however, further reducing agent increases had no effect. This behavior is shown in Figure 10 for batches containing PbO and flour or cornstarch. Similar behavior would be expected if graphite or charcoal were substituted as reducing agents.

#### EFFECT OF VARYING THE AMOUNT OF SCAVENGER OXIDE AND FLUX LEVEL

Tests were made in order to determine the amounts of scavenger oxide and flux which, when present in the batch, would result in optimum noble metal recovery. Based on the previously discussed evaluation of scavengers and reducing agents, PbO and charcoal were used in this work. The batch composition ranges in this testing are shown in Table 4. Figures 11 and 12 show plots of Pd, Rh, and Ru recovery as functions of PbO and Na<sub>2</sub>CO<sub>3</sub> in the batch.

Neither Pd nor Rh recoveries were consistently affected by the amount of scavenger oxide or flux addition. Much of the variability in recovery was probably the result of the sampling uncertainty previously discussed. The only significant, consistent effect seen was an increase in Ru recovery as Na<sub>2</sub>CO<sub>3</sub> was decreased to ~10 wt% and PbO to ~20 wt%. The increased Ru recovery may therefore have been due to decreased volatile loss of RuO<sub>4</sub> with increasing melt viscosity. Ruthenium volatility was not determined but will be investigated in future work.

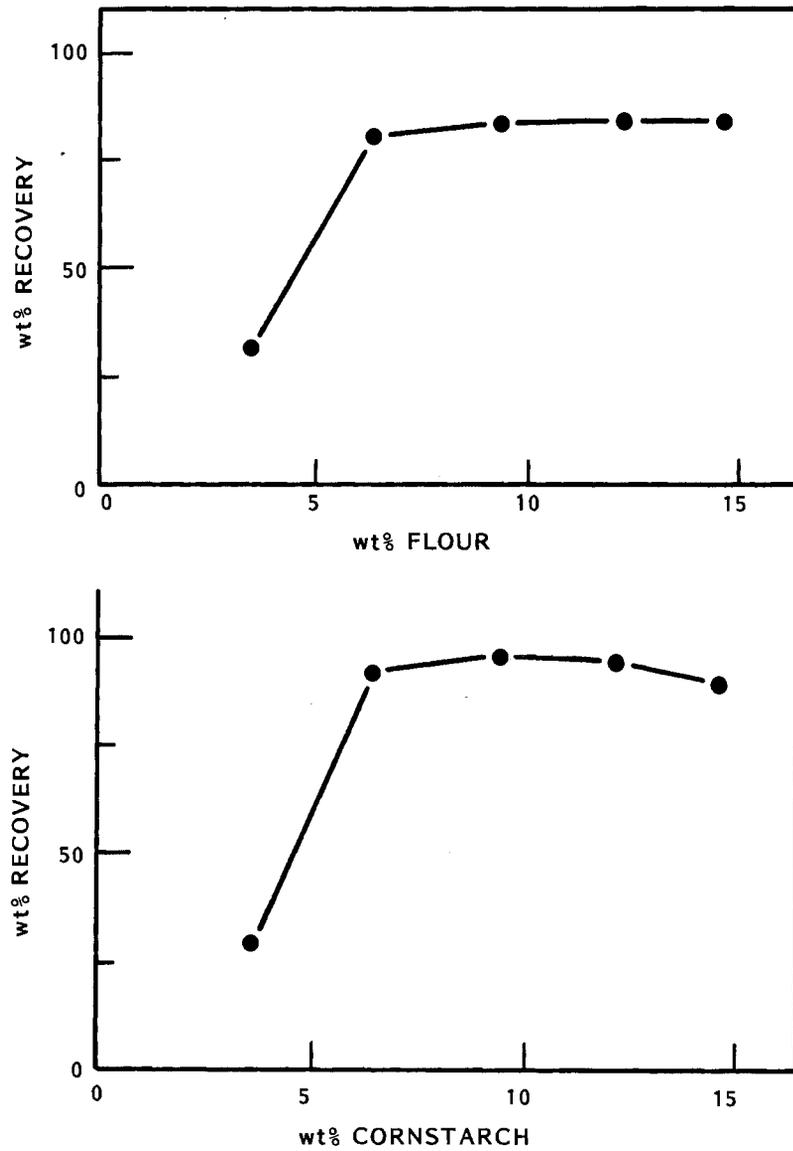


FIGURE 10. Effect of Flour and Cornstarch Levels on Lead Scavenger Recovery

TABLE 4. Batches Used to Test Flux and Scavenger Variations

Component	Tested, g
Simulated FP mixture	15
Glass former	30
Flux ( $\text{Na}_2\text{CO}_3$ )	0 to 30
PbO	10 to 40
Charcoal	4

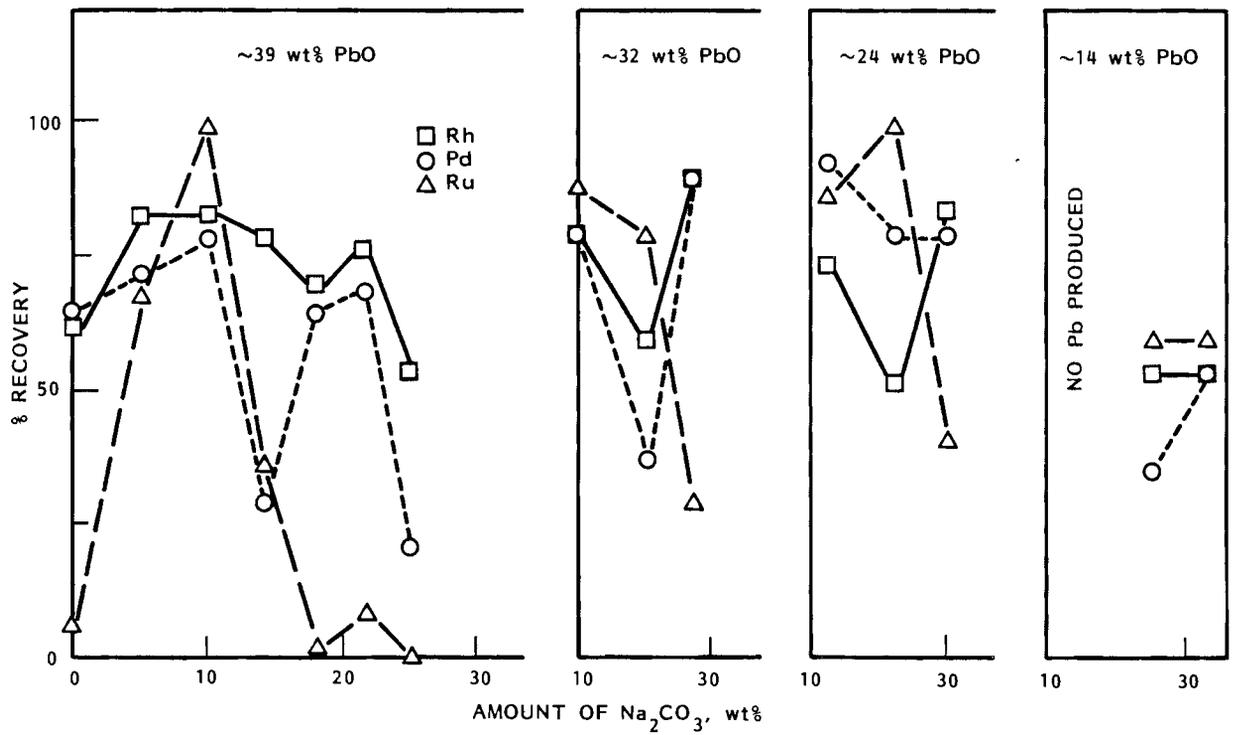


FIGURE 11. Noble Metal Recovery as a Function of  $\text{Na}_2\text{CO}_3$  in Batch at Various  $\text{PbO}$  Levels

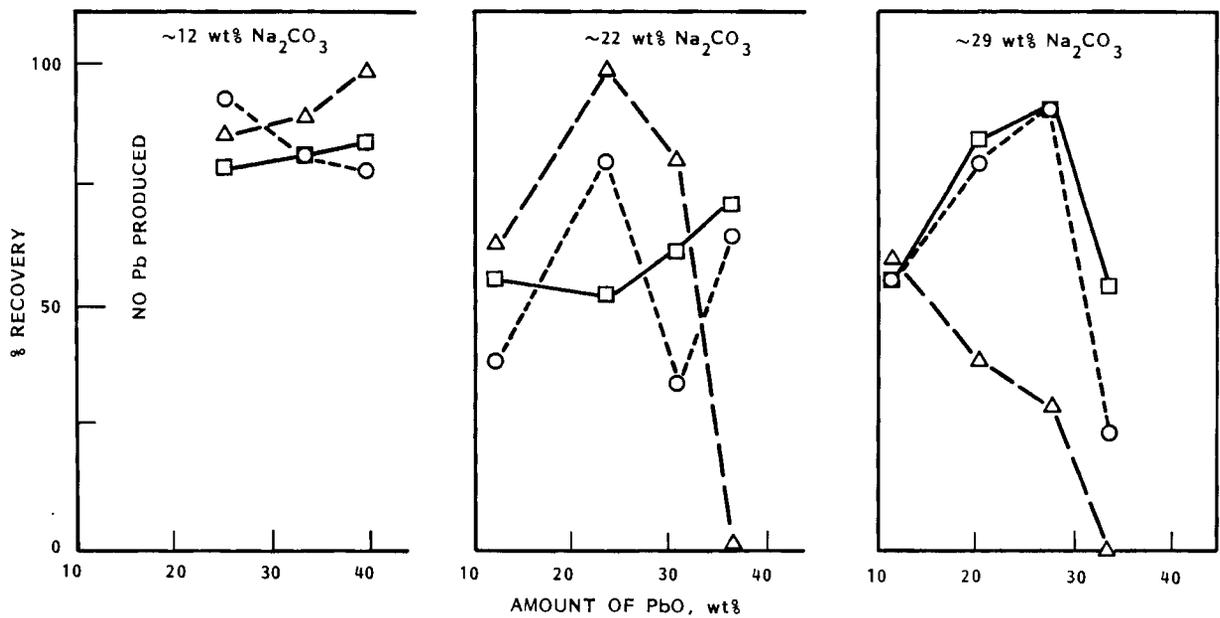


FIGURE 12. Noble Metal Recovery as a Function of  $\text{PbO}$  in Batch at Various  $\text{Na}_2\text{CO}_3$  Levels

Based on these experiments, a batch containing 20 g (25.2 wt%) PbO and 10 g (12.7 wt%) Na<sub>2</sub>CO<sub>3</sub> was chosen as optimum. The batch exhibited excellent noble metal recovery, though the lead was somewhat difficult to separate from the glass. The batch also minimized the additions to the glass needed to achieve separation. By minimizing these additions, the effects of noble metal separation on the quality of the glass produced will be lowered. This is an important consideration if the glass is to be used as a nuclear waste disposal material.

The viscosity of the molten batch is an important factor affecting scavenger separation. The mixture which contained 20 g PbO and 10 g Na<sub>2</sub>CO<sub>3</sub> appeared to have the maximum viscosity which would still allow such separation. This glass viscosity at its 1100°C processing temperature was 20 to 25 poise.

The Na<sub>2</sub>CO<sub>3</sub> has a much greater affect on viscosity than does PbO. This is illustrated in Table 5. An increase of Na<sub>2</sub>CO<sub>3</sub> from 20 to 30 g while holding the PbO at 20g caused a 50% decrease in viscosity. The same increase in PbO at 10 g caused only a 20% decrease in viscosity.

TABLE 5. Viscosities of Recovery Batches as a Function of Temperature and Composition

<u>Composition(a), g</u>		<u>Viscosity at Temperature, poise</u>		
<u>Na<sub>2</sub>CO<sub>3</sub></u>	<u>PbO</u>	<u>1100°C</u>	<u>1000°C</u>	<u>900°C</u>
20	20	6	14	37
30	20	3	7	17
10	20	22	54	225
10	30	16	49	175

(a) Remainder of batch: 15 g fission product oxide simulation, 30 g glass former, 4 g charcoal.

#### BATCH REACTION SEQUENCE INVESTIGATION

An attempt was made to study the reaction sequence in batches used for fire assay noble metal recovery. It was hoped that information on reaction temperatures, reaction rates and other conditions affecting the process would

be found and that characteristic differences would be seen between batches where successful separation was achieved and those from which no scavenger was produced. Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) were used to study the batches. The results from both of these types of analyses were inconclusive. No consistent differences could be seen between fire assay batches from which successful recovery had been achieved, and those in which no scavenger metal was found. For this reason, these data have not been included in this report. Two factors contributed to the difficulty in interpreting the results of these tests. A great number of reactions occurred in the samples. These included release of residual nitrates from the simulated fission-product mixture, decomposition of the reducing agents and  $\text{Na}_2\text{CO}_3$ , and reactions among the various components. The large magnitude of the resulting endotherms and exotherms masked any differences between samples in DTA testing. DSC measurements, which were more sensitive to small changes in a sample, were limited by the instrument to temperatures below  $550^\circ\text{C}$ . This is lower than the temperature where significant reaction began.

## DISCUSSION

In the following section the mechanism of fire assay recovery and conditions necessary for successful recovery are discussed. Subsequent sections address scavenger-reducing agent interaction and properties of the scavenger and glass which affect recovery. Finally, the effects of the various scavengers and reducing agents on the process are discussed.

### FIRE ASSAY RECOVERY MECHANISM

The principle upon which fire assay recovery is based is very simple. The reducing conditions in the melt cause the oxides of Rh, Ru and Pd to be reduced to metal. The scavenger oxide is also reduced. The molten scavenger metal dissolves or collects the noble metals and carries them through the melt as it sinks. Only a minimal number of conditions must be satisfied in order for noble metal recovery to be successful:

- An oxide must be present in the melter batch that will reduce to metal under the given reducing conditions.
- Reducing conditions must be induced and maintained.
- The reduced metal must be molten at the processing temperature used.
- The glass phase of the melt must have a low enough viscosity to allow the molten metal phase to separate.

Palladium and Rh were found to have similar recovery efficiencies in any particular batch used in this work. Ruthenium recovery was generally lower. This was probably due to volatile loss of Ru in the form of  $\text{RuO}_4$ . This occurred before the ruthenium oxide was reduced to the metal. As expected, Ru loss was reduced and recovery increased by increasing the viscosity of the fire assay. This was most effectively accomplished by decreasing the sodium content of the batch.

## SCAVENGER REDUCTION AND SEPARATION

Not all scavenger-reducing agent pairs were capable of producing scavenger metal. This was caused by differences in the reactivities of the reducing agents and in the stabilities of the various scavenger oxides. Copper oxide and tin oxide have significantly higher melting points than the other scavenger oxides, as Table 6 shows. The high melting points of these oxides require that the reducing agent-scavenger reaction occur after the scavenger oxide has dissolved in the glass phase. The lower melting points of PbO, Sb<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> allow reduction to occur directly from the molten oxide before a glass melt has formed. A scavenger oxide's tendency to be reduced in these experiments cannot, however, be predicted from the free energy of reaction with a reducing agent. The free energies for the reactions with silicon and carbon are shown in Table 6. It can be seen that a lower free energy is not consistently associated with the more easily reduced scavengers. As a result, it is evident that kinetic factors control the tendency of the scavenger-reducing agent reaction to reduce the scavenger to metal.

TABLE 6. Free Energies of Reduction of Scavengers by Si and C

<u>Scavenger</u>	<u><math>\Delta F^{\circ}</math> 1100°C (Kcal/mole scavenger metal)</u>	
	<u>Si</u>	<u>C</u>
SnO	38.2	13.6
CuO	63.5	38.8
PbO	51.5	26.8
Bi <sub>2</sub> O <sub>3</sub>	85.0	48.0
Sb <sub>2</sub> O <sub>3</sub>	66.0	29.0

Certain properties of the scavenger metal are important to its suitability for noble metal recovery. These properties are shown in Table 7. The metal must be molten at the processing temperature chosen. Also, its boiling point must be above this temperature. Zinc is an example of a metal that would be unsuitable for fire assay recovery because of its low boiling point, 907°C. Once reduced to the metal, it would boil out of the glass and re-oxidize or deposit elsewhere in the melter or off-gas system.

TABLE 7. Properties Significant to Scavenger Performance<sup>(a)</sup>

Element	Metal Oxide Melting Point, °C	Metal Melting Point, °C	Metal Boiling Point, °C	Density, g/cm <sup>3</sup>
PbO	886	327	1740	11.3
Bi <sub>2</sub> O <sub>3</sub>	817	271	1560	9.8
Sb <sub>2</sub> O <sub>3</sub>	656	630	1750	6.7
CuO	1326	1083	2567	8.9
SnO	1080 <sup>(b)</sup>	232	2260	6.6
ZnO	1975	419	907	7.2

(a) From Weast (1980)

(b) Decomposition temperature

Density is a property that may make some scavenger materials more attractive than others. A high-density metal such as Pb sinks through the glass phase more easily than one such as Sb, which has a lower density. This may be particularly important if a higher-viscosity glass is used.

Graphite and charcoal were the most effective reducing agents because they were the slowest to react with the air in which the batches were heated. A significant portion of these materials remained in the melt once the reaction temperature was reached. The other reducing agents reacted with the atmospheric oxygen in the furnace and were significantly depleted before a molten phase could form to seal out this oxygen. Thus, less of these reductants were present to cause reduction of the scavenger metal oxide. Use of an inert or reducing cover gas in full-scale equipment would largely eliminate this reaction. Use of such a gas might also decrease Ru loss by suppressing formation of volatile RuO<sub>4</sub>. The effects of use of inert and reducing cover gases will be studied in subsequent work.

The viscosity of the melt was found to be an important property that affects fire assay recovery. An excessive viscosity can prevent recovery by not allowing the separation and coalescing of the molten scavenger metal. Because of the melt time used in crucible-scale tests, it was found that the maximum glass viscosity that would allow separation was ~25 poise at the

processing temperature. Melt times in the crucible-scale testing were short in order to prevent re-oxidation of the scavenger metal. Longer residence times in the full-scale equipment may allow separation to occur in higher-viscosity melts. A study of the effect of viscosity on separation in full-scale melters will be required once testing of the technique in this equipment begins.

The viscosity of the melt, however, must not be excessively low. Losses of Ru have been found to be greater in low-viscosity glasses. Also, low-viscosity glasses tend to have poorer leach resistance. This is because the same mechanism affects both properties. Additions to the glass structure that reduce viscosity, such as sodium, do so by substituting easily broken, flexible bonds for stronger Si-O bonds. These weaker bonds are also more subject to chemical attack, leading to decreased leach resistances. Low-viscosity glasses also tend to be more corrosive of melter refractories, leading to increased melter wear.

The viscosity of the glass, then, will have to be a compromise between the requirements of good separation on one hand and adequate chemical durability and melter wear on the other. This will be especially true if the economic viability of the process depends upon the production of an acceptable waste glass during noble metal separation. Such a glass would require no further treatment, such as remelting with additional materials, to increase chemical durability.

Another factor that must be taken into account when formulating a glass composition to be used in fire assay recovery is reduction of glass components from the melt. If elements such as Cu, Ni, or Fe are present in the glass, they may be reduced along with the scavenger oxide. This probably would not have a detrimental affect on noble metal recovery, as all these metals would probably prove to be adequate scavengers. It would, however, complicate noble metal separation from the scavenger, and the loss of these metals from the melt would reduce their beneficial effects on the glass.

#### SCAVENGER EFFECTS

One of the more interesting findings of this study was that scavenger type has little or no effect on noble metal recovery as long as conditions

exist that allow the scavenger oxide to be reduced to a molten metal. Copper, Sn, Sb, Bi and Pb were all found to be effective for noble metal recovery. The choice of scavenger will thus be based on economic or other factors.

The choice of metal used as a scavenger may be influenced by the quality of the glass that results when it is used. This will be most important if no compositional adjustments are to be made to the glass subsequent to fire assay recovery. Melts in which Pb was used as the scavenger were found to produce significantly better glasses than those made with any of the other scavengers. This was probably due to the ability of PbO to enter into the structure of the glass. This allowed any lead not reduced from the melt to be incorporated in the glass. The other scavengers tested had lower solubilities in the glass. Once this capacity was exceeded, a crystalline precipitate or phase separation occurred. This resulted in poor glasses that would probably not be acceptable for long-term storage or disposal.

Within the range of scavenger recoveries observed, noble metal recovery did not correlate with the amount of scavenger produced. Scavenger recovery was highly variable, but nearly complete Pd and Rh separation was achieved in most experiments where scavenger metal was recovered. Thus, a minimum amount of scavenger should be employed in fire assay recovery. This will reduce the scavenger cost, lessen its impact on the quality of the glass produced, and minimize the cost of extracting the noble metals from the scavenger once separation has been achieved.

#### REDUCING AGENT EFFECTS

Reducing conditions are, of course, a requirement for fire assay recovery. The means of achieving them, however, may be unimportant from the recovery standpoint. All reducing agents investigated lead to successful recovery, although there was a small degradation in glass quality when charcoal was used compared to the quality achieved when other reductants were employed. This reduction in quality probably resulted from the ash present in the charcoal.

The amount of reducing agent required in full-scale equipment will be different from that needed in crucible-scale tests. This is due to the different configuration, melting characteristics, and surface-to-volume ratio in

the full-scale equipment. Further crucible-scale testing in a controlled atmosphere needs to be done to study reducing agent effects, while eliminating reaction of the reducing agent with the furnace atmosphere. Additional testing will then be needed in larger-scale equipment to determine how scale-up affects the amount of reducing agent required.

## RECOMMENDATIONS FOR FURTHER STUDY

During the course of this work, a number of areas were identified in which additional study would be helpful.

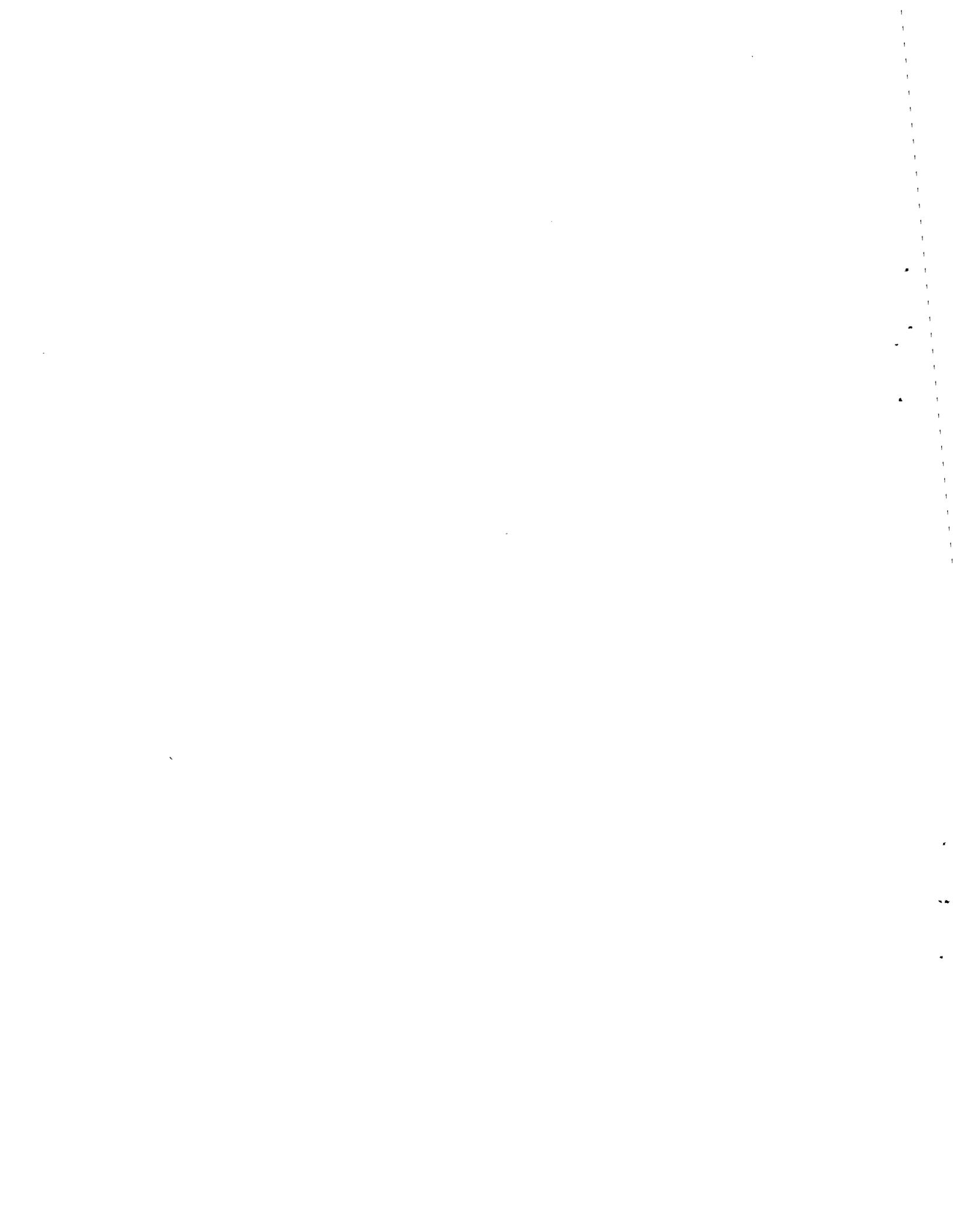
Attention must be given to characterization and optimization of the waste disposal-related properties of the glass produced during separation. The economic feasibility of the process would be enhanced if no further processing is required to produce an acceptable waste glass. Methods of improving the glass properties without sacrificing recovery should be investigated. Also, the trade-offs between recovery and glass quality must be explored.

The recovery achievable from different types of fission-product mixtures should be determined. These other mixtures would include various defense reprocessing mixtures. The effects of a much lower fission-product concentration and differing reprocessing chemicals present in the mixture should be evaluated. Also, the extent to which the recovered noble metals may be contaminated by other radionuclides from the fission product mixture must be studied.

Currently, the most promising method of producing nuclear waste glass is by slurry feeding of an electrically heated continuous melter (Brouns et al. 1980). It should be determined whether fire assay recovery is compatible with slurry feeding. Also, the relationship between viscosity and residence time in the melter, as it relates to scavenger separation, needs to be evaluated. Perhaps a higher-viscosity glass can be tolerated if a longer time is allowed for scavenger-metal separation. High-temperature melting should be investigated as a means of producing a durable glass from which separation is possible.

Finally, further study of the reaction mechanism should be performed. This will allow more fundamental understanding of the fire assay separation technique and may lead to more efficient optimization of the process.

A number of additional areas will be studied by other portions of the program within which this work was done. These include process design, systems studies and the potential use of fission product noble metals.



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