

RECOVERY OF VALUABLE METALS FROM HIGH-LEVEL RADIOACTIVE WASTE

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Processing steps of the recovery of valuable metals from spent nuclear fuel are studied by means of experiments of lead extraction from high level radioactive waste (HLW) and selective separation of noble metals from simulated waste. Lead extraction and cupellation are found to be effective to recover valuable metals from the actual insoluble residue in dissolver solution of spent fuel. As for refining processes of noble metals extracted in lead, selective separation of ruthenium by ozone oxidation method and mutual separation of rhodium and palladium by solvent extraction method, precipitation method and ion exchange method are examined. These methods are found to have high efficiency for refining these three metals. An optimum conceptual flow sheet for recovery of valuable metals from HLW is derived from these experimental studies.

1. Introduction

Spent nuclear fuels contain significant quantities of valuable metals - the platinum-group metals and technetium. The recovery of the platinum-group metals, palladium, rhodium and ruthenium, leads to a new source of these three metals which have uncertainty in supply because of world's limited producers and are increasing in demand because of the growth of high-technology industry. Spent nuclear fuels also contain technetium which is nearly absent in nature and promising in some kinds of fields of material application. Thus there is considerable incentive to recover the platinum group metals from spent nuclear fuel and various processes to recover them have been evaluated on a laboratory scale[1].

Power Reactor and Nuclear Fuel Development Corporation (PNC) began in 1986 to study and has been developing the technologies to recover and utilize three of the platinum-group metals and technetium from spent nuclear fuel as a part of the partitioning program of HLW (OMEGA project) in cooperation with private companies and universities. All the experimental and bibliographic studies were performed under advice of a special committee - The Technical Committee of Recovery and Utilization of Valuable Metals in Spent Nuclear Fuel sponsored by PNC. The committee had prepared the R&D's program after evaluation of possible flows for recovery and utilization of the valuable metals, which had resulted an optimum flow for the recovery.

Some parts of the platinum-group metals exist as the main constituent of the insoluble residue from dissolution stage of spent fuel in Purex process. The recovery of the platinum-group metals from the insoluble residue is simpler and easier than that from HLLW since the residue consists of metallic alloy containing the metals. Thus we have been developing mainly the processes to recover the noble metals from the insoluble residue.

Fig.1 shows the processing steps for recovery and purification of the platinum-group metals from HLW. In this paper we describe the experimental results on each stage in Fig.1, and discuss a conceptual flow sheet for recovery of the platinum-group metals from HLW.

2. Lead extraction

Lead metal was selected as a scavenger in the first stage of separation of the platinum group metals from other fission products and TRU elements. Sodium borate was used as a glass-forming material to fix other constituents of insoluble residue and calcination.

The actual insoluble residue was obtained from the dissolution stage of FBR spent fuel with burn-up 88000 MWD/t. The majority of particle size of the residue was less than $2\ \mu\text{m}$ in diameter. The residue had the composition of 30% Ru, 7.8% Rh, 8.7% Pd, 12% Tc, 23% Mo, 10% Pu and 2.3% U. The irradiated fuel was dissolved under the mild condition so that some part of plutonium and uranium oxide remained to be undissolved. This enabled to estimate the decontamination factor of TRU elements. The residue of 0.45g was mixed with granular lead metal and sodium borate powder in weight ratio of 50 to 1 and 20 to 1 respectively. Table 1 shows the condition of the lead extraction. The mixture was placed in a mullite crucible and then melted at 800°C for 3hr in the air. Another extraction temperature, 1100°C was used in order to examine influence of temperature on phase separation. After melting the mixture was cooled in the furnace and the lead metal called Pb button was separated from the glass. All the operation of lead extraction test was performed in a hot cell.

The distribution of the platinum-group metals in the Pb button was determined by electron probe microanalysis. Rhodium and lead existed in the Pb button uniformly while ruthenium segregated in the upper part of the Pb button close to the boundary between lead and glass. In some extraction conditions a Pb button was not formed and rather small metal phases were dispersed in the glass. Rhodium and lead seem to be alloy with lead. Technetium existed in the same area where ruthenium segregated in the Pb button. On the other hand, ruthenium, rhodium and palladium were not detected in the glass as if the Pb button formation was not perfect. The volatile fraction of ruthenium was not determined in the hot test, however the cold test gave no indication of volatilization of ruthenium while lead extraction at the same condition.

Radioactivities of the glass as well as the lead were measured to determine the decontamination factors of TRU elements. As shown in Table 1 the decontamination factors for Pu, Am and Cm were more than 200.

3. Cupellation

As the platinum-group metals are contained in a Pb button, Pb separation at early stage may be effective to make the following processes easier. Cupellation method is applied to roughly remove lead from lead-platinum group elements alloy to obtain noble metal bead.

Lead button containing the platinum metals were heated on a magnesia crucible or a calcium phosphate crucible (cupel) at 850-1050°C in the air, and then a metal bead were obtained. The main constituent of the bead was platinum group metals, therefore this method was proved to be available for Pb separation process from Pb button. This treatment is optional and not essential for the following separation processes, so that it possible to dissolve Pb button directly without cupellation.

4. Ruthenium separation

The Pb button, containing the platinum group metals (Ru, Rh, Pd), Tc and Mo, is obtained at the Pb extraction stage as before. After that, the Pb button is dissolved with nitric acid solution and Ru is separated selectively from this solution by ozone oxidation method. Ruthenium is purified by taking advantage of volatility of RuO₄. Ozone gas oxidation process is applied for purification of ruthenium in the sludge from the dissolution treatment. Ozone gas bubbling in nitric acid solution is also effective to remove very small quantity of ruthenium in it. This treatment makes it possible to operate the following processes for mutual separation of rhodium and palladium in a glove box owing to decrease of the activity mainly caused by ¹⁰⁶Ru.

The quaternary Mo-Ru-Rh-Pd alloy was prepared as the simulated insoluble residue based on the method reported by Naito et al. [2]. The composition of the alloy is that of fission produced noble metal alloys and has the ε phase structure. Appropriate amounts of Mo, Ru, Rh and Pd metal powders, all with high purity (99.9%), were mixed and pressed into pellet and then sintered at 1723K in vacuum for 3 hours. The pellets were pulverized to fine powder. The particle size of the powder was adjusted to be 3 μm in average using a vibration mill and a membrane filter.

The Pb metal called Pb button of 5g was separated after the lead extraction of the simulated insoluble residue. The Pb button was dissolved with boiling 3M nitric acid (100ml) for 3 hours, using a flask with a reflux condenser. After dissolution the nitric acid solution was filtrated with a 0.45 μm membrane filter to remove the undissolved powder.

The experimental apparatus employed for Ru separation system is shown diagrammatically in Fig.2. The sample, which was 50mg of the undissolved powder or 50ml of the dissolution fraction after Pb button dissolution process, was transferred to the oxidation reactor at 298K. And then ozone was supplied to the reactor from the reservoir by nitrogen carrier for 4 hours. The operation for the oxidation reaction was repeated 3 times for the undissolved powder and 2 times for the dissolution fraction with every one batch. The chemical compositions of each stage were determined with ICP-AES and ICP-massspectrometry. The distribution of the platinum-group metals in the powder samples was analyzed by electron probe microanalysis.

Fourteen experiments for the undissolved powder were performed and the average value of the results is shown in Fig.3. The recovery of Ru which was converted into RuO₄ and collected in the absorption bottle, was more than 98% in this procedure. Only 2% of Ru was remained in the undissolved powder after the ozone oxidation process. Through this operation nearly all of Rh, Pd and Mo were remained in the undissolved powder and less than 0.1% of those were found respectively in the Ru fraction recovered. The remainder of Ru which is not reacted in this procedure seems to be existed as alloy powder based on the EPMA observation. So a sample for re-extraction with lead was prepared by collecting the remainder of fourteen experiments and a recovery experiment of Ru was performed all over again. The recovery of Ru including a loss due to the lead extraction was higher than 93%. Thus total recovery efficiency of Ru from the undissolved powder was more than 99.8% through the ozone oxidation process coupled with the re-extraction by lead.

The separation of Ru in the solution was also performed by ozone gas bubbling into the dissolution fraction. The recovery of Ru was more than 93% in this procedure. Finally it was found that the transference rate of Ru from the insoluble residue into the dissolution fraction could be decreased less than 1.5×10^{-5} using the ozone oxidation.

5. Mutual separation of rhodium and palladium

Various techniques, which are precipitation, solvent extraction, ion exchange and so on, had been studied or used in the platinum group metals refining industry. Among these techniques, solvent extraction of Pd by amine or sulfide extraction is considered to be promising for Pd separation from the nitric acid solution. Some tests for these extractants, therefore, have been carried out. On the other hand, mutual separation of other elements (Rh, Mo, Pb) by solvent extraction or ion exchange method was considered not to be suitable because a good extractant or an ion exchanger had not been found. On this study, precipitation separation method by adding chemical agents were, therefore, has been studied as refining process of Rh, because Rh is most promising element to be used in common industry.

Tri-n-octylamine (TNOA) is one of amine extractants promising for Pd extraction. The mixture of 10% TNOA and CCl_4 or n-dodecane was used for the present study. Extraction experiments were carried out under the condition of O/A=1 for 30 minutes mixing at room temperature. Distribution ratios are almost coincident whether CCl_4 was used for diluent or n-dodecane, however the third phase formation is observed on either solvent. Dodecyl alcohol (5%) addition to either solvent is enough to prevent formation of third phase, and settling time is rather short (1-2 minutes). Nitric acid concentration dependence on distribution ratios of metals by 10% TNOA/n-dodecane extractions is shown in Fig 4. It is seen that distribution ratio of Pb decreases with increasing acidity, and the values are not so high that Pd is extracted effectively at over 3N nitric acid concentration.

Table 2 shows the results of Pd back extraction from 10% TNOA/n-dodecane by various aqueous solutions under the condition of O/A=1 for 5 minutes mixing at room temperature. Palladium is back extracted to 1 wt% thiourea ($\text{CS}(\text{NH}_2)_2$) solution, though it is not done to each other solution. Especially, when ammonia is used, precipitates are formed so that phase separation is difficult. And more than 99% of Pd is stripped by reduction with a hydride solution from the thiourea solution. Chemical form of Pd recovered is powder metal. Thiourea solution, therefore, would be suitable back extraction reagent.

Furthermore the back extraction efficiency was not changed even if thiourea content was changed from 0.1 Wt% to 5wt%. Thiourea is less than 3N nitric acid solution is also available for back extraction and it is useful to promote phase separation, but it is decomposed in 6N nitric acid.

Recently DHS (di-hexyl sulfide) has been studied as a promising extractant of Pd. While most of sulfide extractants are chemically unstable, DHS is rather stable for practical use. Pd extraction study of DHS were hence carried out. Shellsol AB (aromatic solvent) and n-dodecane were selected as diluents. The extraction conditions were those same as TNOA experiments, and DHS content was 10%. Fig.5 shows nitric acid content dependence on distribution ratios of metals by 10% DHS/n-dodecane, which are almost same values as those when shellsol AB is used for a diluent instead of n-dodecane. From this figure, it is seen that the distribution ratios of Pd are extremely high and they are not dependent on nitric acid concentration.

Some reagents for Pd back extraction from 10% DHS/n-dodecane were tested it as TNOA experiments. As shown in table 3, ammonia solution and thiourea solution are effective reagents. To recover Pd from ammonia solution, however, is difficult, though it is easy from thiourea solution by reduction with a hydride solution. Consequently thiourea solution is suitable back extraction reagent from DHS same as TNOA.

Rhodium, Mo and Pb would be contained in the raffinate of Pd extraction process. Neutralization precipitation method was adopted for the Pb separation process. If acetic acid is added to the raffinate before neutralization, Pb would remain in the solution and other elements would be precipitated. This is because Pb acetate is not decomposed by neutralization, though the others are precipitated by hydrolysis with neutralization. pH dependence on the Pb separation was investigated. After adding 20wt% acetic acid, precipitation reaction was executed for 1 hour at room temperature, where pH of the solution was prepared by adding ammonia (<pH10) and sodium hydroxide (pH 10-12). The results are shown in Fig 6. It is seen that more than 90% of Rh and Mo are precipitated as hydroxide at pH8-10 and Mo is dissolved again as molybdate at pH 12, while more than 80% of Pb remains in the solution. More than 99% of Pb is recovered as $\text{Pb}(\text{CO}_3)_2$ from the neutralized solution by adding carbonate to the solution. The chemical form of recovered Pb may be suitable to be returned to the lead extraction process, because $\text{Pb}(\text{CO}_3)_2$ is decomposed easily by heating. The recovery of Pb precipitate would be higher if these procedures are repeated, so that the neutralization method at pH 8-10 would be suitable for Pb separation.

The precipitate recovered on neutralization of the raffinate would contain Rh, Mo and small amount of Pb. As can be seen from Fig.6 mentioned above, more than 80% of Mo is not precipitated in the solution prepared at pH 12 by adding sodium hydroxide but more than 90% of Rh is precipitated. Mutual separation of Rh and Mo, therefore, would be achieved roughly using the precipitation separation method for the precipitate recovered on the Pb separation. As the precipitation separation, it may be appropriate method to dissolve Mo selectively from the precipitate by washing it with ammonia or sodium hydroxide of over pH12. Although Mo is dissolved selectively actually by this method, a small amount of Mo and Pb remain in the Rh precipitate.

Some resin were tested for Rh purification by means of batchwise adsorption. From this test, it is found that chelate resin CS-346 (Sumichelate), amideoxime type, has good performance for Rh purification. The adsorption behavior of CS-346 is shown in Fig.7. It is seen from this figure that Rh would be purified by passing the solution through a column of CS-346 after dissolution of the Rh precipitate with acid solution. On the other hand, coprecipitation method with selenium (Se) or tellurium (Te) was also studied for Rh separation, as this method had been used as analytical method. It was experimentally evaluated that the coprecipitation method was not suitable for practical process because of its long reaction time.

The results presented above indicate that a flow sheet shown in Fig.8 is desirable for a mutual separation process of palladium and rhodium in nitric acid solution. The starting solution of this process flow is the nitric acid solution containing Pb, Pd, Rh and Mo. Palladium is separated selectively from the solution using DHS extraction process, and it is back extracted to thiourea solution, so that it is recovered as metal by reduction agents. On the other hand, the raffinate is added with acetic acid and ammonia solution, so that Pb is recovered to be returned to the former process. The precipitate is treated with sodium hydroxide solution to be separated to Mo and Rh fractions. Rh would be refined finally using chelate resin.

6. Conceptual flow sheet

Based on the results described above, the flow sheet for recovery of noble metals from HLW has been established, that is shown in Fig.9. Lead extraction method is chosen for the first step to separate the noble metals from other fission products because of compatibility with vitrification of HLLW for geologic disposal. After the lead extraction, the cupellation method is applied to roughly remove lead from lead-platinum group elements alloy to obtain noble metal bead. Then the bead is dissolved in nitric acid. Ruthenium in the bead is almost not dissolved in nitric acid, therefore sludge mainly containing ruthenium is separated by filtration. After the separation of ruthenium, aqueous processes are applied for mutual separation of rhodium and palladium.

7. Conclusion

We have determined the conceptual flow sheet as for platinum group metals containing in the insoluble residue. Each separation method used in the flow sheet shown in Fig.9 has high separation factor enough for practical use. It is required to perform the recovery steps continuously and determine the final recovery efficiencies of platinum group metals in order to confirm the effectivity of the flow sheet. The objective of this study is to establish a flow sheet for recovery of the valuable metals from HLW. We are planning to modify the flow sheet for recovery of other valuable metals, especially technetium.

References

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- [2] K.Naito, T.Matsui, H.Nakahira, M.Kitagawa and H.Okada, J. Nucl. Mater., 184, 30(1991).

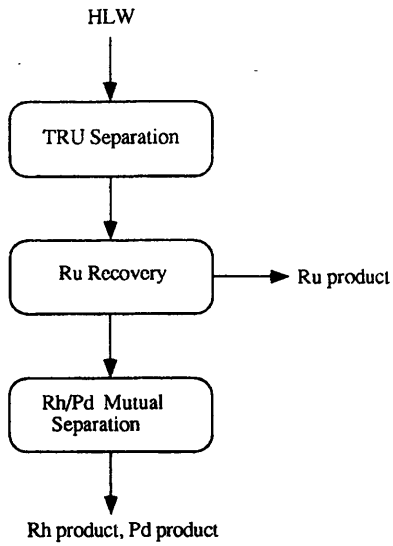


Table 1 Decontamination factors of lead extraction for some TRU nuclides

Nuclide	Activity in Lead (A) [kBq/g]	Activity in Glass (B) [kBq/g]	DF (B/A)
$^{239}\text{Pu} + ^{240}\text{Pu}$	1.1×10^2	1.5×10^{-3}	140
^{241}Am	2.0×10^2	5.9×10^{-4}	300
^{242}Cm	5.1	1.2×10^{-3}	240
^{244}Cm	1.7×10^2	4.4×10^{-4}	260

Fig.1 Processing steps for recovery and purification of the platinum group metals from HLW

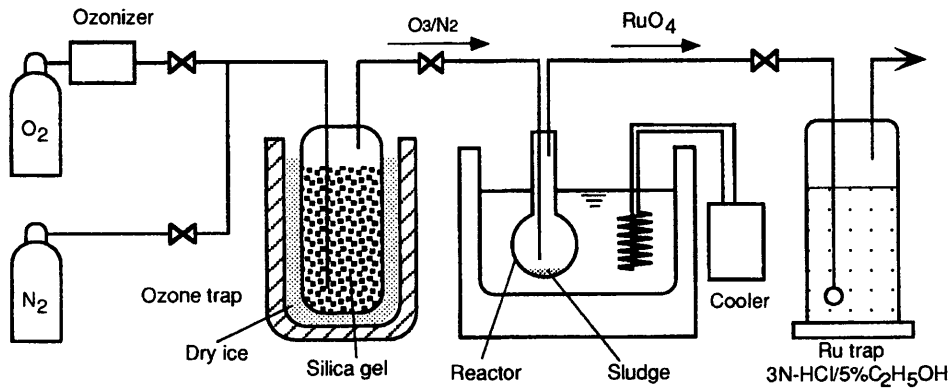


Fig.2 Apparatus for ruthenium oxidation recovery

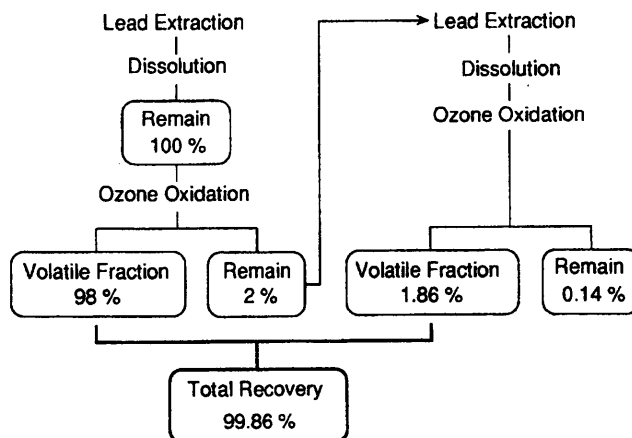


Fig.3 Total efficiency of Ru recovery by ozone oxidation method

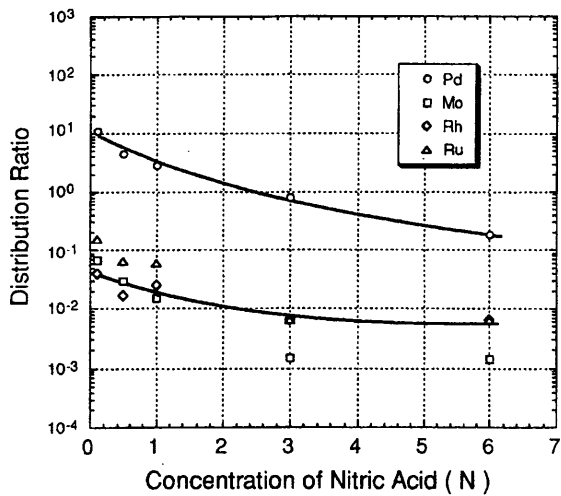


Fig.4 Distribution ratios of metals by 10%TNOA in n-dodecane as a function of nitric acid concentration

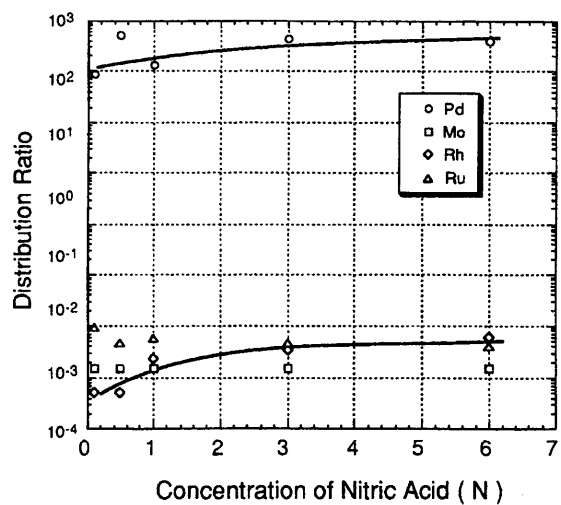


Fig.5 Distribution ratios of metals by 10%DHS in n-dodecane as a function of nitric acid concentration

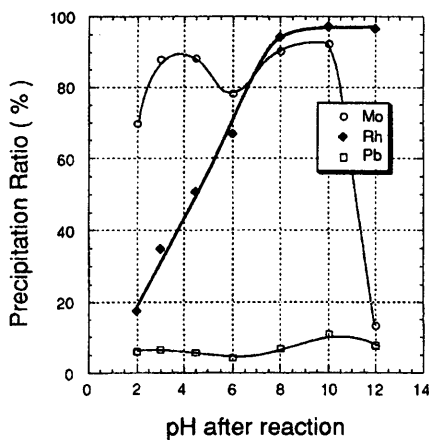


Fig.6 Lead separation from metals precipitate rate of Pb, Rh, Mo as a function of pH by precipitation method (neutralization)

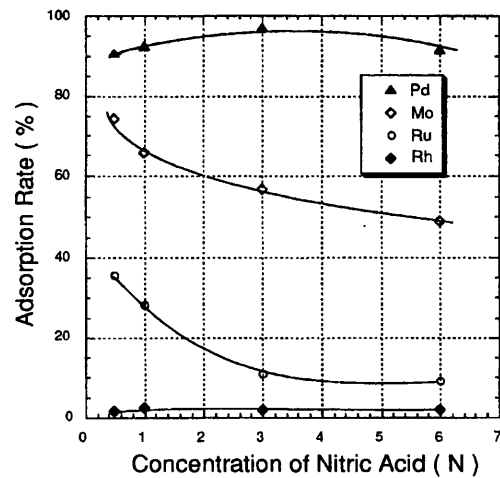


Fig.7 Adsorption rate of metals as a function of nitric acid concentration by chelata resin CS-346

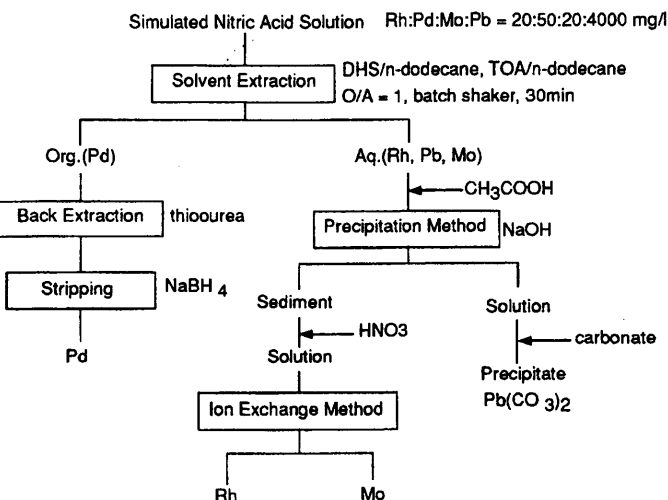


Fig.8 Flow sheet for mutual separation of platinum group metals

Table 2 Palladium back extraction from TNOA/n-dodecane by various aqueous solution

Back Extraction Agent	Back Extraction Rate (%)
Acid	
0.1N HNO ₃	7
6.0N HNO ₃	25
0.1N HClO ₄	26
3.0N HClO ₄	18
Alkali	
6.0M NH ₄ OH	>99
0.5M NaOH	8
4.0M NaOH	23
0.5M Na ₂ CO ₃	2
Others	
1.0wt% (NaH ₂)CS	>99
20wt% Na ₂ S ₂ O ₃	86

Table 3 Palladium back extraction from DHS/n-dodecane by various aqueous solution

Back Extraction Agent	Back Extraction Rate (%)
Acid	
0.1N HNO ₃	N.D.
6.0N HNO ₃	N.D.
0.1N HClO ₄	N.D.
3.0N HClO ₄	N.D.
Alkali	
6.0M NH ₄ OH	>99
0.5M NaOH	9
4.0M NaOH	25
0.5M Na ₂ CO ₃	27
Others	
1.0wt% (NaH ₂)CS	>99
20wt% Na ₂ S ₂ O ₃	73

N.D. : not detected

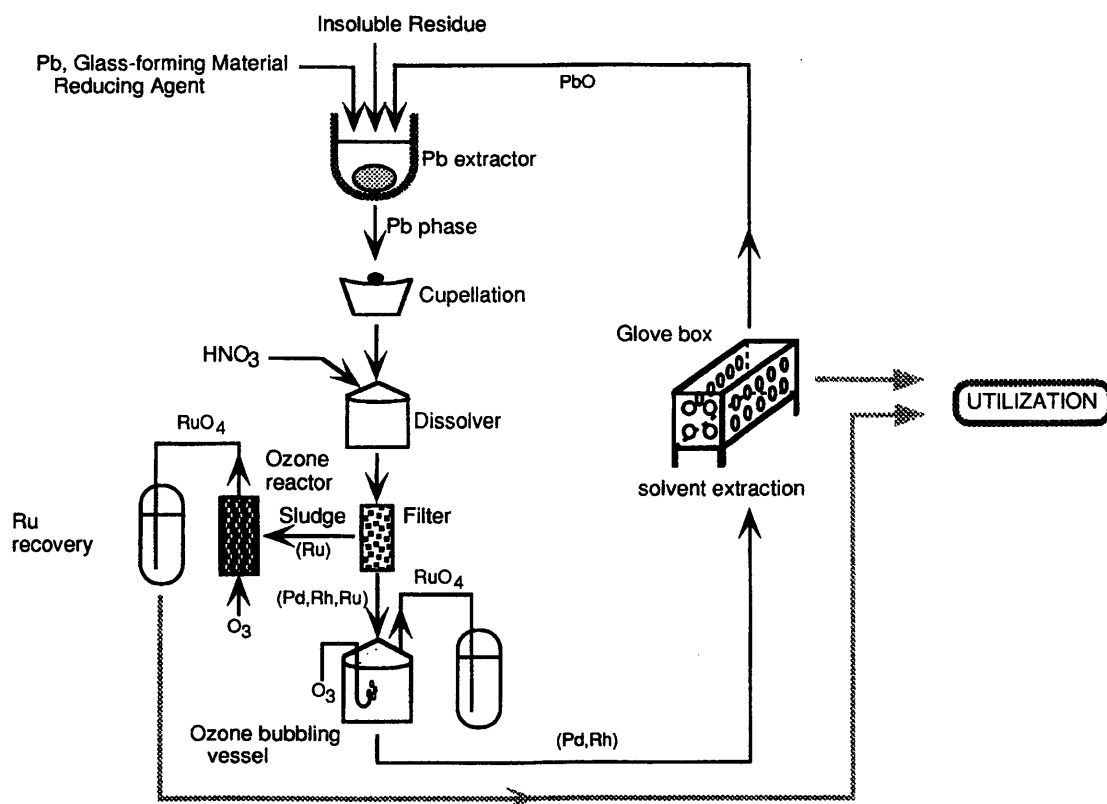


Fig.9 Conceptual flow sheet for recovery of noble metals from insoluble residue