

# Recovery of Value Fission Platinoids from Spent Nuclear Fuel

## PART II: SEPARATION PROCESSES

By Zdenek Kolarik

Retired from Forschungszentrum Karlsruhe, POB 3640, 76021 Karlsruhe, Germany

Present address: Kolberger Str. 9, 76139 Karlsruhe, Germany

and Edouard V. Renard

A. A. Bochvar All-Russian Institute of Inorganic Materials, 123060 Moscow, Russia

*Several processes are reviewed for recovering fission platinoids from radioactive liquids and solid material that typically originate during the reprocessing of spent nuclear fuel by the Purex process. The liquids are radioactive high-level liquid waste and the solution obtained on dissolving the spent nuclear fuel in nitric acid (dissolver solution). The solid is the undissolved fuel residue (dissolver residue). The processes described here have been particularly developed to recover platinoids or, if aimed at the separation of actinides, platinoid recovery is included. Hydrometallurgical processes are predominantly based on solvent extraction, electrodeposition and ion exchange, and less frequently on precipitation and extraction chromatography. Pyrochemical processes are based on extraction or distillation.*

In Part I of this paper, general aspects of the recovery of fission platinoids from wastes resulting from reprocessing spent nuclear fuels by the Purex process were described (1). The main platinoid fractions are released from the Purex process in the radioactive high-level liquid waste (HLLW) and in the undissolved residue of the fuel. The platinoids of main interest: palladium (Pd) and rhodium (Rh), exist in aqueous nitrate solutions typically as Pd(II) and Rh(III). The behaviour of the platinoids in basic separation operations was also reviewed in Part I, and solvent extraction and electrolytic deposition were shown to be the most effective methods for use in separation processes to recover fission platinoids.

In this paper, separation processes for the recovery of platinoids from HLLW and undissolved residues are reviewed, from hydrometallurgical processes (ion exchange, solvent extraction and electrochemical procedures) to pyrometallurgical processes. With one exception, the processes are all described in periodical, patent and report literature. Before the various processes are discussed, some important criteria have to be noted when

planning and developing separation processes. The most important are:

- no significant amounts of additional waste should be produced, and
- no reagents should be added which would interfere with vitrification of the final waste.

Thus, for example, solvent extraction supported by salting-out with large amounts of inert salts, or ion exchange comprising elution with concentrated salt solution, are not acceptable. In addition, gas evolution or the use of highly combustible chemicals must be avoided. Chemicals having unsatisfactory radiation and chemical stability must not be used; however, in certain cases, the lack of stability can be compensated for by extraordinary efficiency or selectivity. Finally, the only separation procedures of interest are those which can be started with acid solutions, as even moderate denitration or neutralisation of the HLLW (say to  $< 2 \text{ M HNO}_3$ ) inevitably causes precipitation of hydroxides or other solids.

As already mentioned, there are two principal aspects to separating fission platinoids:

- The whole group (Pd, Rh, ruthenium (Ru)) is

Platinoids and Tc Recovered by Elutions in the Hanford Ion Exchange Process				
Order of elution	Eluant (38 l each)	Amounts of metals eluted, g		
		Pd	Rh	Tc
1	1 M HNO <sub>3</sub>	0.1	trace	0.8
2	3 M HNO <sub>3</sub>	0.5	0.8	3.8
3	6 M HNO <sub>3</sub>	0.6	1.2	6.1
4	6 M HNO <sub>3</sub>	trace	0.3	0.5
Total metals eluted by HNO <sub>3</sub> solutions		1.2	2.3	11.2
5	10 M NH <sub>4</sub> OH	8	nil	0.1
6	10 M NH <sub>4</sub> OH	2	nil	trace
Total metals eluted by NH <sub>4</sub> OH solutions		10	nil	0.1
Overall metals eluted		11.2	2.3	11.3
Overall metals adsorbed		12	3	11

separated from the HLLW to aid the vitrification.

- Valuable platinoids – primarily Pd and secondly Rh – are selectively separated.

Processes with different principal objectives have been developed or conceived. Although the recovery of fission platinoids is the primary objective in some cases, in others the main objective is to separate actinides or long-lived fission products from HLLW, and platinoid recovery is only achieved if additional process steps are included. Not all the processes aim to obtain individual platinoids in a more or less pure state. Some processes merely result in a mixture of two or three fission platinoids as products.

In only a few cases has process development included all the necessary steps, namely laboratory batch and continuous-flow experiments and subsequent continuous-flow tests with real HLLW. Typically, development has not gone beyond the laboratory scale, and few processes were tested with real HLLW.

Some of the early process designs are hardly applicable now because they do not fulfil the criteria specified above. However, they are reviewed in order to show the increasing tendency to respect the criteria. Purely conceptual process flowsheets based on compiled information are not reviewed here. Such designs may be published before the

start of experimental work as a basis for planning process development, or they may be only mere considerations. The only flowsheets to be critically reviewed here will be those that are at least partly based on original experimental data.

## Hydrometallurgical Separation from HLLW

### Hanford (U.S.A.) Ion Exchange Process

This process (2, 3) aims to separate platinoids from the supernatant of the Hanford alkaline wastes originated in the production of plutonium for nuclear weapons. The process was developed as long ago as the 1960s, using anion exchange as the principal separation method, and tested on an expanded laboratory scale but not extended to large-scale production operation.

In a typical test, around 12 g Pd, 3 g Rh and 11 g technetium (Tc) were adsorbed from about 4000–6000 l of supernatant on a 6 l column of *Amberlite IRA-401* (20–50 mesh) at a flow rate of 4–12 l min<sup>-1</sup>. (A 7 l column of *Amberlite XE-238* became plugged under similar conditions after 200 l throughput.) Successive elutions with 38 l portions of HNO<sub>3</sub> and NH<sub>4</sub>OH solutions removed Rh from the column together with part of the Pd and the major part of the Tc. The Table gives the amounts of eluted metals and compares the over-

all metal amounts gained with metal amounts adsorbed.

Using the reversed phase chromatographic technique (extraction chromatography) Pd could be sorbed from the supernatant on a column of a trifluorochloroethylene polymer (Plaskon) carrying *methyltricaprylammonium chloride* as an extractant. The capacity of the sorbent at 30% extractant content was 31 mg Pd g<sup>-1</sup> of sorbent. A > 90% fraction of Pd was eluted with 10 bed volumes of 10 M NH<sub>4</sub>OH. Rh together with Tc was sorbed, in the next step of the process, from the Pd-free supernatant on a column of *Amberlite XE-238*. To prevent gassing and heat evolution in the succeeding elution with diluted HNO<sub>3</sub>, any nitrite, carbonate and hydroxyl ions were first removed from the column by successive washings with water, 0.1 M HNO<sub>3</sub> and 0.25 M HNO<sub>3</sub> (2 bed volumes of each). The elution of Rh was advised to be subsequently accomplished with 2 bed volumes of 1 M HNO<sub>3</sub>, 3 bed volumes of 3 M HNO<sub>3</sub> and 5 bed volumes of 6 M HNO<sub>3</sub> (2).

Thus, in the former route, sorption from the supernatant with subsequent elution steps yielded two fractions. One fraction, obtained by elution with HNO<sub>3</sub> solutions, contained all the Rh, all the Tc and eventually ~ 10% of the Pd inventory. The other fraction, obtained by elution with NH<sub>4</sub>OH solution, contained the major part of the Pd contaminated by ~ 1% of the Tc inventory. This incomplete separation was attained after a number of time consuming operations – taking far too long for today's requirements. Moreover, if Pd and Rh were sorbed from typical waste – acidic HLLW – the Rh sorption would not be efficient enough.

Also hardly applicable in a modern process would be the subsequent, rather laborious, separation and purification of the platinoids in the two fractions. To purify the raw Pd product in the NH<sub>4</sub>OH eluate of <sup>106</sup>Ru, <sup>137</sup>Cs and <sup>60</sup>Co, the ammonia eluate was evaporated by a factor of 5 and concentrated HCl was added to give pH 1–3. The resulting Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> solid was dissolved in aqua regia and reprecipitated twice. Precipitation of Pd(II) as its *dimethylglyoximate* was the last step (3).

To separate Rh in the raw product from Tc, the acid eluate was concentrated by evaporation by a

factor of 20. Rh(III) precipitated quantitatively, presumably as a hydrous oxide, accompanied by ~ 2% Tc and all of the <sup>106</sup>Ru, <sup>137</sup>Cs and <sup>60</sup>Co. The Rh solid was then roasted at 500°C for 8 hours followed by leaching with aqua regia; this removed part of the <sup>137</sup>Cs and <sup>60</sup>Co. The remaining solid was then fused with NaHSO<sub>4</sub> at 500°C for 8 hours and dissolved in water. Filtration of the obtained solution removed part of the <sup>106</sup>Ru. Precipitation as hydroxide separated Rh from <sup>137</sup>Cs. Dissolving the Rh(III) hydroxide in 6 M HCl, evaporating to dryness, and redissolving in water, followed by repeated precipitation of ammonium hexanitritorhodate (NH<sub>4</sub>)<sub>3</sub>Rh(NO<sub>2</sub>)<sub>6</sub> (3 times) removed the remaining parts of <sup>106</sup>Ru and <sup>60</sup>Co (3).

#### Indian Solvent Extraction Process

In this process (4), Pd(II) is extracted from simulated HLLW in two successive contacts with barren (not loaded with the metal to be extracted) 0.01 M *triisobutylphosphine sulfide* (TIPS) in Solvesso 100. The two combined portions of the loaded solvent are scrubbed with 2 M HNO<sub>3</sub> and Pd(II) is stripped by 0.01 M thiourea. *Diocetyl sulfide* and *α-benzoin oxime* can also extract Pd(II) effectively but, compared to TIPS, the sulfide has lower loading capacity for Pd(II), and the oxime exhibits lower radiation stability.

Only laboratory data have been obtained for this process, which could indeed be a reasonable starting point for further process development, provided that Rh recovery is not required.

#### Japanese Solvent Extraction Process

This is a partitioning process (5, 6) that has been in development at the Japan Atomic Energy Research Institute (JAERI, Tokai-mura) since the 1970s. Initially it was aimed at separating actinides from partially denitrated HLLW by extraction into diisodecylphosphoric acid in an alkane mixture, leaving most fission products in the raffinate. More recently, the process has been extended to include a separation step, in which platinoids are separated together with Tc. In one option the separation step involves further denitration of the raffinate by formic acid, in which, at pH > 2, the platinoids are precipitated as metals together with

hydrated TcO<sub>2</sub>. Tc is then selectively leached under the oxidation to Tc(VII) using oxygen, ozone or hydrogen peroxide, while the platinoids remain in the precipitate.

Alternatively, a column of active carbon adsorbs all the Pd(II) and all the Tc(VII), as well as 16% Rh(III) and 49% Ru(III)NO. Tc(VII) is eluted with 2 M KSCN + 4 M NaOH, accompanied by 41% Ru(III)NO, 2% Rh(III) and 18% Pd(II). The major part of the Pd(II) (82%) and small fractions of Ru(III)NO (8%) and Rh(III) (14%) are retained on the column.

The process, although excellent for separating actinides from HLLW, is little suited to recover platinoids. Obtaining a precipitate that contains all three platinoids is hardly satisfactory even as an intermediate step, and the chromatographic procedure yields incompletely separated platinoids.

#### Swedish Solvent Extraction Process

This process (7) is primarily aimed at separating actinides from HLLW. Pu, Np, Tc and I are expected to be extracted in a first step by 0.2 M *Aliquat 336* in diisopropylbenzene at 3.4 M HNO<sub>3</sub>. Then, according to a mathematical simulation, 80% Ru and 100% Pd are predicted to be extracted at 3 M HNO<sub>3</sub> by 50% *tributyl phosphate* in aliphatic kerosene. Full stripping is to be accomplished by 9 M HNO<sub>3</sub>.

Irrespective of the complexity of the process (three various extractants are being used in three process cycles) it only assumes that a Pd/Ru mixture will be obtained. No data on the behaviour of Rh are given and no experimental tests of the platinoid recovery have been reported.

#### Russian Solvent Extraction Process

This process (8) is the most recent development in the field, utilising the extractability of Pd(II) by trialkyl amine and quaternary ammonium extractants in aromatic diluents from 3 M HNO<sub>3</sub> saturated with NO + NO<sub>2</sub>. To develop the process, Pd(II) was shown to be moderately extracted by *tributyl*, *methyldioctyl*, *trioctyl*, *triisooctyl*, *tridecyl* and *tridodecyl amines*, and efficiently extracted by *trialkylbenzyl* and *trialkylmethyl ammonium nitrates* and by *Aliquat 336* (9). The efficiency of the Pd(II)

extraction by *trioctylamine* and *Aliquat 336* in diethylbenzene is suppressed when the contacted phases are irradiated by gamma rays, but is still high enough even at a dose of 100 W h<sup>-1</sup> (10).

To extract > 99% Pd(II) at 3 M HNO<sub>3</sub> and room temperature, seven phase contacts with 0.5 M *Aliquat 336* or 14 phase contacts with 1 M *trioctylamine* in benzene are needed at a phase volume ratio of organic/aqueous (org/aq) = 1/5. The loaded organic phase is then scrubbed, again at room temperature, with 1 M HNO<sub>3</sub> at org/aq = 10. Pd(II) is stripped into 6 M HNO<sub>3</sub> at 52.5°C and org/aq = 5. The overall Pd(II) yield is 97–98%. Ag(I), Sb(III), Ru(III)NO, Zr(IV), Am(III), Np(V), Ce(III), Sr(II) and Cs(I) are weakly extracted and are satisfactorily, or even very efficiently, separated from Pd(II). Pu(IV) and U(VI), although extracted together with Pd(II), are separated because they are essentially not stripped. Tc(VII) is not separated, being extracted and partially stripped simultaneously with Pd(II).

The process is promising for Pd recovery. It concentrates Pd(II) by a factor of 25 and separates it from the bulk of important fission products and minor actinides. Nevertheless, addition to the process of a final purification step, in which Tc would be efficiently separated from Pd, is necessary. The process is still in development and tests with real HLLW as well as scale up are planned.

#### American Extraction Chromatographic Process

This process (11) was developed for the U.S. Atomic Energy Commission in the early 1970s. It is suggested in this process that the HLLW should be successively contacted with three separate beds of impregnated carbon. The first bed which carries *dimethylglyoxime* adsorbs only Pd, the second bed, carrying *diacetyl disulfide*, adsorbs only Tc, and the third bed carrying *N-phenylthiourea* adsorbs Ru together with Rh. The three loaded beds are then separately calcined, and Pd and Tc are leached from the ash of the first and second beds, respectively. The ash of the third bed is stored to allow the radioactivity to decay.

In addition to the disadvantages of extraction chromatography, in this case mainly losses of the

complexants from the carbon support, the impossibility of regenerating the extractants and the necessity of incinerating large amounts of carbon represent a serious drawback. We are not aware of any reports of further developments.

### Two Japanese Precipitation Processes

These represent research work from the early 1990s and use neither solvent extraction nor ion exchange (12, 13). The first process (12) elaborated in joint work by university and industrial researchers is aimed both at reprocessing spent fuel and at partitioning HLLW. It suggests that the fuel should be dissolved in HCl or a HCl/HNO<sub>3</sub> mixture. The solution is then reduced by hydrazine and, after addition of SnCl<sub>2</sub>, platinumoids are precipitated as Cs salts of chlorostannate complexes. Separation of U and Pu from fission products is accomplished in subsequent steps. However, the lack of selectivity and the contamination of the HLLW with HCl and Sn(II) render the process unattractive.

In another process (13), the actinides, fission lanthanides and fission alkaline earth elements are supposed to be precipitated from HLLW as oxalates at 1–3 M HNO<sub>3</sub>. Without being supported by data, the platinumoids are said to remain in the supernatant solution together with the alkali elements. The procedure, mentioned here for completeness, holds no promise of platinumoid recovery.

### Two American Combined Processes

These two processes (14, 15) were suggested as a result of industrial research.

The first process described is aimed at recovering Tc, but also includes optional recovery of platinumoids. The simulated HLLW was made alkaline (pH ≥ 9) by Ca(OH)<sub>2</sub> to precipitate fission products, among them the platinumoids, and to leave Tc(VII) in solution. The precipitate was optionally dissolved in dilute nitric acid and the platinumoids were then cathodically deposited. However, some fractions of the platinumoids remained in the solution with the Tc(VII) after the addition of Ca(OH)<sub>2</sub>. These were codeposited cathodically, with the Tc, in another electrolysis step. The deposit was then stripped with 5.3 M HNO<sub>3</sub>, the solution was made

alkaline, and Tc(VII) was extracted into 2,4-dimethylpyridine, leaving the platinumoids in the aqueous phase (14).

Salination of HLLW with a large amount of Ca(NO<sub>3</sub>)<sub>2</sub> would inadequately increase the amount of solids in the subsequent treatment of the waste and would nowadays be quite unacceptable. Adding Ca(OH)<sub>2</sub> might perhaps be acceptable after prior denitration of the HLLW. However, individual separation of the platinumoid is missing from this process, and as the platinumoids are split between an electrode deposit and an aqueous raffinate, the process is of no interest.

In the flowsheet of the second process (15), the simulated HLLW was neutralised by 50% aqueous ammonia from an initial 8 M to 0.2 M HNO<sub>3</sub>. The platinumoids and Tc(VII) were then cathodically deposited at –0.40 V vs. Ag/AgCl at a current density decreasing from an initial 70 mA cm<sup>-2</sup> to a final 0.3 mA cm<sup>-2</sup>. About 99% of Pd, Rh and Tc, and 60% of Ru were plated over a period of ~ 48 hours. Treatment of the deposit with HNO<sub>3</sub> dissolved the Pd, Ru and Tc, while Rh was converted to flakes suspended in the resulting solution (15).

The same objections as before arise regarding the neutralisation of the HLLW and the incomplete separation. There are no known reports concerned with developing these processes beyond the laboratory scale.

### Japanese Combined Process

This is based on a flowsheet developed by university-industrial research in the 1990s (16). It is mentioned here to give an example of a rather confusing concept that is intended to accomplish both the reprocessing of spent fuel and the partitioning of the waste. It utilises the ability of U(VI) and Pu(VI) to form soluble carbonate complexes in order to remove the major part of the fission products as hydroxides or carbonates.

The flowsheet is useless for the recovery of platinumoids (and barely useful for its other objectives). Part of the Ru is removed as RuO<sub>4</sub> during dissolution of the fuel in dilute nitric or hydrochloric acid under simultaneous oxidation. The remainder of the Ru, and the bulk of the Pd and Rh are distributed into a number of process

streams, such as: the insoluble residue after fuel dissolution; the Cs tetraphenylborate product; the U/Pu product; the waste fraction containing Na, Tc and Mo; and the waste fraction containing Te, Mo and Zr.

#### Japanese Electrochemical Process

This platinoid recovery process (17) is one of the results of extended research work performed at the Power Reactor and Nuclear Fuel Corporation (Tokai-mura). The work is aimed at improving the Purex process, for example, by introducing electrochemical operations which reduce the salt content in the HLLW and so facilitate the final waste treatment. Constant-current electrolytic deposition of Pd at the optimal  $-0.1$  V vs. SCE is a promising method to recover Pd from HLLW that contains 3 M  $\text{HNO}_3$ . In long-term electrolysis  $> 90\%$  Pd is deposited, but Rh deposition is very slow. Its advantage is that the operation does not produce secondary waste. Thus the operation is of potential use in a future process for partitioning the HLLW, if installed and operated on a large scale.

### Hydrometallurgical Separation from Dissolver Solution and Solubilised Dissolver Residue

#### Japanese Electrochemical Process Option

Without giving details, electrolytic deposition is said to be a candidate method for removing unspecified platinoids (and Tc) from the dissolver solution without producing secondary waste (17).

#### French Solvent Extraction Process

This process (18) involves extraction of Pd(II) by a 0.034 M solution of *6,9,12-tritribiheptadecane* in chloroform. As much as 86% Pd is extracted in one phase contact from a solution containing  $214 \text{ g l}^{-1}$  U(VI),  $0.55 \text{ g l}^{-1}$  Pu(IV), 1 M  $\text{HNO}_3$ ,  $15.4 \text{ mg l}^{-1}$  Pd, and  $0.84 \text{ GBq l}^{-1}$  gamma radioactivity of fission products. After the extraction and after one scrubbing phase contact with 1 M  $\text{HNO}_3$ , the level of gamma radioactivity per mg Pd is reduced by a factor of  $3 \times 10^5$ . A one-step stripping with water yields a solution containing  $5 \text{ mg l}^{-1}$  U,  $< 0.5 \text{ mg l}^{-1}$  Pu,  $13.3 \text{ mg l}^{-1}$  Pd, and  $2.7 \text{ kBq l}^{-1}$  gamma radioactivity (phase volume ratios have obviously been

1/1 in all steps). It is important that the extraction equilibrium is attained in 5 minutes.

These results lead us to expect good separation and decontamination efficiency when using counter-current extractors. Indeed, it would be very desirable to replace the chloroform by a less volatile and, preferably, halogen-free diluent. However, the applicability of the process could be hindered by the extractant having insufficient chemical or radiation stability and, eventually, by its high price. It is unfortunate that the source (18) gives no information about the behaviour of Rh.

#### Japanese Solvent Extraction Process

This method (19) was developed in the late 1980s/early 1990s to be linked with extraction into Pb buttons (see Japanese Extraction Process 1 (21) below). A solution obtained by dissolving a Pb button in dilute nitric acid contains Pd, Rh, Mo, excess Pb, and 0.1–6 M  $\text{HNO}_3$ . Only Pd(II) is extracted into 10% *dibexyl sulfide* in dodecane. The Pd(II) is stripped with 1 wt.% thiourea and reduced to metal by a hydride reagent. Acetic acid is added, to a concentration of 20 wt.%, to the aqueous phase left over from the extraction step and ammonia is used to adjust the pH to 8–10. Lead (90–95%) is left in the supernatant and a precipitate containing Mo(VI) and Rh(III) is filtered off and redissolved in diluted  $\text{HNO}_3$ . These two elements are then separated on an *amide oxime chelating resin (CS-346 Sumichelate)*.

The process, only briefly described in (19), is a plausible completion for a pyrometallurgical process. However, it could be simpler to add the Pb button solution to the HLLW, and then recover all the Pd from the HLLW, provided that the considerable Pb(II) content does not interfere with further waste treatment.

### Pyrometallurgical Separation from HLLW

#### Japanese Process

A super-high-temperature process (20) suggests calcination of HLLW at  $\sim 700^\circ\text{C}$ , followed by the removal of Cs and Rb by sublimation at  $\sim 1000^\circ\text{C}$ . The platinoids can then be reduced at  $\sim 1600^\circ\text{C}$  without adding reductants, or can be reduced in

the presence of nitrides, such as AlN, BN, TiN or Si<sub>3</sub>N<sub>4</sub>. Experiments with simulated HLLW have shown that a molten metallic phase is formed which, after cooling, contains the platinoids as Pd metal and as a Ru-Fe alloy. The phase also contains Mo in metallic form and corrosion products in the form of Cr-Ni, Fe-Ni and Cr-Fe-Ni alloys. Rh is also expected to be present in the metallic phase, but its behaviour has not been investigated. Stable oxides form the other phase, which contains zirconium, actinides, lanthanides and alkaline earth elements.

Clearly the platinoids are incompletely separated in this process, and it is difficult to assess how many further process steps would be needed to obtain pure products.

## Pyrometallurgical Separation from Dissolver Residue

### Japanese Extraction Process 1

This process has been developed by Japanese industrial and university researchers since the 1980s (21). It is based on extraction into a Pb or PbO<sub>2</sub> button coexisting with a glass phase. Melting Pb with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> or B<sub>2</sub>O<sub>3</sub>, as glass forming constituents, and the dissolver residue, in the ratio 50:10:1 by weight, at 750–1100°C under bubbling air produces a PbO<sub>2</sub> button containing the platinoids. The Mo is vaporised during the melting. Melting the above components in an argon (Ar) atmosphere yields a Pb metal button containing 95–98% of the Pd, 87–97% of the Rh and 91–95% of the Ru together with 2–13% of the Mo. CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> (simulating actinides and crud components) are directed into the glass phase both under bubbling air and in the Ar atmosphere. To remove the Pb, the button can first be melted for 0.5–1 hours with Zn at 650°C in an Ar atmosphere. Subsequent cooling to 390°C removes Pb in liquid form, leaving a solid Zn phase containing 74–90% of the platinoids and Mo. Zn can finally be removed by evaporation.

Alternatively, the Pb or PbO<sub>2</sub> button can be dissolved in boiling 3 M or 6 M nitric acid. As much as ~ 90% of the Pd but only ~ 30% of the Rh is dissolved after 3–12 hours. The Rh yield can be improved to ~ 90% by a small addition of Bi at

the melting step. The fraction of Ru transferred during the dissolution into solution is as little as ~ 0.024%, both with and without the Bi addition. Pd and Rh can subsequently be separated by an aqueous method, such as described above (19).

A common feature of this and the next two processes is that the platinoids are incompletely separated from each other and from the other fission products, especially Mo. The pyrometallurgical operations serve mainly to solubilise the residue. Further separation steps, with a hydrometallurgical treatment as an optimal procedure, are necessary. This will make the recovery of the platinoids rather complicated.

### Japanese Extraction Process 2

This process (22, 23), analogous to Japanese Extraction Process 1 (21) based on extraction into a lead phase, was developed at the Power Reactor and Nuclear Fuel Development Corporation (Tokai-mura) in the 1980s. It was tested in cold runs with simulated residue and in hot runs with true residue. The hot residue contained, in wt. %: 6.1 Pd, 20.6 Ru, 5.5 Tc, 22.1 Mo, 1.85 Pu and 12.0 U (the Rh content was not given). The hot residue was mixed with Pb metal and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (at a ratio of 1:50:10) and two phases formed during melting at 800°C. As much as ~ 100% of the Pd, most of the Rh, but only 60–80% of the Ru, Mo and Tc were extracted into the Pb phase. Pd and Rh were homogeneously dispersed in the Pb phase. Ru, Mo and Tc were concentrated near the boundary of the Pb phase where Mo formed a mixed oxide with Pb. Pu and U were partitioned to the glass phase and their concentration in the Pb phase was below the detection limit of an electron probe microanalyser. A 3 M solution of HNO<sub>3</sub> (probably boiling, but not specified in the source) was then used to dissolve the Pb phase together with most of the Pd and several tens of per cent of Mo. Most of the Rh and Ru and the rest of the Mo remained in a solid residue.

### American Extraction Process

As mentioned in Part I (1), in 1981 it was suggested that fission Ru could be separated to obtain the radioactive isotopes <sup>103</sup>Ru and <sup>106</sup>Ru, precursors

of the stable isotopes  $^{103}\text{Rh}$  and  $^{106}\text{Pd}$ , respectively (24). Molten Mg is expected to leach Ru, Rh, Pd, Ag and Cd from the dissolver residue, while Mo and Tc are left in the solid. The Mg phase is then contacted with a U/Cr eutectic at  $950^\circ\text{C}$  or with a U/Fe eutectic at  $750^\circ\text{C}$ . Ru is transferred to the eutectic phase, where it forms an  $\sim 0.1$  at.% solution. Additional decontamination of Ru by removing the radioactive Rh and Pd can be achieved by contacting the loaded eutectic with a fresh portion of molten Mg. The solidified eutectic is stored to allow the  $^{106}\text{Ru}$  and  $^{103}\text{Ru}$  to decay to stable  $^{106}\text{Pd}$  and  $^{103}\text{Rh}$ , respectively. The stable isotopes can then be recovered into a Mg phase when the eutectic is melted and contacted with molten Mg. A conventional method can then be used to separate and recover  $^{106}\text{Pd}$  and  $^{103}\text{Rh}$ .

### Japanese Distillation Process

In the first step of this process (25), performed at ambient temperature, Ru is oxidised to  $\text{RuO}_4$  by ozone and distilled off together with  $\text{Tc}_2\text{O}_7$  and part of the Pb oxide. Mo and the remaining Pb are then distilled from the solid residue in an air or oxygen stream at  $\geq 1100^\circ\text{C}$ . Finally, Pd is distilled in vacuum at  $\geq 1230^\circ\text{C}$ , leaving Rh in the solid. All three platinumoids are mutually separated, but the separation efficiency is unknown.

Let us remember the poor applicability of large scale  $\text{RuO}_4$  distillation, due to the tetroxide being easily reduced to  $\text{RuO}_2$  in the gaseous phase. The dioxide then forms a deposit on the walls of the piping and reaction vessels which is extremely difficult to remove.

### Conclusions

Fission platinumoids, Pd, Rh and Ru, with Pd and Rh being of most interest, can best be recovered from spent nuclear fuel, namely from the HLLW and the dissolver solution by a hydrometallurgical process. Solvent extraction and electrolytic deposition are the most promising methods, less so are precipitation and ion exchange or extraction chromatography.

While numerous processes have been developed, few have been tested with real HLLW. Indeed, many of the processes developed have not

gone beyond the laboratory scale. However, some are promising as a starting point for further research. In some processes the mutual separation of the platinumoids is the final goal, but not in others.

To separate the platinumoids from the dissolver residue, a pyrometallurgical treatment appears to be the only feasible option. This treatment can convert the residue to a form soluble in dilute nitric acid. However, with the present state of knowledge, the platinumoids are neither mutually separated nor decontaminated from other fission products. Subsequent hydrometallurgical separation is therefore needed. One possibility that should be checked is to combine the residue solution with the HLLW, instead of treating it separately.

### References

- 1 Z. Kolarik and E. V. Renard, *Platinum Metals Rev.*, 2003, 47, (2), 74
- 2 J. V. Panesko, Report ARH-733, Atlantic Richfield Hanford Co., Richland, WA, U.S.A., 1968
- 3 J. V. Panesko, Report ARH-911, Atlantic Richfield Hanford Co., Richland, WA, U.S.A., 1968
- 4 G. H. Rizvi, J. N. Mathur, M. S. Murali and R. H. Iyer, *Sep. Sci. Technol.*, 1996, 31, (13), 1805
- 5 M. Kubota, *Radiochim. Acta*, 1993, 63, 91
- 6 M. Kubota, I. Yamaguchi, Y. Morita, Y. Kondou, K. Shirahasi, I. Yamagishi and T. Fujiwara, Proc. Int. Conf. Future Nucl. Systems: Emerging Fuel Cycles and Waste Disposal Options (Global '93), 12–17 Sept., 1993, Seattle, WA, U.S.A., Am. Nucl. Soc., La Grange Park, IL, U.S.A., 1993, p. 588
- 7 A. Landgren, J.-O. Liljenzin and M. Skålberg, Proc. ISEC '96 – Value Adding Through Solvent Extraction, 19–23 March, 1996, Melbourne, Australia, Vol. 2, p. 1315
- 8 E. A. Mezhev, V. V. Druzhenkov and A. N. Sirotnin, *Radiokhimiya*, 2002, 44, (2), 136; *Radiochemistry*, 2002, 44, (2), 146
- 9 E. A. Mezhev, V. A. Kuchumov and V. V. Druzhenkov, *Radiokhimiya*, 2002, 44, (2), 126; *Radiochemistry*, 2002, 44, (2), 135
- 10 E. A. Mezhev, I. A. Kulikov and E. G. Teterin, *Radiokhimiya*, 2002, 44, (2), 131; *Radiochemistry*, 2002, 44, (2), 141
- 11 R. H. Moore, *U.S. Patent* 3,848,048; 1974
- 12 Y. Asano, T. Yamamura, H. Tomiyasu, K. Mizumachi, Y. Ikeda and Y. Wada, Proc. Int. Topical Meeting Nucl. and Hazardous Waste Management (Spectrum '94), 14–18 Aug., 1994, Atlanta, GA, U.S.A., Am. Nucl. Soc., La Grange Park, IL, U.S.A., 1994, p. 836
- 13 Y. Akai and R. Fujita, *J. Nucl. Sci. Technol.*, 1995, 32, (10), 1064

- 14 W. W. Carlin, *U.S. Patent* 3,890,244; 1975
- 15 W. W. Carlin, W. B. Darlington and D. W. Dubois, *U.S. Patent* 3,891,741; 1975
- 16 Y. Asano, N. Asanuma, T. Ito, M. Kataoka, S. Fujino, T. Yamamura, W. Sugiyama, H. Tomiyasu, K. Mizumachi, Y. Ikeda, Y. Wada and M. Asou, *Nucl. Technol.*, 1997, 120, 198
- 17 M. Ozawa, H. Hirano, Y. Koma, Y. Tanaka and T. Kawata, Proc. Int. Conf. Evaluation Emerging Nucl. Fuel Cycle Systems (Global '95), 11–14 Sept., 1995, Versailles, France, p. 585
- 18 V. Guyon, J. Foos, A. Guy, T. Moutarde, R. Chomel, M. Draye and M. Lemaire, *Sep. Sci. Technol.*, 1995, 30, (7–9), 1961
- 19 K. Kirishima, H. Shibayama, H. Nakahira, H. Shimauchi, M. Myochin, Y. Wada, K. Kawase and Y. Kishimoto, Proc. Int. Conf. Nucl. Waste Management Environ. Remed., 5–11 Sept., 1993, Prague, Czech Republic, ASME, New York, NY, U.S.A., 1993, Vol. 1, p. 667
- 20 M. Uno, Y. Kadotani, H. Kinoshita and C. Miyake, *J. Nucl. Sci. Technol.*, 1996, 33, (12), 973
- 21 K. Naito, T. Matsui, H. Nakahira, M. Kitagawa and H. Okada, *J. Nucl. Mater.*, 1991, 184, 30
- 22 Y. Wada, K. Kirisima, K. Wada, K. Kawase and N. Sasao, Proc. 1989, Joint Int. Waste Management Conf., 22–28 Oct., 1989, Kyoto, Japan, ASME, New York, NY, U.S.A., 1989, Vol. 2, p. 233
- 23 Y. Wada, K. Kirisima, K. Wada, K. Kawase and N. Sasao, Trans. ENS/ANS-Foratom Conf. (ENC '90), 23–28 Sept., 1990, Lyon, France, Verlag TÜV Rheinland, Köln, Germany, 1990, Vol. IV, p. 2285
- 24 F. J. Smith and H. F. McDuffie, *Sep. Sci. Technol.*, 1981, 16, (9), 1071
- 25 T. Matsui and R. Sasaki, unpublished results

#### The Authors

Zdenek Kolarik retired from the Forschungszentrum Karlsruhe in 1998. He was a member of the research staff in the Institute of Hot Chemistry and then in the Institute of Nuclear Waste. His particular interest was separation chemistry, especially solvent extraction. He participated in work aimed to refine reprocessing of spent nuclear fuel by the Purex process and adapting the process to fast breeder fuel. He also participated in developing a process to separate actinides from radioactive high-level liquid wastes.

Edouard Renard is a group leader at the A. A. Bochvar All-Russian Institute of Inorganic Materials, Moscow. He works in separation chemistry, particularly with solvent extraction. His research work has been directed to further the development of the Purex process for reprocessing fast breeder fuel and recently to the development of a process for the recovery of fission products from radioactive high-level liquid wastes.

## The Platinum-Enhanced Activity of Antibacterial Silver

Silver (Ag) has valuable antibacterial and purifying properties, and for centuries was used to keep potable liquids pure. It has also been used in many medical applications, ranging from wound dressings to attacking Legionnaires' disease. Its antibacterial activity depends on the balance between the activity of  $\text{Ag}^+$  ions, which kill the bacteria, and the total amount of Ag released from a coating. If the amount of Ag released is too high, cytotoxicity will result. The released  $\text{Ag}^+$  ions act by displacing other essential metal ions, such as those of calcium or zinc, from biological material. In order to enhance the antibacterial performance of Ag, it is necessary to increase the concentration of  $\text{Ag}^+$  ions relative to that of metallic Ag released from the coating.

Researchers from Enterprise Ireland, and Biomatech in France, have now investigated whether platinum (Pt) could enhance the release of  $\text{Ag}^+$  ions from antibacterial Ag coatings (D. P. Dowling, A. J. Betts, C. Pope, M. L. McConnell, R. Eloy and M. N. Arnaud, *Surf. Coat. Technol.*, 2003, 163–164, 637–640). As Ag is more active than Pt in the galvanic (electrochemical) series, Pt should

enhance  $\text{Ag}^+$  ion formation through galvanic action. To evaluate this, chronoamperometric experiments were performed on Ag-Pt alloys (0.5 and 3.0% Pt) in pH 8.00 borax buffer solutions containing 0.02 mol  $\text{l}^{-1}$  HCl at  $20 \pm 2^\circ\text{C}$ . Resulting current-time curves showed that  $\text{Ag}^+$  formation increased with Pt addition by up to 100%.

Antibacterial Ag and Ag/Pt coatings were deposited onto a range of polyurethane and silicone polymers using a combination of magnetron sputtering and neutral atom beam plasma sources. The magnetron sputtering target was prepared from 1% Pt in a Ag matrix; this sputtered Ag/Pt coatings with thicknesses in the range 5–12 nm.

The bacterial adhesion and bactericidal effects of the Ag and Ag/Pt coated polymers were tested using *Staphylococcus epidermidis*, and the cytotoxicity was tested using fibroblast cells. Adding 1% Pt significantly enhanced the antibacterial effectiveness of the Ag coatings. For silicone, which has highly mobile polymer chains, up to a 2 log reduction in bacterial adhesion was achieved for 5 nm thick Ag/1% Pt coatings. Cytotoxicity was not observed.