Recovery of noble metals from spent nuclear fuels

by

Zekeriya Altac

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I. INTRODUCTION

Spent fuels contain significant quantities of three of the noble metals, ruthenium, rhodium, and palladium plus the related element technetium. We shall refer to these three Platinum Group Metals (PGM) as "noble metals" in this work. The estimated value of these noble metals (about 4 kgs in 1 tonne of discharge commercial nuclear reactor) in 1979 was $ 15,000 [1,2].

Noble metals are used in a wide variety of electronic-electrical devices, in the petroleum, chemical, and pharmaceutical industries, and as catalyts for conversion of oil to gasoline and other products. They are also used in dentistry and medicine, jewelry, brazing alloys, synthetic fiber production, fuel cells, jet engines, and many other uses. Increasingly large quantities are being requested for industrial, military, space, and other applications. Thus, noble metals are very valuable and extremely useful in the U.S economy.

A significant factor for the U.S is uncertainty of supply of these metals. Nearly all of the world's supply of natural noble metals is extracted from deposits in the Soviet Union, the Republic of South Africa, and Canada. The United States' production of noble metals is small; the only mine operating to recover noble metals is in Alaska, and a very limited quantity is recovered during base metal refining. The total yearly world production of noble metals is about 196 tonnes, and the U.S relies on importing over 90% of its requirements (about 30 tonnes) to meet domestic needs each year [1,3]. Since the supply of these isotopes or elements is largely from foreign sources, they are

considered strategic materials by the Federal Emergency Management Agency. Thus, there is a considerable incentive to recover them from nuclear fuels.

This study is concerned with the recovery of fission product noble metals from long cooled (about 10 years or more) spent fuels, and proposes a plant design to recover them efficiently and economically.

II. LITERATURE REVIEW

Since 1946, the Oak Ridge National Laboratory has been isolating and purifying radioisotopes and making them available to other organizations for development and industrial purposes. In recent years, the demand for a few of the fission products including noble metals has been increased sharply, and the recovery of these isotopes has been initiated at other sites.

During 1960-64, attention at ORNL and Hanford was directed at development of methods that are applicable to large scale recovery of these isotopes [4]. Early recovery methods were primarily based on selective precipitation techniques. More recent developments have emphasized the use of solvent extraction, ion exchange, and pyrometallurgy as means of separating and purifying the radioisotopes.

Most of the work on fission product recovery has been conducted on aqueous waste from the Purex (TBP) solvent extraction process variants which are now used world-wide for separating fission products [5].

The ORNL studied lab scale recovery of fission products from Purex waste [6]. An accomplishment of the study was that a method was developed to recover Sr-90. The procedure involved elimination of sulphate ion from the waste solution at 55 to 60% nitric acid and recovering Sr from an almost pure nitrate system at greater than 85% nitric acid.

Wischow and Horner at ORNL have summarized the flowsheet tests and process chemistry studies in the development of a solvent extraction flowsheet for the recovery of Sr-90 from Purex waste solution [7].

As a part of its waste management program, Hanford investigated ion-exchange and solvent extraction processes for the extraction of long-lived fission products from various Purex plant waste streams. Several flowsheets were made available [8].

Again as a part of its waste management program, Pacific Northwest Laboratory (PNL) has developed processes for the recovery of selected fission products from Redox and Purex plant wastes. Solvent extraction, ion-exchange, and precipitation processes have been studied. An ion-exchange facility for the large scale purification of Pm-147 was installed at PNL [9].

In 1973, Exxon Nuclear Co. carried out a study for DOE on the recovery of various isotopes from commercial nuclear fuel wastes. A similar study was carried out in 1980 by PNL for DOE. Exxon studied recovery of radioisotopes from Purex wastes generated by the reprocessing of high exposure oxide fuels. PNL studied recovery from Zirflex acid wastes. Exxon did not consider Ru recovery, but PNL did. Exxon selected an ion-exchange process for recovery of Cs from commercial waste. PNL used phosphotungstic acid (PTA) precipitation for Cs recovery. The concentrations of the isotopes of interest are much greater in the Exxon study than in the purex ZAW study of PNL [3].

Rather substantial quantities of selected fission products have been made available by the USAEC pilot plants at Oak Ridge and Hanford, permitting a wide variety of radiation application development programs to proceed. The results of these programs have appeared in the open literature. In the last decade, attention at the Oak Ridge Fission

Product Development Laboratory has been largely devoted to isotope conversion and encapsulation rather than recovery from raw waste [10]. Solvent extraction and ion-exchange have now been developed for most of the fission products of interest. These highly selective processes have the advantages of potentially very high recoveries and purification.

Recent advances at Lawrence Livermore Laboratory in laser separation of radioactive from stable isotopes of the same elements are encouraging and reported to be effective. Preliminary cost estimates for the separation of radiactive from nonradioactive isotopes by this technique are reported to be for Pd, Rh, and Ru $ 0.47, $ 0.23, $ 0.93/g respectively. Further study of Ru is needed to define the catalytic potential of this metal [11]. Before the laser separation technique could be beneficially applied, gross separation of fission products, especially noble metals, from spent fuels must be made.

As a consequence of the large amount of research and development work which has been done in recent years in the field of fission product recovery and purification, the designer of a fission product plant is faced with an almost bewildering plenitude of proven and workable processes. Since capital and operating costs for separating noble metals from spent fuel are currently controlling commercial viability, this is the area where technological change and innovation can have the most favorable impact. Applications of wet chemistry separation techniques have so far been more costly than importation of metals from conventional sources. A discounted cash flow analysis with a 15% monetary recovery annually showed that fission product noble metals were

not economically competetive in 1976 at this high capital change rate [11].

In recognition of this business sensitivity, the Pacific Northwest Laboratory (PNL), Battle Memorial Institute, started some scouting studies in 1979 of concepts for simplifying separation flowsheets. One other criterion used in guiding the work was to keep new processes compatible with existing glass fixation methods for nuclear wastes. A process called "lead button" or "lead extraction process" was developed. In order to test the concept, PNL conducted two scouting experiments using simulated and nonsimulated fission products (30,000 MWd exposure fuel) and made melts using these wastes mixed with lead oxide and charcoal in porcelain crucibles at 1100° C. Noble metal recoveries averaged 80% for the metals [1]. These very preliminary results encouraged the PNL researchers to expect that process recovery cost for these noble metals would be reduced over wet separation techniques.

A parallel program to evaluate other methods for noble metal recovery from spent fuel reprocessing liquids was conducted at PNL. Beaker-scale screening tests were initiated for three potential recovery processes, identified through patent and other technical literature searches. These are a sugar denitration process, a chelate-impregnated carbon absorbent process, and an amine-borane resin process. Applicability of these process is still under investigation [12].

III. THEORY AND EXPERIMENTAL WORK

The Pacific Northwest Laboratory's, PNL, method to recover fission product noble metals consists of combining a mixture of fission product waste with glass forming chemicals, a metal oxide, and a reducing agent. When this mixture is melted at 1100° C, the metal oxide is reduced and forms a separate phase containing the noble metals as metals in solution. This phase flows to the bottom of the container. The remainder of the mixture forms a glass that is suitable for nuclear waste storage. This glass waste floats on the top of the molten metal. Figure 1 taken from the PNL work, shows how the lead extraction process for recovering noble metals from fission products might be integrated into a nuclear waste/vitrification scheme. Fission products, scavenger oxide, reducing agent, and glass formers would be fed and melted in a melter. The lead, containing noble metals, would then be processed by conventional methods to separate the noble metals and recover for reuse.

In sections III.1, 2, and 3, the pertinent PNL work is described. The PNL carried out a study for DOE which was aimed at examining a variation of the technique as a method for recovering Pd, Ru, and Rh from fission product mixtures. The work reported was performed using a nonradioactive oxide simulation of a fission product mixture. First, a number of different scavengers (Sn, Bi, Sb, Cu, Pb) and reducing agents (graphite, flour, sugar, silicon, cornstrach, charcoal) were tested, and the effect that each had on recovery 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
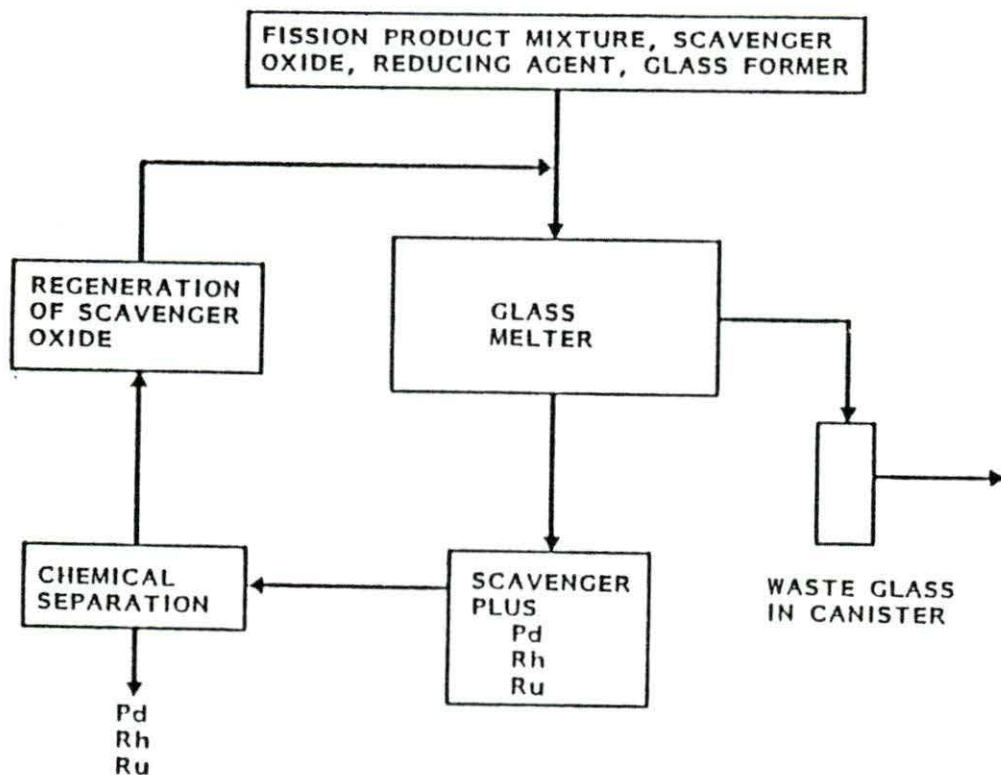
FIGURE 1.   Schematic recovery of noble metals incorporated into
             nuclear waste glass production [13]

amounts of these materials needed for successful recovery.   Several

conclusions were reached during the course of the work.   The most

noteworthy are summarized below;

    1.   The recovery was found to depend only on reduction of

       scavenger oxide to metal.   When such reduction was

       achieved, no significant difference in noble metal

       recovery efficiency was found amoung the scavengers

studied. These include PbO, SnO, CuO, Bi_2O_3, and Sb_2O_3.

2. Not all reducing agents studied were able to reduce all scavenger oxides to metal. Only graphite would reduce SnO and CuO. However, Sb_2O_3, Bi_2O_3, and PbO were reduced by all of the reducing agents tested.

3. Palladium, Rh, and Ru recoveries of about 90% were achieved in "crucible-scale" tests with lead used as scavenger.

4. Lead appeared to exhibit the best scavenger characteristics at a low cost. It extracts the noble metals and does not appear to have a detrimental effect on the quality of the glass produced.

5. Glass viscosity was an important property of the melt. An excessively high viscosity hampered separation of the scavenger metal whereas a low viscosity led to increased volatile loss of RuO_4.

6. The glasses that were produced 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. The glasses were produced from the batches containing PbO as a scavenger and charcoal as a reducing agent.

7. Only three experiments were performed using real fission products; technetium recoveries also were observed with the other noble metal recoveries found to be in the

expected range. The technetium recoveries in these experiments were respectively none, 1 %, and 11 %. Further evaluations are needed to determine the Tc recovery conditions.

Having reached those conclusions, the PNL researchers decided to continue the experiments using only lead oxide as scavenger and charcoal as reducing agent. In the experiments recovery efficiencies with different charge compositions, viscosity effects, and PbO/reducing agent recoveries were explored.

III.1. PbO/Reducing Agent Requirements

The amount of PbO and charcoal required to reduce a melt that optimizes the recovery of noble metals was identified. Experiments were completed where the quantities of PbO and charcoal were varied but the glass mixture including the simulated fission product content was kept constant. The numbers in the circles are percentages of lead fed to the melt and separated from the glass mixture. The noble metal recovery was nearly independent of scavenger recovery. These data show that a minimum of 20 wt% PbO must be fed for proper recovery. Charcoal must be fed at between 4 to 17 wt% or two to four times the stoichiometry requirement for PbO reduction if adequate recovery is to be achieved. If PbO or charcoal additions are below these values, the recovery drops off. These data show that charcoal or PbO additions are not critical to acceptable recovery as long as they are within the reasonable limits identified here. The results are shown in Figure 2.
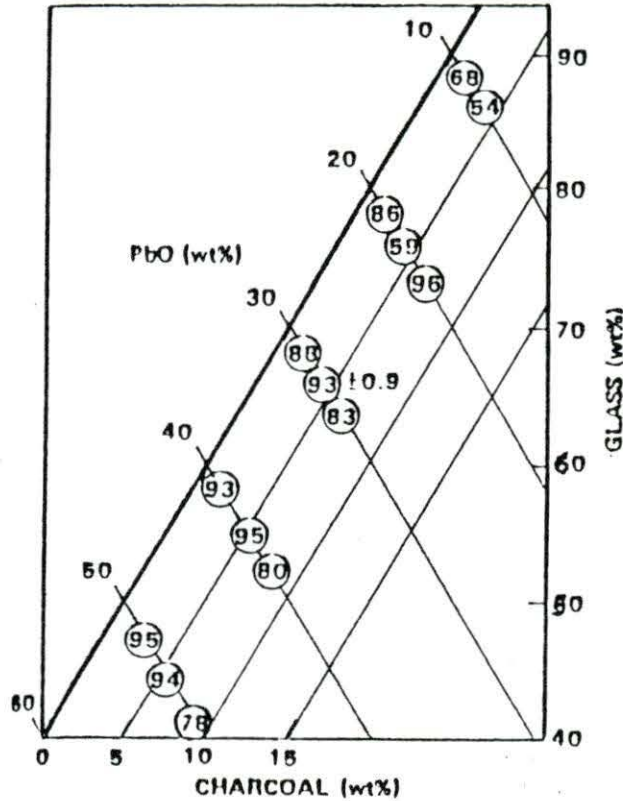
FIGURE 2.   Lead recovery as a function of feed composition [1]

III.2.   Effect of the Amount of PbO and the Flux Level

Tests were made in order to determine the amounts of PbO and flux which, when present in the batch, would result in optimum noble metal recovery.   The batch composition ranges in this testing are shown in Table 1.

Figures 3 and 4 show plots of Pd, Rh, and Ru recovery as functions of PbO and Na_2CO_3 in the batch.   Neither Pd nor Rh recoveries were consistently affected by the amount of PbO or flux addition.   Much of

TABLE 1.   Batches used to test flux and scavenger variations [13]

Component	tested, g
Simulated FP Mixture	15
Glass Former	30
Flux(Na_2CO_3)	0 to 30
PbO	10 to 40
Charcoal	4

the variability in recovery was probably the result of the sampling

uncertainty. The only significant effect seen consistently was an

increase in Ru recovery as Na_2CO_3 was decreased to about 10 wt% and PbO

to 20 wt%. The increased Ru recovery may therefore have been due to

decreased volatile loss of RuO_4 with increasing melt viscosity. Based

on the experiments, a batch containing 25.2 wt% PbO and 12.7 wt% Na_2CO_3

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 the

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.

III.3. Viscosity Effects

The viscosity of the molten batch is an important factor affecting

PbO separation. Low viscosity usually correlates with ability to

separate the scavenger phase from the melt. However, the need to reduce
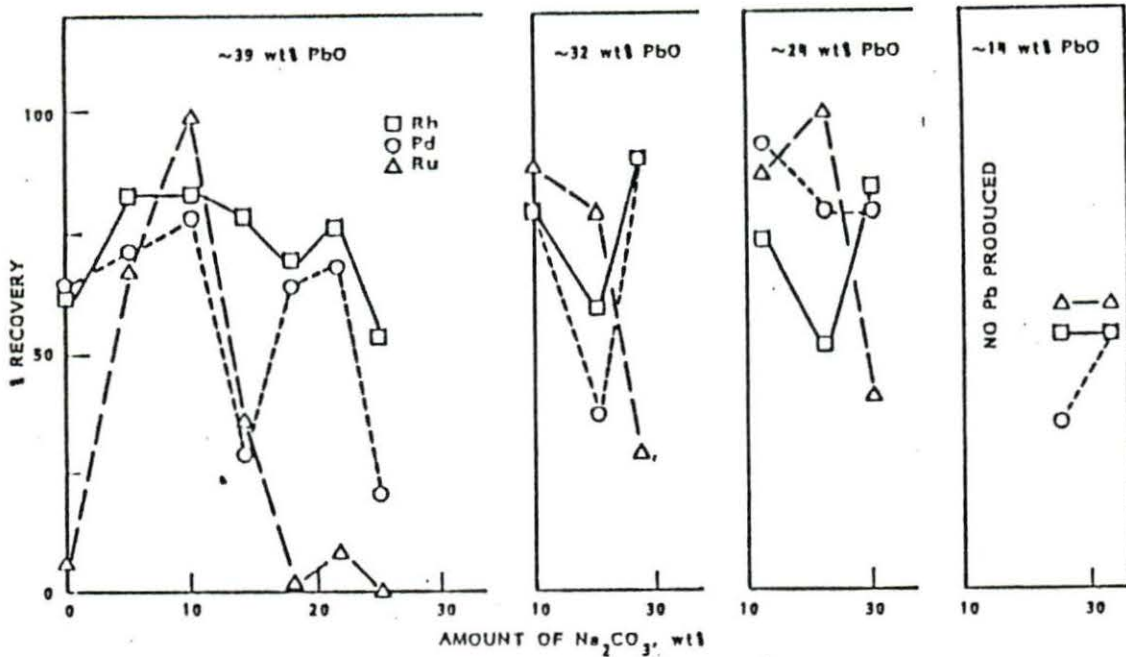
FIGURE 3.   Noble metal recovery as a function of Na_2CO_3 in batch at various PbO levels [13]

the amount of flux was recognized for two reasons, First, low viscosity melts usually produce less durable waste disposal glasses than do high viscosity melts.   Second, the electrical resistivity of the glass is too low, so that the current density at the melter will be too high, causing accelerated electrode wear and improper melter operation.   Several approaches were taken to identify the effect of flux on recovery.   Early efforts in recovering lead from higher viscosity glasses usually did not produce molten lead.   Further work demonstrated that additions of reactive ingredients may allow recovery from high viscosity glasses. The results of a number of these experiments are shown in Table 2.
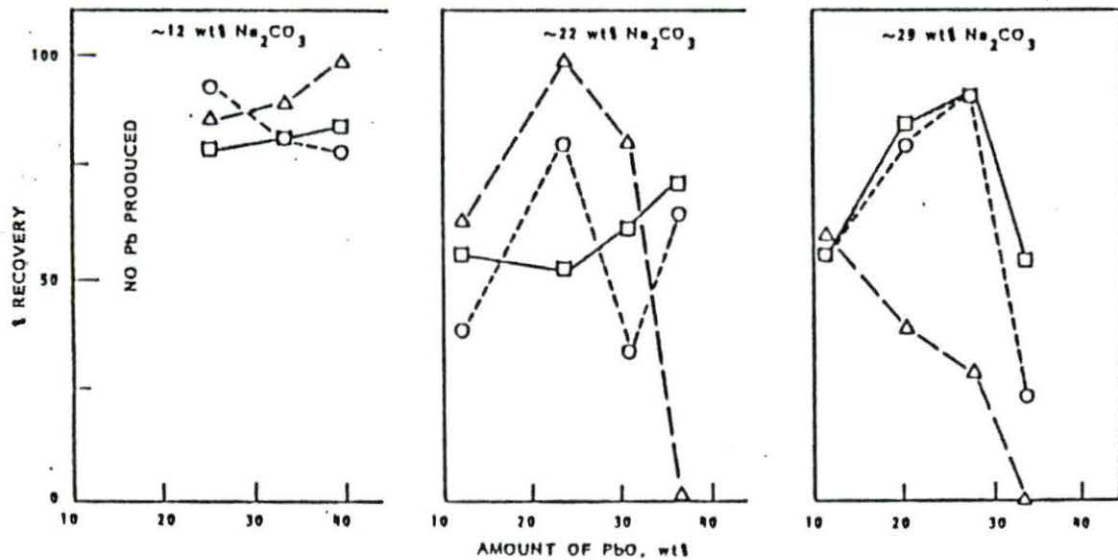
FIGURE 4.   Noble metal recovery as a function of PbO in batch at various Na$_2$CO$_3$ levels [13]

Greater than 80% noble metal recovery has been achieved in melts with glasses in the 50 to 80 P range. This is significant as it indicates that extremely low viscosity glasses are not required for recovery. The Na$_2$CO$_3$ has a much greater effect on viscosity than does PbO. This is illustrated in Table 3. Glasses having viscosities in the 50 to 80 P (1050° C) range should be acceptable for waste disposal. The relationship between viscosity, alkaline-oxide content, and resistivity of waste glasses was also determined. The relationship between resistivity and viscosity is important in noble metal recovery. Figure 5 shows the electrical resistivities of the six glasses tested as a

TABLE 2.   Compositions and noble metal recoveries from higher
            viscosity glasses [1]

Component	Composition (wt%)				
PW-4b-7 [1]	25	25	25	25	30
Frit-165 [2]	--	25	12.5	50	60
Glass Mix [3],[4]	50	25	37.5	--	--
PbO	25	25	25	25	10
Charcoal [5]	2	2	2	2	4
Glass Viscosity at 1050° C (P)	10	80	50	120	120

Noble Metal	Recovery (%)				
Palladium	84	79	80	*	*
Ruthenium	83	77	77	*	*
Rhodium	92	83	87	*	*

    [1] Duplicates commercial Purex waste with minimum processing
chemicals.
    [2] Frit-165; SiO_2, 68 wt%; B_2O_3, 10 wt%; Na_2O,
13 wt%; LiO_2, 7 wt%; MgO, 1 wt%; and ZrO_2, 1 wt%.
    [3] A premelted and crushed mixture of 63.1 wt% Frit 76-101 [4]
and 36.9 wt% Na_2O
    [4] Frit 76-101; 64.2 wt% SiO_2, 15.3 wt% B_2O_3,
4.5 wt% Na_2O, 8.0 wt% ZnO, 3.2 wt% CaO, and 4.8 wt% TiO_2.
    [5] Two or four times these stoichiometric amounts
required for reduction.
    * No lead Produced.

function of alkaline-oxide content at different glass viscosities. As
shown, the glass melt with a viscosity of 10 P probably could not be
processed in existing equipment. However, glasses with viscosity of 50
P or above could be melted as their electrical resistivity is acceptable
for proper melter operation.

TABLE 3.   Viscosities of recovery batches as a function of temperature
            and composition [13]

Composition (%)		Viscosity at Temperature, P		
Na$_2$CO$_3$	PbO	1100° C	1000° C	900° C
22.4	22.4	6	14	37
30.0	20.0	3	7	17
12.6	25.3	22	54	225
11.2	33.7	16	49	175

III.4. Recovery of Noble Metals From Lead Mixture

The recovery of noble metals from the lead mixture is a
conventional purely metallurgical method. The PNL work was carried only
to the point of noble metal extraction. However, the noble metals in
lead are very dilute, and concentration is desirable. This
concentration process called "recovery" is explained here.

When a proper amount of Zn is added to the mixture and kept at
constant temperature, say about 330° C, in the lead rich region of Pb-Zn
phase diagram, zinc is compeletely dissolved in lead. The noble metals
are insoluble in Pb-Zn mixture. If the temperature is decreased to 320°
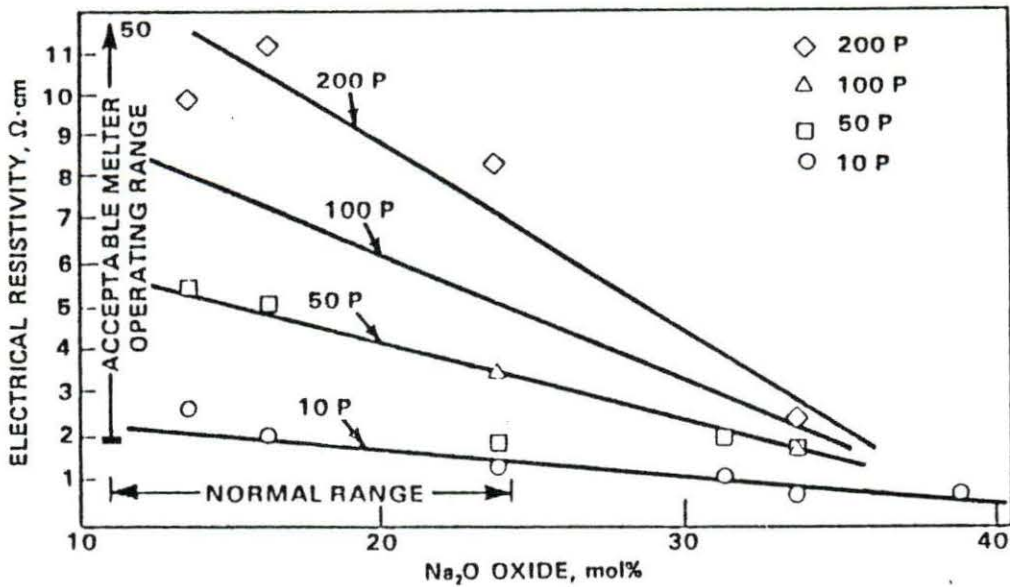
FIGURE 5.   Electrical resistivity of various viscosity glasses as a
function of Na$_2$O content (1050° C) [1]

C, which is in the liquid plus solid Pb region, two phases are formed.

This process is called fractional solidification. Solidification is

heterogeneous and is initiated by the presence of solid noble metal

particles in the liquid phase. In practice, it is often necessary to

"seed" the melt with foreign particles to promote nucleation. This

method allows us to enrich the noble metal content of the solid lead

mixture, while recovering most of the lead as liquid for recycle. The

recovery efficiency of lead is a function of the amount of Zn added, the

temperature at which this "squeezing" is performed, and performance of

squeezing (used filter efficiency, temperature variations during

squeezing etc.). Squeezing is a process in which a liquid is separated

from a solid by compressing the mixture in order to filter the solids.
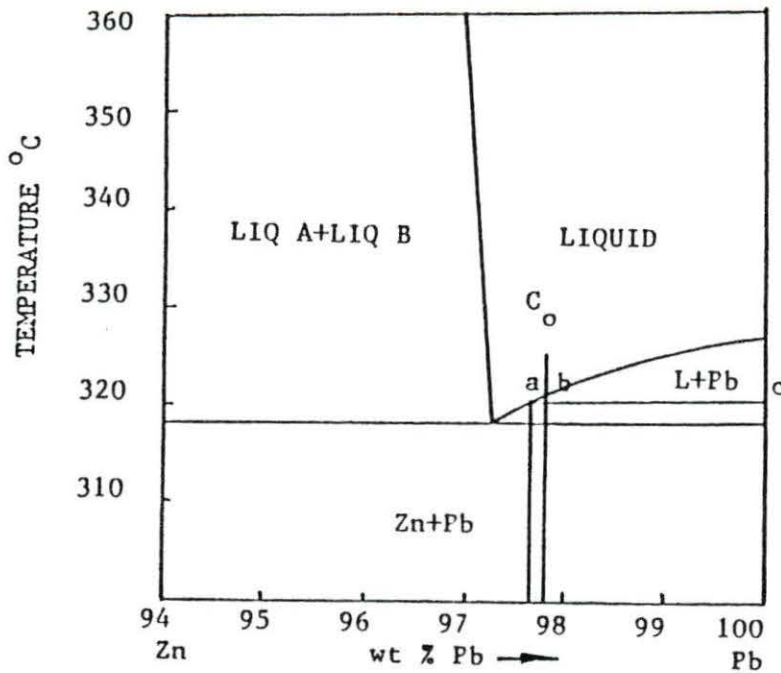
FIGURE 6.   Pb rich region of Pb-Zn phase diagram [14]

We take as an example a lead plus noble metal mixture containing

99.7 wt% Pb. We calculate the amount of the phases and of recovery

using the Pb-Zn equilibrium diagram. An addition of 2.35 wt% Zn to the

mixture changes the composition of Pb+NMs to 97.8 wt% Pb and 2.0 wt% Zn.

It is possible to work with the Pb-Zn diagram only because it remains

unchanged even though we have noble metal impurities. To determine the

actual chemical composition of Pb-Zn-NM alloy, in the equilibrium at

320° C in a two phase region (Liquid+Pb), a horizontal line, called a

tie line, is drawn to the boundaries of the field. These points of intersection are dropped to the base line and composition is read directly (Figure 6). Point a, when dropped to the base line, will give the composition of the liquid phase constituting the mixture. In this case, the liquid composition is 97.6 wt% Pb and 2.4 wt% Zn. Point c, when dropped to the base line, gives the composition of solid Pb which is 100 wt%.

To determine the relative amounts of the two phases in equilibrium at 320° C, a vertical line representing the alloy, C_0, is drawn. The vertical line divides the horizontal line into two parts whose lengths are inversely proportional to the amounts of phases present. This is known as the lever rule. In Figure 6, the vertical line representing 97.8 wt% Pb, divides the horizontal tie line into two parts, ab and bc. If the entire length of the tie line is taken to represent 100 %, or total weight of the two phases present at 320° C, the lever rule is expressed as

Liquid %= bc/ac   Solid %= ab/ac

If the tie line is removed from the phase diagrams and numerical values are inserted, one finds that the amount of the two phases are 6.38 wt% solid Pb+NMs, and 93.62 wt% liquid.

IV. DESIGN

In this chapter, we present the design of a system (1000 t/y) and plant area for the extraction and the concentration of noble metals. The designed plant will operate 330 d/y for 30 years with 100% rated capacity.

IV.1. Feed Materials

Feed materials are high level Purex waste (PW), frit, sodium carbonate, lead oxide, and charcoal. The feed composition was chosen as 20 wt% PW, 50 wt% glass mixture, 26 wt% lead oxide, 4 wt% charcoal. The glass mixture contains 17 wt% Na_2CO_3, 21 wt% Frit-165, and 62 wt% Frit 76-101. These combinations were chosen as a result of experiments performed in PNL (Chapter III), and give optimum noble metal recovery efficiencies combined with high quality glass. The glass mixture results in a glass viscosity in the range 50 to 80 P.

IV.1.1. Purex Waste

Selected Purex waste is LWR uranium fuel of 30,000 MWd/MT burnup, 10 years cooled, and contains 1870 g Ru, 366 g Rh, 1355 g Pd, and 768 g Tc/MTHM [2]. The waste is in solid form, 1.66g/cm³, and is transported from storage tanks at the Purex plant.

IV.1.2. Glass Mixture

IV.1.2.1. Frit   The frit to be used is a combination of two different frits. These are Frit-165 and Frit 76-101. They are added to the melter as a premelted solid that has been crushed and sized to a

-20,+80 mesh range. The frits are widely used in nuclear waste
vitrification.

    IV.1.2.2. Sodium Carbonate   Sodium carbonate decomposes under
melter conditions and produces sodium oxide and carbon dioxide. Sodium
oxide is a flux material, which is needed in order to adjust and
maintain a 50-80 P viscosity range in the melter for proper melter
operation, and to obtain a good quality durable glass that can be
disposed without further processing. It is charged to the melter in
solid form crushed and sized to a -20,+80 mesh range.

IV.1.3. Lead Oxide and Charcoal

    Lead oxide is the scavenger used to extract noble metals, while
charcoal is used as reducing agent. They both are crushed and sized to
-50 mesh.

IV.2. Extraction Plant

IV.2.1. Feed Tanks

    It is assumed that the plant is a sub-division of a Purex plant
and that Purex waste is supplied from waste storage tanks. In the
extraction plant, five feed tanks are provided for PbO, charcoal,
Na_2CO_3, Frit-165, and Frit 76-101. All of the tanks are cylinders of
4.92 m^3 volume, 2.5 m high and 0.85 m radius. The cylinder bottom is
welded to a cone (50 cm high). The feed tank capacities for PbO,
Na_2CO_3, charcoal, Frit-165, Frit 76-101 are 83.6, 11.6, 7.86, 2.16, 2.03
tons respectively. Each tank is furnished with a automatic balance that
permits metering a material feed rate of 148.8 kg/h for PbO, 22.83 kg/h

for charcoal, 48.5 kg/h for Na_2CO_3, 59.9 kg/h for Frit-165, and 176.9 kg/h for Frit 76-101.

IV.2.2. Material Handling

As was indicated, the Purex waste comes from a Purex reprocessing plant. The highly radioactive waste is transported by conveyors which are totally shielded with lead or concrete. To prevent contamination, the conveyor should be enclosed in a tube so that dusts can be withdrawn through filters. This conveyor ends at the waste feed tank in the bunker where the other materials are also fed. The bunker should be similarly enclosed. The speed of the conveyor is 38 cm/min with 5 kg/m conveying capacity (feed rate 114.14 kg/h).

The other materials to be fed are brought in barrels and unloaded in a storage room (13 m x 5 m) built next to the plant. A portable flat-belt conveyor is used to move the materials to the feed tanks, and make reload easier. Five windows are provided between the plant and storage room for material handling from the room to the tanks. The belt is 36 cm wide and 7 m long, and is made from high carbon steel. It gives the flexibility to use in loading five materials into feed tanks and can be switched easily from one job to another.

A belt conveyor is passed from the bottom of the feed tanks; it is inclined at 26° after a 10.5 m flat route. The materials are elevated to 3 m height which is the level of the top of the mixer bunker. Maximum belt speed is 13 m/min and it is rolled on steel rollers (3.5 cm rad., 30 cm wide). The belt speed during the operation is kept at 152.2 cm/min with 5 kg/m belt carrying capacity.

The bunker receiving all of the materials is shielded to prevent gamma ray exposure originating mainly from Cs-137 and Sr-90 which makes 65% of the total radiation from ten year cooled Purex waste, which contains 0.711 g Sr-90/kg and 0.516 g Cs-137/kg [2]. The radioactivity of Sr-90 and Cs-137 are 87 and 139 Ci/g isotope respectively [3]. Therefore, the total radioactivity contribution including Y-90, daughter of Sr-90, is about 243 Ci/kg Purex Waste.
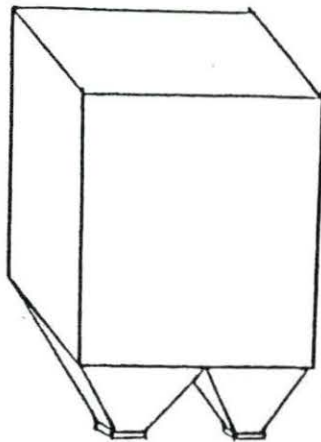
FIGURE 7.   The front view of the mixer bunker

The bunker is designed to have two taps to feed two melters. The taps are furnished with automatic balances to meter and adjust a material feed rate of 285.35 kg/h for each melter.

IV.2.3. Melter

The melter design presented here is based on one designed for the PNL pilot plant. This design has been changed to include:

(a) Changes recommended by PNL

(b) Changes required by the lead extraction process. These include redesign of the melter floor and provision of freeze valve and extraction tube for recovery of the lead-noble metal mixture.

Alternating current, passing through the molten glass between two electrodes, maintains the glass at 1100° C to 1200° C and supplies the heat necessary to fuse the metal oxides and glass formers into a homogeneous glass material. At this temperature also, PbO and noble metals are reduced by charcoal. As the molten glass accumulates in the melter tank, it flows out of the tank through an underflow throat, up a riser passage along a discharge trough, off a discharge lip and into a receiving canister; meanwhile, the noble metal and lead mixture accumulates at the bottom of the melter.

Two melters are operated in parallel. This type of melter is a new design, and while it has been proven that it can be operated in small capacities, the performance of larger capacity melters is unknown. Therefore, the design of very large melters should be and has been avoided. Also this duplication enables the plant to operate at a reduced rate in case of failure during operation. We therefore expect
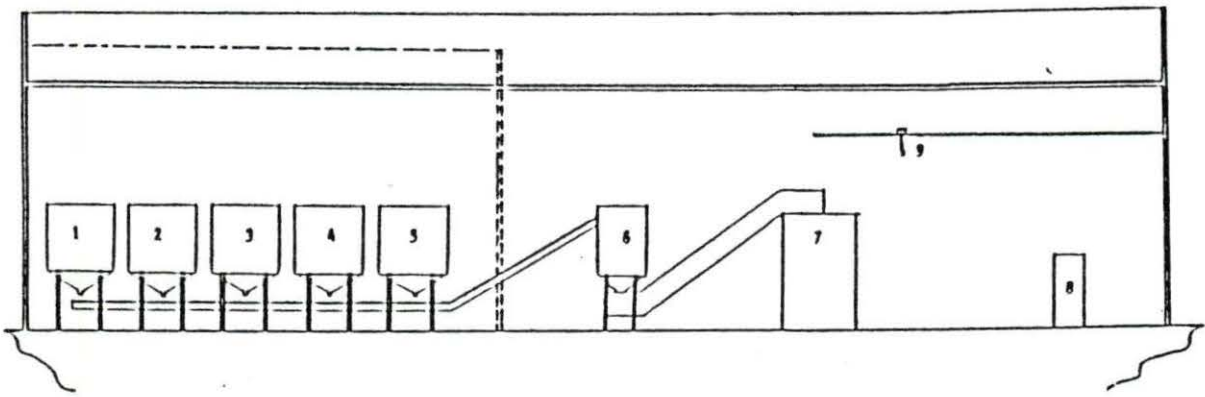
1- Na_2CO_3 Feed Tank
2- Charcoal Feed Tank
3- PbO Feed Tank
4- Frit-165 Feed Tank
5- Frit 76-101 Feed Tank
6- Mixer Bunker
7- Melter
8- Squeezer
9- Crane

FIGURE 8.   Front view of the extraction plant
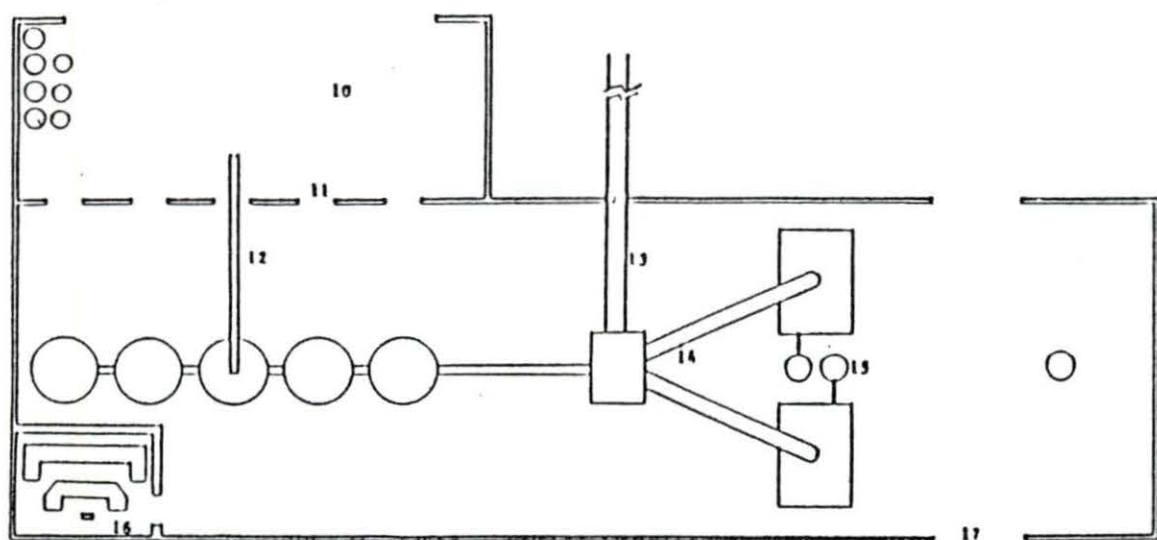
10- Storage Room
11- Windows
12- Portable Conveyor
13- Purex waste Transportation Line
14- Melter Feed Lines
15- Argon Gas Feed Tanks
16- Control Room
17- Door

FIGURE 9.   Top view of the extraction plant

that the plant will be operable at more than 70% of its rated capacity. Additionally, small adjustments in feed rate, glass removal rate etc., might be made with a potential for further capacity increase.

It is assumed that recovery efficiencies of the noble metals are 77 % Ru, 87 % Rh, and 80 % Pd. The assumption is based on the PNL experiments and arguments presented in Chapter III. These experiments were bench-scale, and, recognizing the difficulty of determining precisely the noble metal recovered from 20 g fission product mixture, it can be hoped that industrial scale recovery efficiencies will be higher than our assumed values, possibly up to 90%. Thus, we consider these assumed values to be conservative.

The power required is about 200 Kw. Two viewports are included in the design of the melter to enable visual data to be accumulated on the operation of the melter. The axes of the viewports are inclined 45° to the surface of the lid. One viewport is in the melter section, the other in the discharge section. The melter has also a glass sample access port. This port enables one to obtain glass samples in order to detect noble metal losses, using an Argon Plasma spectometer.

IV.2.3.1. Size   The electric melter is shown in detail in Figure 10. The melter tank is 93 cm wide and 142 cm long. However, 5 cm thick electrodes entirely cover each end of the melter tank. This reduces the effective tank length to 132 cm and its surface area to 1.23 m². The melt is 45 cm deep, giving the tank volume of 647.1 l. The bottom of the melter is inclined 8° in order to permit the metal mixture to flow freely towards the freeze valve. The melter is rectangular in

external dimensions; 2.90 m long, 1.77 m wide, and 2.17 m high.

IV.2.3.2. Refractories   Because of its high corrosion
resistance, the fused cast chrome alumina refractory, Monofrax K-3[1], is
used wherever contact with molten glass and metal is expected. This
includes the tank lining, the throat, the riser, and the discharge
trough. Void free K-3 blocks, 10cmx15cmx46cm, are used for the 10-cm-
thick lining and throat. Similar blocks with machined semicircular
grooves are used for the riser and for the discharge trough. Zirmul[2],
8cmx31cmx46cm, paving blocks--a zirconia stabilized mullite--are used as
backup refractory for any glass or lead mixture that penetrates the K-3
through the block-to-block joints in the floor and sides of the melter;
these blocks also provide an additional thermal barrier. A 32-cm layer
of Zirmul is provided under the K-3 floor blocks, and an 8 cm layer is
provided behind the K-3 walls. Alfrax 66[3], a high alumina castable
refractory is poured into the 8 cm space between outer melter walls and
the 1 cm thick crushable expansion Joint Board[4] that lines 1 cm thick
Inconel 601[5] containment box. The Alfrax and Joint Board provide the
bulk of the thermal insulation for the melter tank and the Joint Board

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[1] Registered Trademark of the Carborundum Corp; Refractories
Division, Falconer, New York.

[2] Registered Trademark of the Charles Taylor Sons Comp;
Cincinnati, Ohio.

[3] Registered Trademark of the Carborundum Co; Niagara Falls, NY.

[4] Registered Trademark of Huntington Alloys Division of the
International Nickel Co; Huntington, West Virginia.

[5] Registered Trademark of the Carborundum Co; Niagara Falls, NY.

Legend:
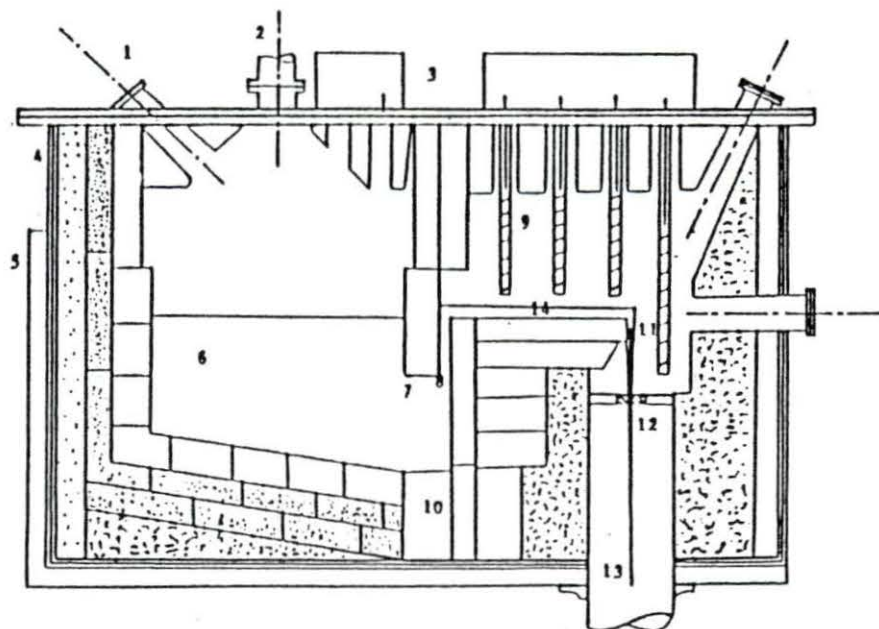
▢ HONOFRAX K-3 BRICKS

▢ ZIRHUL BRICKS

▨ ALFRAX

▨ FIRE BRICKS

1- View Port
2- Feed Inlet
3- Heat Cover Element Boxes
4- Inconel 601 Containment Vessel
5- Water Cooling Jackets
6- Molten Glass
7- Undrflow Throat
8- Riser
9- Silicon Carbide Heaters
10- Freeze Valve
11- Discharge lip
12- Knife Operated Valve
13- Discharge Tube
14- Discharge Trough

FIGURE 10.   Melter tank east-west cross section
[Adapted From Reference 15]

provides a means for absorbing the refractory expansion as the melter is initially brought up to its operating temperature.

A 3 cm thick mica sheet is installed between the Inconel containment vessel and the Jóint Board to provide a measure of electrical insulation between the glass and the containment vessel in the event of intrusion of the glass into the tank refractory lining. To minimize corrosion around the discharge throat, the throat and riser should be fabricated from a single monolithic K-3 block. All of the tank liner refractories should be positioned vertically instead of horizontally to minimize corrosion of the horizontal joints. Refractories should be cemented with appropriate refractory cements.

IV.2.3.3. Freeze Valve   The melter tank is provided a freeze valve type bottom discharge valve (Figure 11). This valve is intended to enable the melter tank to discharge the molten lead and noble metal mixture accumulated at the bottom of the melter. The valve body is machined from Inconel-690 bar. The discharge passage is 3.8 cm in diameter. To prevent metal from freezing in the valve, a heater is provided in the valve. During operation 0.74 m/min of cooling air at 0.38 kg/cm is passed through the freeze valve cooling passages, extracting about 1 Kw of heat from the Inconel valve body block; this reduces its temperature to about 250° C and freezes any metal mixture in the passage. Two 1500 watt resistance heaters, positioned on either side of the valve body, provide the heat required to thaw the metal that is normally frozen in the passage.

Heater

Air
Out

Air In
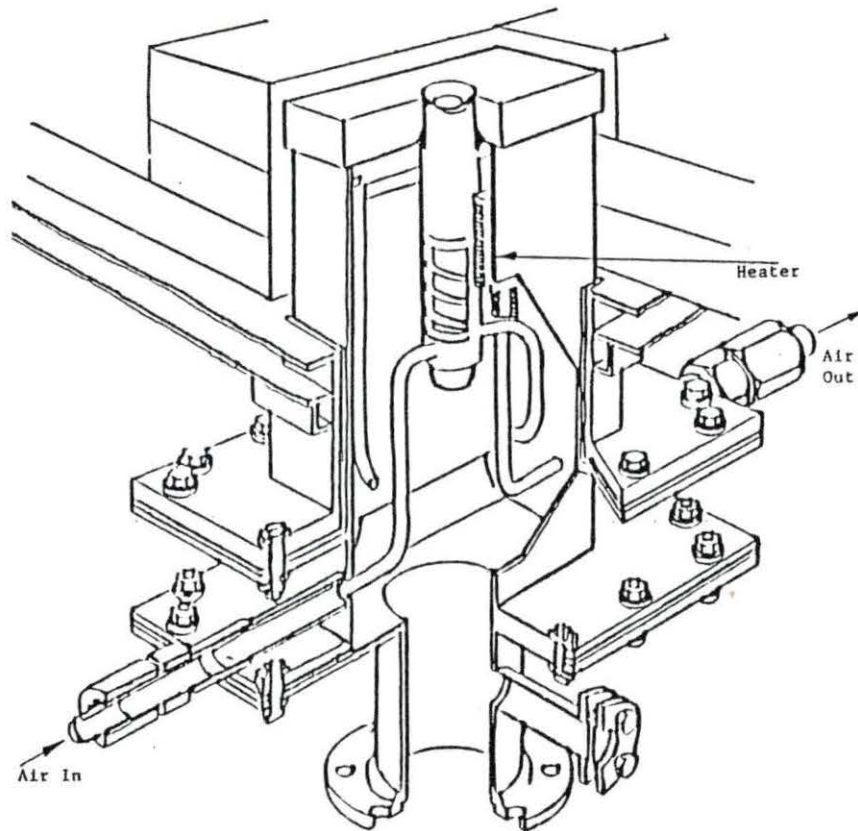
FIGURE 11.   Bottom freeze valve [15]

IV.2.3.4. Electrodes   The electrodes consist of slabs of Inconel-690 5 cm thick, 86 cm wide, and 90 cm tall. The electrodes weigh about 312 kg each. The power connections to the electrodes are made on electrode ducts that protrude above the melter lid. Serpentine cooling air passages are covered with 6 mm thick Inconel-690 plate welded to these terminations. These enable cooling air inlet and outlet connections to be made at the top end of the electrode duct above the melter lid.

A 10 cm foot is added to each electrode (Figure 12). This is one of the modification recommended by PNL. The shorter electric current path length at the bottom of the melter increases the heat source there, and helps make a more homogeneous glass. Each of the electrodes has a 6 mm diameter hole drilled on the centerline of the electrode 1.6 cm back from the front face of the electrode and extending to within 1 cm of the bottom of the electrode. These holes extend to the top of the electrode ducts with Inconel tubing and are used as thermowells.

IV.2.3.5. Lids   An Inconel-601 flange, 10 cm wide and 2.5 cm thick, extends completely around the top of the edge of the containment vessel. Another Inconel-601 plate, 2.5 cm thick, welded with two side flanges, connects the two sides together outlining the melter tank. The bottom part of the melter rests on a 1 m high concrete step which has been formed as shown in Figure 13. This enables an easy removal of glass and metal mixture.

Each of the lids is fitted with an 18 cm thick layer of LDS moldable ceramic refractory on its underside. The melting cavity lid
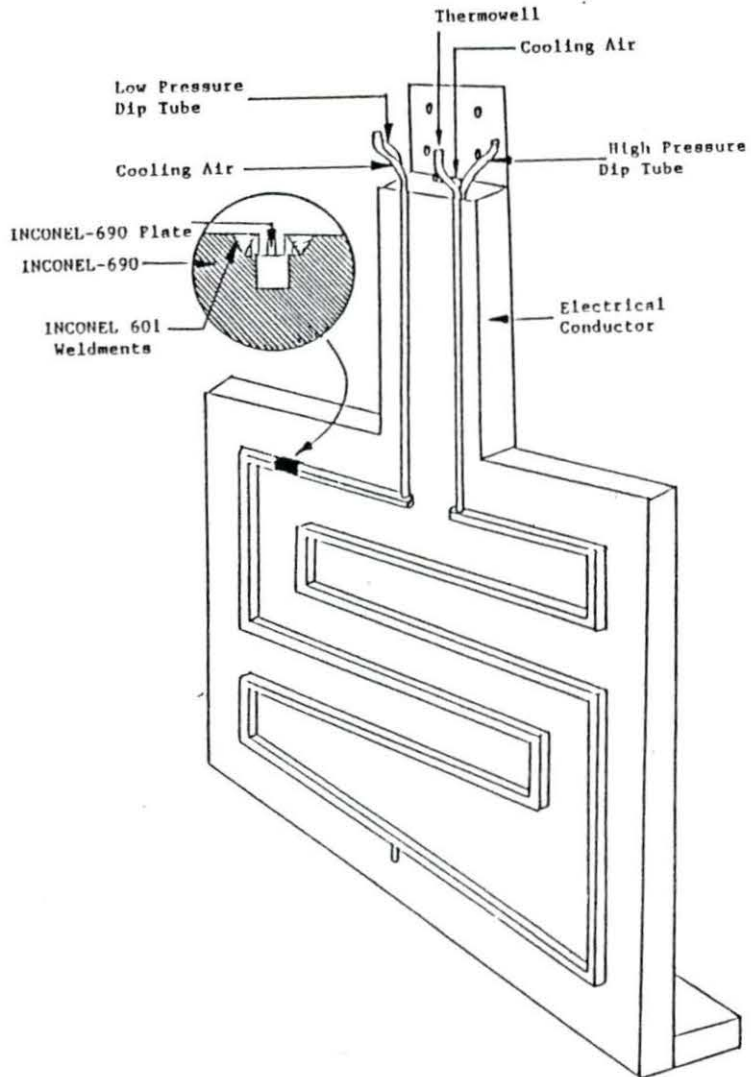
FIGURE 12.   Slab-type electrode (back-side view)
            [Adapted From Reference 15]
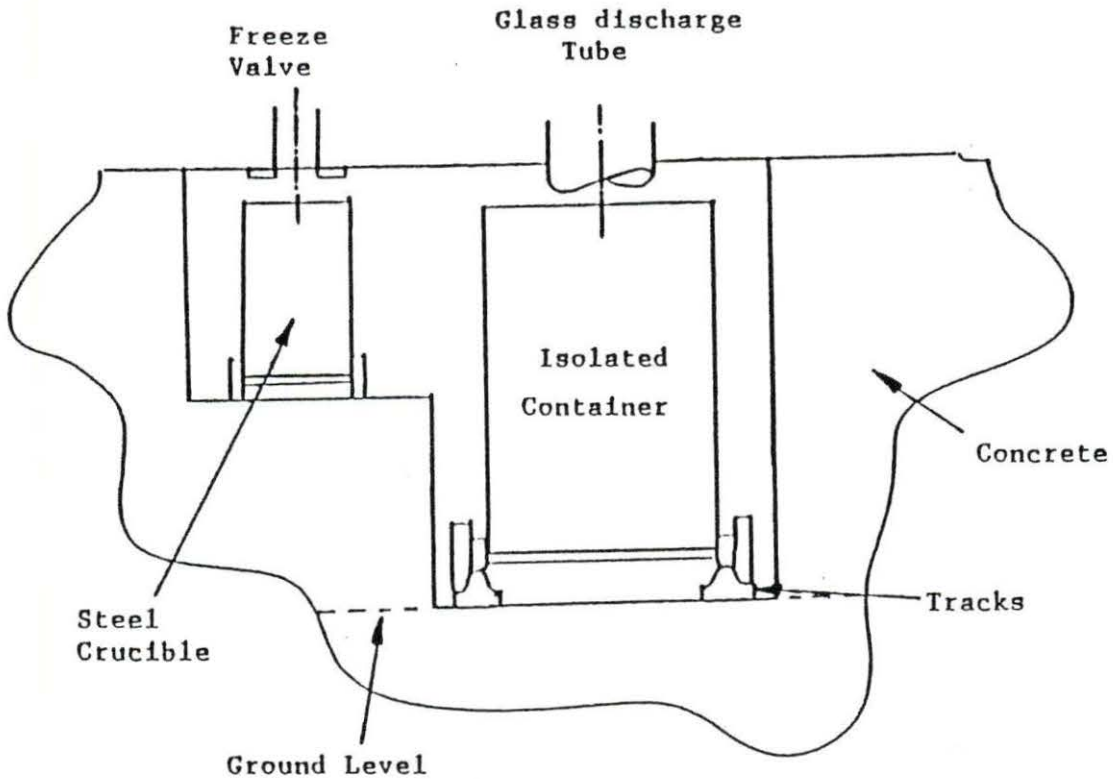
FIGURE 13.   Schematic of discharge system

and insulation layer are penetrated by several openings. There are two

rectangular openings for power ducts, an opening for a viscometer, 13

holes for sturtup silicon carbide heaters, four for space thermocouples,

three for vapor space instruments, one for a pressure gauge and valve,

and one for an airlock. The discharge section lid and its insulation

layer are penetrated by four holes for the discharge section silicon

carbide heaters.

IV.2.3.6. Airlock   An airlock system is required in the feed transportation line from the bunker to the melter. A standard airlock valve, consisting of spherical valves, separated with a 5 liter intervening chamber, is used for this purpose. Each spherical valve is air driven and requires only a quarter run to go from fully open to dust-tight seal. The air operators are electrically controlled and are sequenced to operate the valves intermittently. Position sensing switches inhibit the opening of either valve unless the other valve is fully closed, thereby, reducing the air in-leakage to the melter.

IV.2.3.7. Silicon Carbide Heaters   Auxiliary heat is supplied to the discharge trough and to the discharge face to maintain the refractories at about the melter glass temperature and minimize the thermal strains in the refractories, and to maintain desired glass properties as the glass is discharged to the receiving canister. Six silicon carbide resistance-heating elements penetrate the discharge section lid and insulation, and extend down into a 30-cm-widex110-cm-longx96-cm-tall cavity over the discharge trough. An airtight box on the discharge section lid covers the upper end of the heater elements and prevents air from leaking into the melter. The six elements are wired in parallel and each element is rated at 5.3 Kw (19.8 Kw max). The maximum recommended temperature is 1250° C. Two other silicon carbide heating elements are positioned in a similar manner in front of the discharge face. These heaters are slightly larger than the discharge trough heaters (8.45 Kw each with a 162 V max operating voltage), and extend down below the lid of the discharge trough. These

two heaters are used to keep the Inconel discharge lid hot to minimize
the tendency of the glass to curl back under the discharge trough as it
pours.

IV.2.3.8. Discharge System   Zirmul blocks are used above the
discharge trough and around the discharge face to form the trough and
discharge cavities. A 55-cm-long and 24-cm-dia Inconel cylinder is
welded to the containment box floor, axially in line with the drop point
from the discharge lip. Standard pressed insulation fire bricks fills
the void from the Inconel bottom of the melter box to the top of the
outer discharge tube.

A 50-cm-long flanged section of flexible stainless steel pipe is
used to make a sealed, flexible connection between melter and receiving
canister. One end of the flanged pipe is connected directly to the
discharge tube flange assembly discussed previously and the other end is
connected to a 20-cm pneumatic-operated knife valve. When the receiving
canister is not in the place, the knife valve is closed to stop the flow
of air into the melter. The closed knife valve also prevents accidental
discharges of glass from the melter system.

The removal system is detailed in Figure 13. The glass canisters
are placed into a cylindrical steel container which is lined with fire
bricks so that during and after the discharge, cooling is slowed. Slow
cooling results in a glass which has minimum cracks in it (The more the
cracks, the greater the surface area in the glass, and therefore, the
greater the risk of leaching by repository ground water). The cylinder
has a diameter of 65 cm and height of 90 cm. The thickness of the

lining is 10 cm. Canisters, 40 cm in diameter and 75 cm high, are used

for this purpose. The cylindrical container rests on a 75 cm x 75 cm

cast iron dolly with thickness of 5 cm and four wheels are provided.

The wheeled container travels on tracks, 4.5 m long and 0.80 m wide.

After the canister is filled, the container is remotely moved, first to

a limited circulation room for further controlled cooling, and finally

to a storage or disposal site.

A similar method is used to remove the metal mixture, except that

the steel crucible is not provided with insulation but a tracked dolly

with four wheels is provided. The discharge of the metal mixture is

one-shot and there is no need for it to be cooled slowly, as it moves

directly to the squeeze operation. Both glass canister, after cooling,

or the crucible that contain lead plus noble metals are transported by a

lift truck. The truck could be shielded or, preferably, unmanned or

remotely operated.

IV.2.3.9. Inner Refractory Coolers (IRC)   Slab-type coolers (8

cm thick, 38 cm wide, and 51 cm tall) are located in the midst of the

refractories in the discharge end of the containment box. The purpose

of the coolers is to inhibit glass leakage from the melter tank. The

heat loss to these coolers runs about 2.87 Kw each.

IV.2.3.10. Cooling Jackets   Cooling jackets are built into the

containment box to control the cold side temperature of the

refractories, to prevent molten glass and metal mixture from completely

penetrating the refractory walls to the containment box, and to assist

in cooling the Inconel electrodes. The cooling jackets are located on

three sides of the containment box. The unjacketed fourth side is at the discharge end of the melter where refractory temperature are not severe. The heat losses run about 0.8 Kw.

IV.2.4. Gas Feed and Evacuation System

In order to increase ruthenium recovery, an inert gas atmosphere is recommended. The inert gas is argon, and is fed from tanks which are situated between the two melters. Two argon gas tanks are available, one for each melter. The tanks, each 2.1 m³, feed the melter after accumulated gas in the melters is removed. Feeding is by an installed vacuum pump. The maximum pressure allowed in the melter is 1.5 atm; the vacuum pump evacuates the $CO/CO_2/Ar$ gas mixture when melter tank pressure exceeds 1.5 atm. This limit is set in order to obtain optimum conditions for reduction reactions and noble metal extraction.

The carbon dioxide and monoxide release rate is 5.03 m³/h which means that pressure buildup is very slow.

IV.2.5. Squeezer

In order to separate solid Pb plus noble metals from the liquid Pb-Zn metal mixture, fractional solidification is applied (Chapter III). For this solidification and separation, a squeezer was designed. The squeezer is 75 cm in diameter and 110 cm in height. The squeezer is placed on a concrete foot, 70 cm high.

The squeezer consists of an adapted compression testing machine. In operation a plunger moves downward relative to the metal causing any liquid in the crucible to pass through a filter. The outside of the
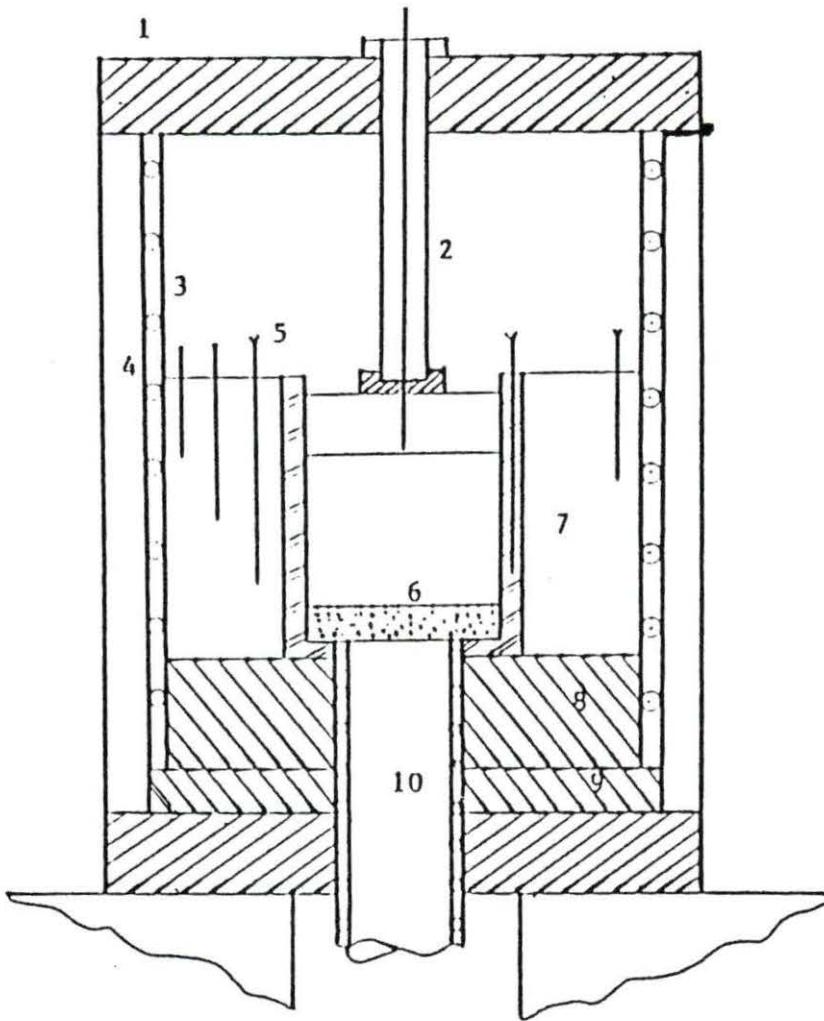
1- Top Lid
2- Plunger
3- Heating Coils
4- Isolation
5- Thermocouples
6- Alumina Filter
7- Brass Ring
8- Fire Bricks
9- Cast Iron
10- Discharge Section

FIGURE 14.   Squeezer

squeezer is well-insulated to reduce heat losses and create conditions for well-controlled temperature solidification (fractional solidification).

The crucible, which holds the liquid metal mixture, is made of stainless steel and is 25 cm in diameter and 35 cm in height. The plunger is carefully aligned with the crucible axis. The crucible also holds a 6 cm thick porous alumina filter with a pore size of 200 to 300 micro meter. The liquid metal is placed in the crucible directly above the filter.

The design includes a brass ring, 27 cm inside dia. and 77 cm outside dia., and bearing insulation designed so that minimum temperature differences occur in the liquid metal mixture. The brass ring is coated with 1 mm steel in order to protect brass from oxidation.

The top lid of the squeezer is movable which permits us to remove the crucible and replace it with another one. The crucible is a special design and is used only in squeezing. A crane is available for all lifting operations. The squeezer is covered by a steel containment box. The bottom is cast iron (10 cm high), and on top of it fire bricks (20 cm high). Cast iron absorbs the stresses that occur during squeezing and fire bricks are used for insulation purposes.

The squeezer requires 40 Kw to operate and 30 Kw in standby. The squeezer is basically surrounded by a cylindrical heating coil which is supplied with energy either directly from the network (line frequency) or through a frequency convertor. The magnetic field generated by the coil is the energy carrier to the charge. Also a heating coil, smaller

in diameter, is provided to prevent squeezed metal from freezing in the discharge tube.

IV.2.6. Instrumentation

IV.2.6.1. Argon Plasma Spectrometer   The APS is ideally suited for the analysis of liquid samples. It provides highly simplified operation and relieves the operator from the burden of interpreting and analyzing the spectra. A radio frequency generator supplies power to generate an intense oscillating magnetic field, forming and sustaining the plasma. A pneumatic nebulizer aspirates solutions into the center of the plasma, where temperatures up to 8,000 ° K are rapidly reached. Analyte species are reduced to atomic form and subsequently emit energy at their characteristic wavelengths. The emitted light enters a monochromator where it is dispersed by a diffraction grating. The exit slit isolates the wavelength of interest, allowing it to enter the photomultiplier tube where precise intensity measurements are converted to electric signals. A computer then converts the signals into concentration units and presents its findings to the operator. The recommended spectrometer is ARL 3410 'ICP'.[6] It is 171 cm high, 161 cm wide, and 75 cm deep, and weighs 432 kg. The spectrometer is furnished with IBM PC XT microcomputer with 640 Kbytes memory.

The spectrometer is situated in the basement of the control room, and the radioactivity in the basement is carefully monitored by

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[6] Registered Trademark of the Applied Research Lab, Sunland, Calif.

sensitive detectors. The samples to be analyzed are remotely taken from

the discharge section by an automatic sampler and transported

pneumatically to ARL 3410 ICP. The torch section of the spectrometer is

shielded in such way that no radioactive gas release from the torch to

the room is permitted. This gas is partially condensed and collected in

steel tanks located next to the spectrometer and for later disposal.

Output of the ARL 3410 ICP is made to the IBM PC XT microcomputer which

is located in the control room.

TABLE 4.   Typical noble metal APS detection limits [16]

Metal	Detection Limit (ppm)
Pd	0.040
Ru	0.050
Rh	0.010
Pb	0.005

Typical noble metal APS detection limits are given in Table 4.

Although these detection limits are not as low as for techniques such as

neutron activation, the APS does offer the most rapid and accurate

method available for simultaneous determination of trace concentrations.

IV.2.6.2. Thermocouples   The thermocouples are used to monitor

temperatures throughout the melter. Table 5 shows the location of

thermocouples. The "K" type is used (40 T/Cs). Extension wires are

connected to a readout device on a panel in the control room. To

protect thermocouples from harmful atmospheres and corrosive fluids, or

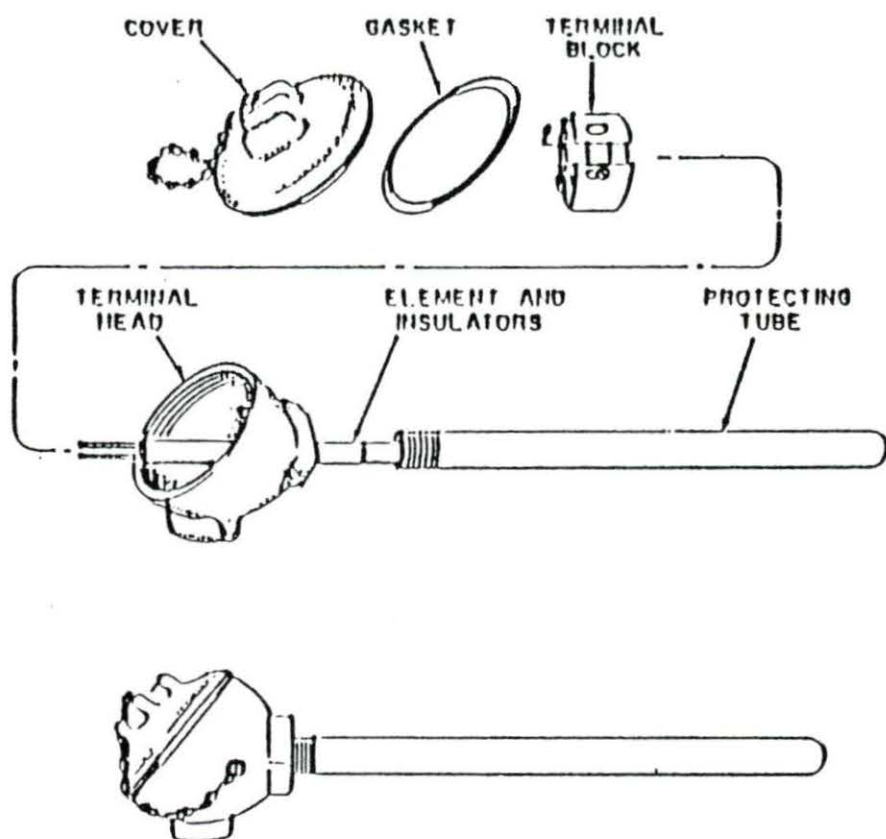FIGURE 15.   A view of TC assembly and protecting tube [17]

mechanical damage, protecting tubes or wells are supplied to support the
thermocouples.

Thermocoupes are needed in both melter and squeezer. Four
thermocouples are inserted inside the wall of the squeezer crucible,
another in the center of the plunger. About 24 thermocouples are
inserted in the brass ring (Figure 17). The thermocouples employed

TABLE 5.   List of thermocouple locations in the melter

Thermocouple Number	Location
1	N Electrode Probe, 9 in. in Level
2	N Electrode Probe, 6 in. in Level
3	N Electrode Probe, 3 in. in Level
4	N Electrode Probe, 0 in. in Level
5	N Electrode Cooling Air Outlet
6	Tank Sub-Floor Corner
7-9	Melter Tank West Wall
8	Tank Sub-Floor Center
10	Auxiliary Tank Heaters N
11	West Wall Center-Top
12	West Wall Center-Middle
13	West Wall Center-Bottom
14	Feed Nozzle Cooler
15	Glass Probe, 18 in. in Level
16	Glass Probe, 15 in. in Level
17	Glass Probe, 12 in. in Level
18	Glass Probe, 9 in. in Level
19	Glass Probe, 6 in. in Level
20	Glass Probe, 3 in. in Level
21	Glass Probe, 0 in. in Level
22	Freeze Valve Shell Top
23	Auxiliary Tank Heaters S
24	Freeze Valve Nozzle
25	S Electrode Cooling Air
26	S Electrode Cooling Air
27	N IRC-Top
28	N IRC-Middle
29	N IRC-Bottom
30	Discharge Through Sub-Floor
31	Discharge Through-1
32	Discharge Through-2
33	Discharge Through Cooler
34	Discharge Tube
35	Discharge Face
36	S IRC-Top
37	S IRC-Middle
38	S IRC-Bottom
39	S IRC Air Outlet
40	Tank Sub-Floor Discharge

should never show temperature differences exceeding 1° C. To accomplish

that the thermocouples should be periodically checked and calibrated.
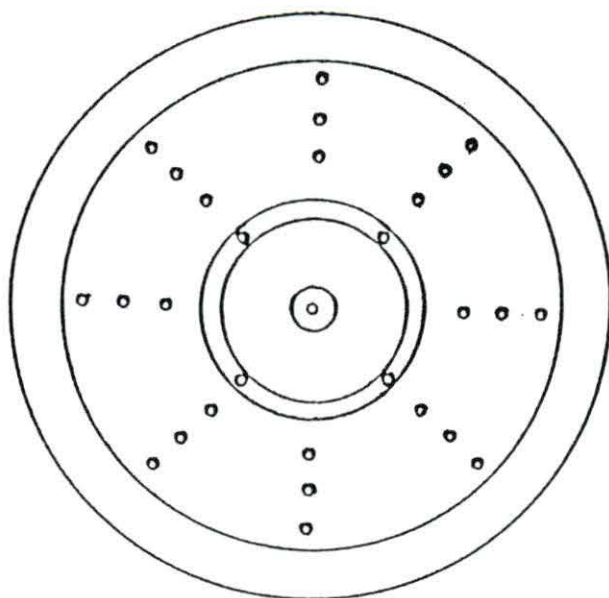
o   Thermocouples

FIGURE 16.   Thermocouple locations in the squeezer

IV.2.6.3. Rotational Spindle Viscometer   The design pressure

and temperature of this instrument are 1.5 atm and 1400° C. It is

capable of measuring viscosities in the 0-500 P range. Viscosity is

measured by sensing the torque required to rotate a spindle continuously

in the molten glass. A measuring head is installed on the melter tank.

The temperature of the mounting flange on which the viscometer is placed

should not exceed 315° C. To prevent this, a cooling pad between flange

and viscometer was designed. The baffle tube is 1 m in length and 3 cm
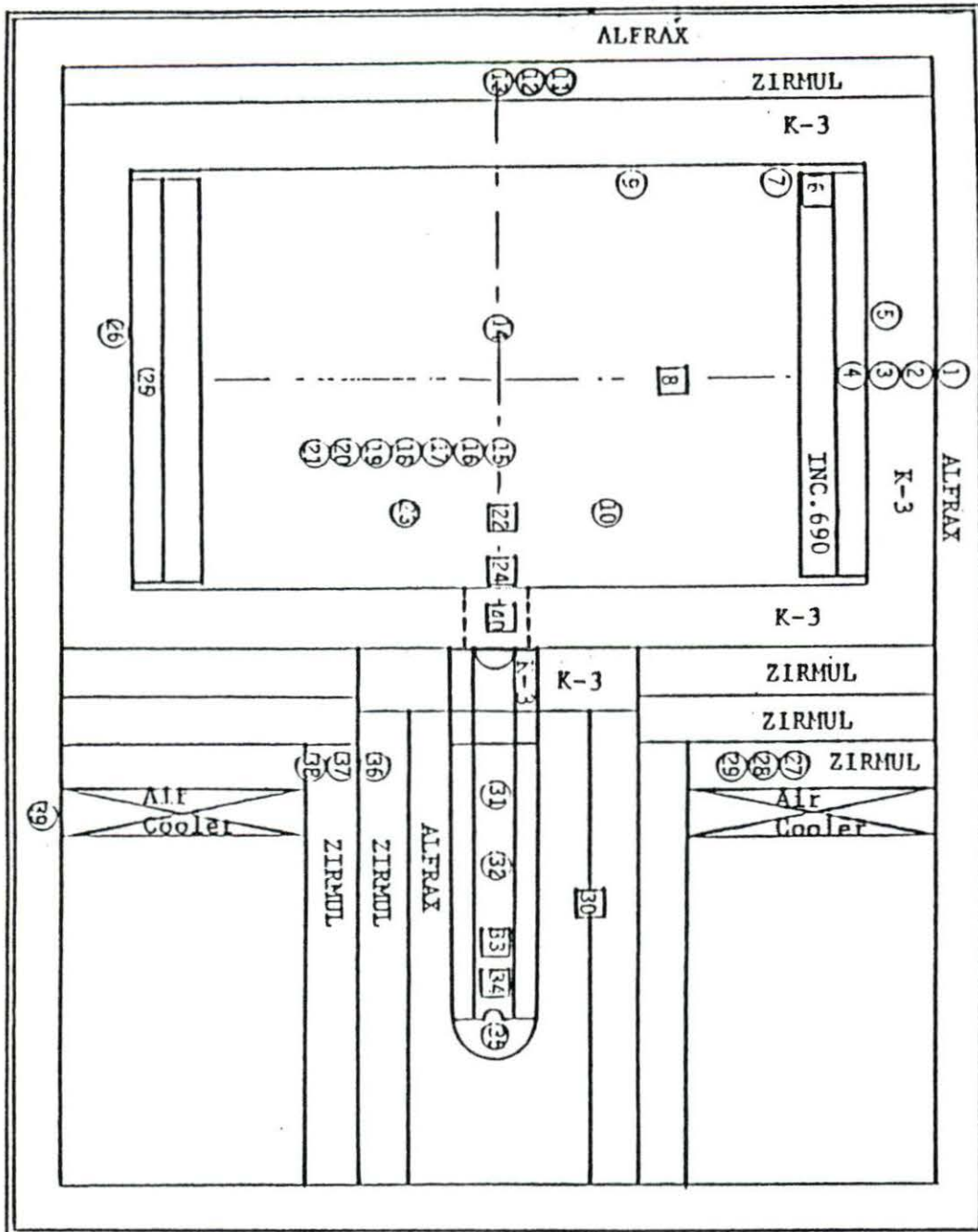
FIGURE 17.   Thermocouple locations in the melter
[Adapted from Reference 15]
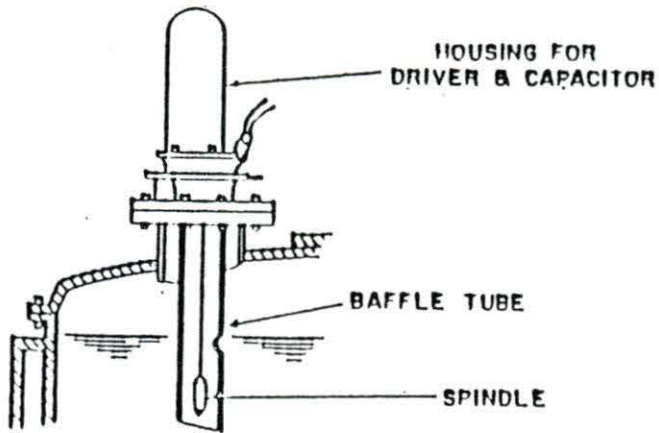
FIGURE 18.   Rotational spindle viscometer [17]

in diameter.

IV.3.   Plant Products

IV.3.1. Metal Mixture

Having fed the melter, rections occur and two products are
obtained. One is Pb plus noble metals, and the other is the glass. The
metal mixture contains 1765 ppm Ru, 345 ppm Rh, 1279 ppm Pd, and 99.66
wt% Pb. The metal mixture production rate is 60.46 kg/h per melter. In
order to enrich the Pb with noble metals, fractional solidification and
squeezing processes are performed (Chapter III.4). After Zn addition (2
% of Pb present), 1.205 kg Zn/h, the metal mixture contains 1730.5 ppm
Ru, 338.6 ppm Rh, 1253.9 ppm Pd, 1.954 wt % Zn and 97.71 wt % Pb. This
mixture is squeezed in the squeezer. Two phases are obtained. The

liquid phase, 59.1 kg/h, contains 97.6 wt % Pb and 2.4 wt % Zn. The solid phase, 2.565 kg/h per melter, contains 4.16 wt % Ru, 0.82 wt % Rh, 3.02 wt % Pd, and 92 wt % Pb. It is this solid phase that is sold as plant product.

As was indicated previously, our Purex waste is at least 10 years cooled. Realistically by the year 2000, the commercial nuclear wastes in the U.S will be at least 12 years cooled [18]. Knowing that the radioactivity of the noble metals is reduced to 0.082% of their radioactivity at discharge in 10 years, the radioactivity of longer cooled Purex waste will be smaller. Therefore, less radioactivity is contributed by noble metals, especially by Ru-106. Nevertheless, the radioactivity of the lead alloy is found to be 1.3675 Ci/kg alloy (Appendix A) which needs to be reduced to a safe level that does not cause any radiation hazard to the personnel who purify the alloy, or to users of these metals. If this alloy is stored for ten more years, the radioactivity of the alloy will be reduced to about 1.55 mCi/kg alloy. Here the radioactivity is mostly contributed by Pd-107 which is a low energy (0.035 MeV) beta emitter.

If we assume, in the worst case 10% Tc recovery, we get about 0.19 wt % Tc in the alloy. This is completely Tc-99 isotope (2.13×10^5 years), having about 0.017 Ci/gTc radioactivity. That is not desired because it will contribute 0.0323 mCi/kg alloy and last as long as the noble metals are used.

IV.3.2. Glass

Glass (vitrified waste) contains 27 wt % Purex waste, 3.25 wt % PbO (12.5 wt % of the total PbO charge), and 69.75 wt % of glass (from frits and flux). The glass is homogeneous in appearance. In addition, the resistance to leaching of the glass tested in PNL was found to be close to that of waste glasses [13]. As long as the charge requirements are met and the viscosity maintained at the proper level, the glass should have properties that will be acceptable for waste disposal.

V. ECONOMIC ASSESSMENT

This section contains an economic assessment of two cases in terms
of their capital and operating costs. In the first alternative (Case
I), the assumption is that the waste vitrification facility would be
incorporated into the Purex complex which would bear the vitrification
facility cost. Space would be available within the Purex complex. The
second alternative case (Case II) is that the extraction and
vitrification facility, described in detail in Chapter IV, is provided.
In the economic assessment, the difference between the two cases
represents the marginal cost of providing for noble metal recovery.

V.1. Capital Costs

Building a plant requires investment of capital to purchase land,
to construct buildings, to install equipment, and to provide cash to
permit purchase of supplies and to pay salaries until the venture begins
to pay its way in the form of profits. In our case, the largest cost
items expected in both of the cases are construction cost and the land
cost. Because the land at a Purex complex is always designated for the
handling of wastes, the opportunity cost (the value of the land in its
next best alternative use) is considered zero. The types of facility
and equipment do not differ very much between Case I and Case II. In
Case I, feed tanks are needed for Frit-165, Frit 76-101, and Na_2CO_3 .
The electric melters will be conventional vitrification melters;
therefore, cheaper melters than those used in Case II. In Case I, there
is no need for a squeezer.

Since the radioactivity of the alloy is high, a ten-year cooling period is required before the noble metals can be used in the industry. To do that the alloy should be stored possibly next to the plant. That is why storage cost is included, covering the construction of the storage facility and the containers the alloy will be stored in.

The factor method was used in estimating capital costs. Factor estimating relies on the principle that a ratio factor exists between the cost of a particular equipment item and the associated nonequipment items that need to be added to the project in order to complete the installation of that item. Standard equipment (feed tanks, bunker, and conveyor) prices were obtained and adjusted for facility design as necessary in this study [19]. The melter, 50 kg/h, designed and installed by PNL in February 1986 The melter cost estimates were obtained by using a 0.6 cost capacity factor. The cost capacity factor for furnaces between 20-200 Kw is given as 0.5 which was used in estimating the squeezer cost.

In factor estimating, there are basically two ways to estimate the capital costs. One takes purchased equipment cost, and the other takes installed equipment cost as the starting point. In this work, we used installed equipment cost, because installed melter cost, which is the bulk of the equipment cost, was available. Later, estimates for nonequipment items that makes the capital cost were obtained by multiplying installed equipment costs with appropriate Lang factors that are provided in references 20, 21, 22 and 23, except for the control and instrumentation costs. These were obtained again from the melter

TABLE 6.   Comparison of the installed equipment costs

ITEM	($) Cost per item	Case I		Case II	
		# of items	Total	# of items	Total
Feed Tanks	5,000	3	15,000	5	25,000
Bunker	7,500	1	7,500	1	7,500
Melters		2	7,500,000	2	8,000,000
Squeezer	1,500,000	-	--	1	1,500,000
Conveyor	$4000/m	70m	280,000	80m	320,000
TOTAL			7,802,500		9,852,500

TABLE 7.   Capital cost distribution

ITEM	CAPITAL COST($)	
	Case I	Case II
Process Equipment	7,802,500	9,852,500
Pipe, Valves, and Fittings	780,200	985,200
Storage	---	1,970,400
Control and Instrumentation	1,960,000	2,450,000
Electrical	390,000	492,000
Building Const.	2,180,000	3,150,000
Eng. Fee (15%)	2,000,000	2,835,000
Contingency(15%)	2,270,000	3,260,000
TOTAL	17,382,700	24,995,100

figures mentioned earlier and adjusted to our case by using an appropriate cost capacity factor.

V.2. Operation Costs.

As far as the materials used are concerned, the Purex waste cost is assumed to be zero. The prices of the raw materials were taken from weekly published Chemicals Marketing Reporter [24], and the required amount of material (displayed in Table 8) was multiplied by the price to find the costs. An estimate of the number and type of personnel required to operate a facility at the proposed capacity is given in Table 9.

TABLE 8.   Materials used and their costs

RAW MATERIALS	$/kg	Case I		Case II	
		t/y	Cost($/y)	t/y	Cost($/y)
Glass Mix.	0.50	3,000	1,500,000	2,500	1,250,000
PbO	0.35	-	-	1,300	455,000
Charcoal	0.20	-	-	200	40,000
Argon	$0.074/ft^3	-	-	560,000 ft^3	41,440
TOTAL			1,500,000		1,786,440

TABLE 9.   Personnel and salaries

PERSONNEL TYPE	$/y SALARY	Case I		Case II	
		Number of Personnel	Total $/y	Number of Personnel	Total $/y
Manager	50,000	1	50,000	1	50,000
Engineer	35,000	2	70,000	2	70,000
Operator	27,000	6	162,000	8	216,000
Technician	22,000	6	132,000	8	176,000
Laborer	18,000	3	54,000	4	72,000
Fringe Benefit (15%)			70,200		87,600
Overhead (50%)			269,100		335,800
TOTAL			807,300		1,007,400

TABLE 10.   Total annual operation costs

	Case I ($/y)	Case II ($/y)	Cost Dif.
Raw Materials	1,500,000	1,786,440	
Electricity	178,200	257,400	
Salaries	807,300	1,007,400	
Investment Cost (15%)	332,460	407,316	
TOTAL	2,817,500	3,458,240	640,740

V.3. Cost Differential

Process chemicals and other process materials, and utility services are included in the determination of the operating costs of the facilities. The operation costs and a cost differential is presented in Table 10. From the design figure of 5000 ton/y of initial waste the glassification cost is $ 0.57/kg in Case I, in Case II this cost increases to $ 0.70/kg. Actually, the $ 0.13/kg increase in annual spending goes to the extraction of noble metals from nuclear waste by the described method.

The vitrified waste can be stored in an appropriate manner, generally away from the public. The cost of storing and disposing of these wastes must be assessed on a site-by-site basis. Obtaining an accurate estimate of the costs of permanent disposal is difficult because the question of acceptable sites for permanent disposal of radioactive wastes has not been settled, and costs are site specific. However, this item will be the same for Case I and Case II.

V.4. Revenue From Sales

Revenue from each facility can be estimated using the quantity of material recovered at the site for each year of operation, multiplying by the sale price of that material, and discounting the future income to present value. To estimate the future revenues, it is necessary to determine the current and future market conditions for the materials being recovered.

Significant quantities of three noble metals will be recovered as lead alloy from the operation of the proposed extraction facility. The consumption of these metals in the U.S is shown in Table 11.

TABLE 11.   Annual noble metal consumption (in Kg) [3]

	1978 (Actual)	1980 (Actual)	1900 (Forecast)	2000 (Forecast)
Pd	28,550	28,370	34,210	42,300
Rh	2,180	2,290	3,580	4,820
Ru	1,800	2,420	3,270	5,290

Palladium is currently used as a component in telephone switching equipment and automobile catalytic converters, as a catalyst in petroleum refining and glass making, and for dental purposes. Demand for this product is expected to grow steadily for the next 10 years and then begin to slow down, when substitutes for its use are found [7].

Rhodium's major uses are as an alloy element to harden Pt and Pd, as plating in jewelry, in electrical parts, automobile catalytic converters, and as a catalyst in a variety of chemical processes. The quantity of rhodium demanded is expected to follow the same trend as that of palladium.

Ruthenium is useful in electronics, electrical applications, and as a catalyst in chemical processes. Its use has been increasing recently because of price and supply advantageous over the other noble metals. For this reason, the demand for ruthenium is expected to

continue to grow, and there should be no problems involved in selling the full annual output from the proposed recovery facility.

In pricing the lead+NM metals alloy, a discount is necessary to make the product attractive aganist imported metals. In this study, a 50% discount was assigned to determine the present worth of sales that must be delayed for ten years. The selling will be performed ten years after extraction. To estimate the selling price of the alloy more accurately, future price forecasts should be studied. However, at a 5% discount rate for ten years, a 40% price discount for present worth at time of extraction of the alloy would result. We, therefore, chose 50% discount for the sake of being conservative.

Market prices of 99.9% purity noble metals are given in Table 12 with the production from the facility described here.

TABLE 12.   Noble metal market prices and production[1] [24]

	PRICE ($/gram)	PRODUCTION (Kg)
Ru	5.46	1,690
Rh	28.93	329
Pd	4.82	1,224

[1] 1985 Market Prices.

As a result, the total revenue from sales becomes $ 7,395,000. The immediate processing consists of extracting the noble metals as a lead alloy. This alloy is processed and purified by the methodology described in Appendix B. No costs are assumed for this last extraction

process; this processing is expected to be performed by private industry, but the sale and processing will not occur until at least 10 years after extraction.

VI. CONCLUSIONS

The noble metals have strategic importance for the U.S economy.
Their domestic production is necessary and must be made. It is well-
known that potential exists for the noble metals to be recovered
economically from spent nuclear fuels. In this study, we first
identified the process (Lead Extraction Process) selected to recover the
noble metals from spent fuel efficiently. The studies performed by PNL
since 1979 and experiments and their results served our aims. The
results were widely used in the design. Some of the design features
that will likely be incorporated into facilities in a mature industry
were explored. We also identified the principal components that make up
the costs of a noble metal extraction and vitrification plant, and of a
waste vitrification plant only, providing some insight about the
relative importance of each component.

One expects to have a waste vitrification facility within a Purex
processing plant. The vitrification facility could be modified so that
one also could recover the strategic noble metals. The modifications
will require about 7.5 million dollars in incremental capital cost and
about 1 million dollars in annual operation cost over that for only
waste vitrification facility; we would still, of course, vitrify the
radioactive spent fuel while recovering the three noble metals as lead
alloy. For a Purex plant owner, this new facility does not become an
economical burden; on the contrary, it becomes a very profitable by-
product operation. The present worth of revenue ten years from now,
computed to be about 7.5 million dollars annual revenue from sales of

the metal alloy greatly exceeds the capital and operating costs. This study demonstrates that the lead extraction process can be applied to industrial use beneficially and economically, and the expected profits are large politically and economically. The design is flexible enough for the future capability of capacity increase. There is no doubt that facilities of this sort will relieve the future industrial demand for noble metals in the U.S.

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VII. APPENDIX A: ACTIVITY CALCULATIONS

After a 12-year cooling period, the noble metal isotopes with the longer half lives are the main concern. These are Ru-106, Pd-107, and Tc-99. The other isotopes of the noble metals decay to a stable state very quickly because of their relatively short half lives. These three radioactive isotope decay chains are given below;

$$Tc^{99} \longrightarrow Ru^{99} \text{ (stable)}$$

$$Ru^{106} \longrightarrow Rh^{106} \longrightarrow Pd^{106} \text{ (stable)}$$

$$Pd^{107} \longrightarrow Ag^{107} \text{ (stable)}$$

Here, predecessors of even shorter life isotopes have been omitted. The number of fissions from reactor spent fuel with 30,000 MWd/MT burnup is found to be, using standard assumptions, 8.0496×10^{22} fissions/kg Spent Fuel. Then the number of nuclides at discharge will be the number of fissions times the fission yield of that decay chain.

$$N^{\circ}_{99} = 4.9255 \times 10^{21} \text{ Mo}^{99} \text{ nuclei/kg SF}$$
$$N^{\circ}_{106} = 3.2335 \times 10^{20} \text{ Tc}^{106} \text{ nuc/kg SF}$$
$$N^{\circ}_{107} = 1.1309 \times 10^{20} \text{ Tc}^{107} \text{ nuc/kg SF}$$

The number of Ru^{106} atoms at discharge for three years exposed fuel can be calculated from

$$N'_{106} = N^{\circ}_{106} [1-\exp(-3 \lambda_{106})]/3/ \lambda_{106}$$

and the number of Ru^{106} atoms after 10 years cooling period is calculated from

$$N_{106} = N'_{106} \exp[- \lambda_{106} tc]$$

where tc is the cooling period, and λ_{106} the decay constant of Ru^{106} (2.153×10^{-8} sec^{-1}) isotope. After 10 years of cooling, the calculated value is then

$$N_{106} = 4.0311 \times 10^{16} \; Ru^{106} \; nuclei/kg \; SF$$

and the activity per kg spent fuel is calculated from,

$$A_{106} = N_{106} \; \lambda_{106}$$

and is equal to 0.023457 Ci/kg SF.

We can calculate the specific quantity of Ru^{106} which is 7.0955×10^{-6} g Ru^{106} /kg SF. Then, the radioactivity per gram Ru^{106} is found to be 3305.8 Ci/g Ru^{106} . The radioactivity contributed by Ru in the alloy is found by multiplying the quantity present in the alloy with its radioactivity; the results in 0.618 Ci/kg alloy.

Since Ru^{106} and Rh^{106} are in equilibrium, Rh^{106} also will contribute as much radioactivity as Ru^{106} (0.618 Ci/kg alloy).

Palladium 107 isotope concentration is almost unchanged after the cooling period because of its very long half life.

$$N_{107} = N^{\circ}_{107} = 1.1309 \times 10^{20} \; Pd^{107} \; nuclei/kg \; SF$$

Activity of Pd^{107} is calculated from,

$$A_{107} = N_{107} \; \lambda_{107}$$

where λ_{107} is the decay constant of Pd^{107} (8.381×10^{-15} sec^{-1}), and the activity of Pd^{107} is found to be 0.01033 mCi/kg SF. The contribution to the alloy by Pd^{107} is 1.165 mCi/kg alloy. The activity calculation of Tc-99 is similar to those of Ru-106 and Pd-107. Here also Tc concentration is unchanged over the cooling period because of its very long half life.

$N_{99} = N^{\circ}_{99} = 4.9255 \times 10^{21}$ Tc^{99} nuclei/kg SF

and the activity is calculated from

$A_{99} = N_{99} \lambda_{99}$

where λ_{99} is the decay constant (1.032×10^{-13} sec^{-1}). The activity of one gram of Tc^{99} is 0.017 Ci, and the contribution to the alloy is 0.01303 Ci/kg alloy. Now, the total radioactivity contributed by three of the noble metals, including Tc, will be the sum of the radioactivities, which is 1.3675 Ci/kg alloy. Ten tears later, this activity will be about 15.5 mCi/kg alloy which could be considered low enough for processing.

VIII. APPENDIX B: PURIFICATION OF NOBLE METALS

Because of the radioactivity of the alloy it can not be purified and used immediately. This alloy has to be stored until radioactive Ru-106 has decayed enough that alloy can be processed.

One might conceive of several schemes for purification of the noble metals from the lead alloy. One possible option was explored during the course of this research. The purification could be accomplished by the methodology identified in Figure 1.

Most of this technology is used commercially, and no long-term development is required to verify its viability for fission products. Since platinum, Os, and Ir are not present to complicate and increase the cost for recovery of Pd, Rh, and Ru, purification should be straightforward and at minimum cost. Thus, purification should be a laboratory-scale operation.

Ruthenium and Rh are insoluble in all acids, including aqua regia. On the other hand, palladium and lead are soluble in acids. Palladium is the only metal of the platinum group to be attacked by nitric acid when in the massive state. Thus, a first separation is based on the solubility of the metals in nitric acid. The alloy is dissolved in hot HNO_3 and filtered; the filtrate contains about 15 % Rh and 85 % Ru. Further separation or purification of Ru and Rh is based on oxidation of Ru to volatile RuO_4 Ruthenium tetroxide exists in two forms, the brown form (m.p.27° C) being more stable, more soluble and less reactive than the yellow form (m.p.25° C). It is volatile even at room temperature, subliming with a moderate partial pressure. Ruthenium is stable in
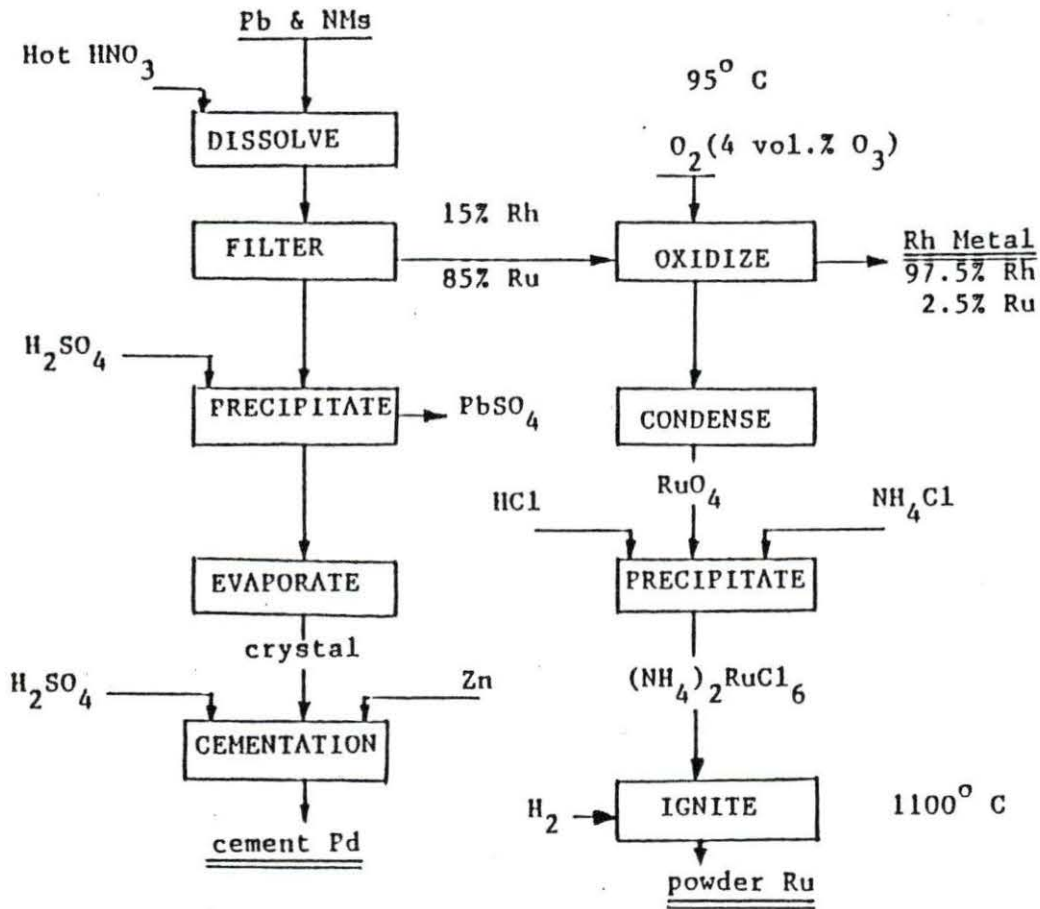
FIGURE 19.   Purification flowsheet of the lead & NM alloy

oxygen at room temperature, but its oxidation is appreciable at 100° C and rapid at 500° C. The main product of oxidation is the dioxide, RuO_2, but above 600° C some tetroxide is formed. To form mostly tetroxide, a strong oxidizing agent is used: that is oxygen enriched with 4 vol % ozone. In laboratory tests at 95° C using this oxygen-ozone mixture, in two hours 97.5% of Ru was volatilized and in ten hours 99.5 % of Ru was volatilized.

During oxidation Rh is not affected; it is an extremely noble metal. It is not attacked by oxygen, water, aqueous solutions of caustic alkalis, solutions of acids, and oxidizing agents including aqua regia. The residue is 97.5 % Rh and 2.5 % Ru metal, but the Ru content can be reduced further by long exposure to the oxidizing agent.

Ruthenium tetroxide is condensed and absorbed in concentrated HCl solution, which reduces it to Ru^{+3} and Ru^{+4} Addition of NH_4Cl to the HCl solution results in the precipitation of ammonium chlororuthenate. The crystals are filtrated off and are ignited to ruthenium black, which is finally reduced at 1000° C in a hydrogen atmosphere to a metal powder. The volatization of tetroxide will require precations to minimize the release to the environment of radioactive Ru-106.

Palladous nitrate and plumbous nitrate are easily formed by the action of nitric acid. The solution is then exposed to H_2SO_4 to precipitate $PbSO_4$ by dissolving the sulphate crystalls in cold water. Palladous sulphate is very soluable in cold water while much of the plumbous sulphate is filtrated off. Palladous sulphate is reacted with sulphuric acid then zinc is added to this solution which results in the

displacement reaction between Pd^{+2} and Zn^o The products are cement palladium, Pd^o , and Zn^{+2} ions in the solution.

IX. AKNOWLEGMENTS