# Recovery of Value Fission Platinoids from Spent Nuclear Fuel

PART I: GENERAL CONSIDERATIONS AND BASIC CHEMISTRY

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

Radioactive high-level liquid wastes originating from reprocessing spent nuclear fuel can be a valuable source of platinum metals. The recovery of fission palladium and rhodium is of particular interest and is being investigated worldwide. The radioactivity of fission platinoids is reduced to a non-hazardous level after decontamination from other fission products by a factor of 10½. The intrinsic radioactivity of fission palladium is weak and can be tolerated in many applications, while that of fission rhodium decays to an acceptable level only after storing for about 30 years. With emphasis on recent achievements, this paper, which covers periodical, report and patent literature, reviews the behaviour of fission platinoids in basic separation operations. Aqueous methods, such as solvent extraction, ion exchange, electrolysis, precipitation and redox reactions, are dealt with as well as pyrochemical methods, such as molten salts/metal extraction and solid phase reactions. A second part, to be published in a later issue, considers separation processes.

The management of fission-produced platinum metals (platinoids), namely ruthenium (Ru), rhodium (Rh) and palladium (Pd), has been developing as a topic of research throughout the history of nuclear chemistry. Efforts directed at separating platinoid radionuclides from irradiated nuclear materials date back to the Manhattan Project in the 1940s. Since the early 1960s intensive research has been undertaken in various fields of nuclear chemistry, with most attention initially being given to two problems:

- First, the behaviour of radioruthenium in the Purex (plutonium uranium extraction) process for reprocessing spent nuclear fuel. Radioruthenium tended to be difficult to separate from uranium and plutonium.
- Second, the behaviour of the platinoids during the waste vitrification process when they form separate phases that cause deterioration in the stability of the glasses.

A third field of research work developed later

when it was recognised that fission platinoids isolated from radioactive high-level liquid wastes (HILWs) were potentially useful products. As a considerable volume of HLLW is produced worldwide each year during reprocessing spent nuclear fuel by the Purex process, the amount of platinoids recovered from the HLLW could contribute towards platinum metals obtained from natural sources (1). Recovering Pd and Rh is of most interest, with less need to recover Ru because of its lower commercial value, and because fission Ru contains a large proportion of the radioisotope <sup>106</sup>Ru.

Recovery of the fission platinoids from HLLW is now considered technically feasible and deserving research effort (1). The level of radioactivity of fission products in the recovered platinoids is acceptable to safety regulations after decontaminating by a factor of 10<sup>10</sup>. Intrinsic radioactivity is then the only remaining source of radiation in the platinoid products.

Fission Pd contains stable isotopes with masses of 104 (17 wt.%), 105 (29 wt.%), 106 (21 wt.%), 108 (12 wt.%) and 110 (4 wt.%), and only one radioactive isotope, namely  $^{107}Pd$  (17 wt.%) with a half-life of  $6.5\times10^6$  years. This long half-life may only be a minor problem because  $^{107}Pd$  is a soft  $\beta$  emitter (maximum energy 0.035 MeV) and the radiation intensity at the surface of fission palladium is only 520 Bq cm $^{-2}$  (2).

A more serious problem could be the radioactivity of fission Rh isotopes, <sup>102</sup>Rh and <sup>102m</sup>Rh, with half-lives of 2.9 and 0.57 years, respectively. These are present in trace mass fractions (fission Rh consists of almost 100% of the stable isotope <sup>103</sup>Rh). Their radioactivity is reduced to an acceptable level after a suitable, and indeed long storage time (≥ 30 years). There are applications for fission rhodium where its radioactivity does not conflict with safety regulations, for instance as components of construction materials for nuclear reactors.

It has been suggested that stable isotopes of Pd and Rh could be exclusively obtained if fission Ru was the only platinoid that was separated. The isotope <sup>106</sup>Ru (half-life 368 days) β-decays through the daughter isotope <sup>106</sup>Rh (half-life 30 seconds) and yields stable <sup>106</sup>Pd, while stable <sup>103</sup>Rh is formed from <sup>103</sup>Ru (half-life 40 days) (3). However, this would leave large and unexploited amounts of Pd and Rh in the radioactive waste.

At present the selective recovery of Pd, Rh and also Ru from HLLWs is the primary object of research activities on fission platinoids. Less attention is being given to investigating group separation of the platinoids, a process aimed at avoiding difficulties in the HLLW vitrification. The problem of satisfactory separation of radioruthenium from uranium and plutonium in the Purex process seems to be largely solved.

The recovery of fission platinoids has been extensively studied in the last decades, for example in Japan (JNC and JAERI) and in the U.S.A. (PNNL). Early work has been reviewed, for instance (1, 4–7), but there are no surveys of recent achievements. This review aims to give up-to-date information on the most recently published results of separation research. Part I also deals with platinoid behaviour during the reprocessing of spent

nuclear fuel and with waste management, but only as far as is necessary to understand the nature of the problem. The review will concentrate on Pd and Rh, with less emphasis on Ru.

## Paths of the Platinoids in the Purex Process and Waste Management

At present, and for the foreseeable future, the hydrometallurgical, solvent extraction-based Purex process will be the one predominantly used for the industrial reprocessing of spent nuclear fuel. The wastes resulting from this process are, and will be, the main source of fission platinoids. However, it is unfortunate that the platinoid inventory mostly splits into waste fractions which differ substantially in their chemical nature. Thus, in the very first chemical step of the process - dissolving the fuel - up to a third of the fission platinoids can remain in an undissolved solid residue where they are components of a quinary Mo-Tc-Rh-Ru-Pd alloy. This solid may be difficult to convert into an aqueous solution by any practical route - so it is not the best source for a hydrometallurgical isolation of the platinoids, but recovering them by a pyrochemical process is quite feasible. It is, however, possible to isolate the platinoids by a hydrometallurgical procedure from the solution obtained on dissolving the fuel (dissolver solution), but this is not advantageous as, at first, large amounts of U(VI) and Pu(IV) present in the dissolver solution could interfere with platinoid separation. Second, the separation could require the addition of chemicals into the dissolver solution which would interfere with the subsequent operations of the Purex process.

The main fraction of the fission platinoids is not extracted with U(VI) and Pu(IV) in the first cycle of the Purex process, and remains in the aqueous raffinate which is released from the process as the HLLW stream. Problems may arise when the extractant, tributyl phosphate, is degraded by radiation and nitric acid. Degradation products, among them dibutyl phosphate, can, for example, form insoluble Pd compounds, which, together with other solids, form the ill-famed interface cruds. This interferes with the process and can cause Pd loss to a material that is difficult to treat.

Ruthenium, present as a nitrosyl complex, is also mainly contained in the HLLW. However, the fraction accompanying uranium and plutonium may be so large that the final products are contaminated with <sup>106</sup>Ru at a higher level than allowed by existing specifications. Extensive studies have been undertaken to solve this problem, ranging from basic chemistry of fission Ru to flowsheet studies. (Removing Ru as the tetroxide from the dissolver solution has even been considered). Nowadays this problem seems to have been resolved by adjusting the flowsheet of the first Purex cycle.

In the HLLW the platinoids are predominantly contained as true solutes. The HLLW stream contains nitric acid at a concentration sufficient to suppress hydrolysis of the elements, and the platinoids can participate, for example, in solvent extraction or ion exchange equilibria. The HLLW is thus a suitable source for hydrometallurgical separation of the fission platinoids. However, the HLLW is not allowed to remain in the same state it was in when released from the Purex process. For intermediate storage, the HLLW is concentrated by a factor of 5 to 25 by evaporation; this can result in the formation of solids and further loss of Pd. For example, Pd can precipitate as phosphate simultaneously with other fission products (phosphoric acid is formed by decomposition of small amounts of butyl phosphates contained in the HLLW).

It must be emphasised that any solids present in the HLLW concentrate could cause severe difficulties in any hydrometallurgical partitioning process. They would seriously impede the separation of platinoids as happens for actinides. It would be very advantageous to partition the HLLW before it is concentrated by evaporation, preferably immediately after its release from the Purex process.

Before vitrification of the HLLW concentrate, the nitric acid is decomposed (denitration) by a suitable reductant, usually formic acid. The reaction proceeds at the boiling point of the reaction mixture and the resulting acidity or even alkalinity is controlled over a wide range (2 M HNO<sub>3</sub> to pH ~ 9) by the amount of formic acid added. The

behaviour of platinoids during the denitration can be very diverse, ranging from hydrolysis in the solution (at pH < 1), through precipitation as hydroxides (at pH 1–2) to reduction to metals (at pH > 2). Many other fission products also precipitate during the denitration, and recovery of the platinoids from the complex solid formed would not be feasible.

During vitrification the platinoids form separate solid phases in the borosilicate glass melts. If allowed to accumulate, these solids can influence the performance of the melter. Once incorporated in a glass, the platinoids are practically inaccessible to chemical recovery.

Acid Purex waste solutions from defence programmes at the Hanford site, U.S.A., were neutralised with the inevitable formation of solids, for long-term storage in tanks. The supernatant (pH is 11–12) is buffered by carbonate ions – one of its components. The platinoids remain in the supernatant. This treatment has not been applied to HLLW from civil programmes; thus, alkaline solutions are not a typical waste form. Nevertheless, for completeness, the behaviour of platinoids during the recovery from such solutions is discussed here.

## Behaviour of Platinoids in Separation Systems

**Properties in Aqueous Solutions** 

The solution chemistry of Pd and Rh has been extensively studied in chloride solutions. The chemistry of Pd and Rh, especially of Rh, in nitrate solution is much less — in fact inadequately — known.

In nitrate solutions Pd is stable in the divalent state. This is also the case in 12 M nitric acid, where indirect evidence indicates the absence of Pd(IV). It has been shown that the crystals obtained by evaporation of the nitrate solutions are only of the Pd(II) compound Pd(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, and not of the Pd(IV) compound Pd(NO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> (8). Rhodium in nitrate solutions is only stable in the trivalent state. Under suitable conditions it can be kept in the less stable tetravalent state.

An important feature of the redox chemistry of platinoid ions is their ease of reduction to metals,

chemically or electrolytically. This can be utilised to separate them and is selective with respect to the non-platinum metals. Strong oxidants, such as permanganate, oxidise Ru to the tetroxide which is gaseous and thus easily removed from solutions. This removal is highly selective with regard to metals present in the HLLW.

Pd(II) does not hydrolyse strongly. Both Pd(II) and particularly Rh(III) are complexed by nitrite ions. A fraction of Rh(III) (9) and probably also of Pd(II) exists as nitrite complexes in the HLLW; nitrous acid formation from nitric acid is induced by the strong radiation. Ruthenium enters the Purex process, passes through and leaves as various complexes of the nitrosyl ion, [RuNO]3+, which forms when the nuclear fuel is dissolved in nitric acid. The coordination chemistry of the [RuNO]3+ ion is very complicated as it can form a series of nitrato, nitrito and nitro complexes in diverse, and often very slow, reactions. The complexed [RuNO]3+ ion seems to be the typical form of Ru in the HLLW, where its nitrate complexes have analogous compositions to those in pure nitric acid solutions (10, 11).

Both Pd(II) and Rh(III) form soluble complexes in the alkaline solutions obtained on neutralising the acidic Purex wastes to pH 11–12. Most fission and corrosion products precipitate as hydroxides or basic salts, but caesium and technetium remain in the supernatant together with the major part of the Pd and Rh. It is difficult to specify the nature of the soluble complexes because the supernatant contains large amounts of complexing anions, such as  $\sim 0.5$  M nitrate,  $\sim 2$  M nitrite,  $\sim 1$  M carbonate and  $\sim 0.3$  M sulfate. The form of Rh(III) in the solution may possibly be the anionic complex [Rh(NO)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $^{-}$  (see (12) and references therein).

All platinoids exhibit a strong affinity to soft-donor complexants, that is, those which bond complexed ions via a nitrogen or sulfur donor atom. This can help in attaining the required selectivity – if such complexants are considered in the choice of extracting, stripping or cluting agents. However, the strong tendency of platinoids to form chloride complexes cannot be made use of because adding hydrochloric acid or metal chlo-

rides to HLLW is unacceptable. The tendency towards slow reaction kinetics in complex-forming reactions is a common feature of the platinoids and can limit the throughput in continuous process operations.

#### Solvent Extraction

Solvent extraction, in conventional liquid-liquid form, is the most practicable method used today for partitioning. Its basic chemistry is well known as is its use in applied chemistry and in large-scale engineering works. Important experience has also been gained from its use in large-scale nuclear separations and from decades of industrial operation of the Purex process. The advantages of solvent extraction operations are:

- high throughput
- ease of continuous operation, and
- ability to keep contact time short between the extractants and the highly radioactive aqueous phase.

It is desirable but not imperative that inexpensive and commercially available extractants are used. Paraffinic diluents are preferred in nuclear separation processes currently in operation.

Extraction chromatography (reversed phase chromatography) is a less useful procedure in solvent extraction, especially for large-scale separation processes. It has all the disadvantages of ion exchange (see below) and loss of extractant from the column is an additional operational hindrance.

In this review, the term 'distribution ratio' has its usual meaning, that is, the ratio of the total concentration of the extracted metal in a particular valence state in the organic phase to the corresponding total concentration in the aqueous phase.

#### Solvating Extractants

The extraction of platinoids in a nitrate form is clearly preferred, as nothing extra needs to be added to the HLLW. Extraction in a nitrite form would also be advantageous, but the concentration of nitrous acid present in the HLLW is not high enough to form extractable complexes. Adding larger amounts of nitrous acid or its precursors to HLLW is quite acceptable, as they can be easily destroyed in the HLLW when no longer required.

Palladium Extraction – The extractability of Pd(II) nitrate by *tributyl phosphate (TBP)* is low. As a function of nitric acid concentration the distribution ratio of Pd(II) attains its highest value of  $\sim 1.3$  with neat TBP and the value of 0.23 with 30% TBP in decane, both have sharp maxima at 0.6–0.7 M HNO<sub>3</sub> (13).

Trialkylphosphine oxides (alkyl = butyl, isoamyl or octyl) in benzene diluent extract Pd(II) nitrate from 0.2–4 M HNO<sub>3</sub> more effectively than TBP. However, the extraction is suppressed by nitric acid and could be of importance only at < 1 M HNO<sub>3</sub> (14).

<u>Bifunctional phosphoryl extractants</u>, such as alkyl-(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxides (alkyl = octyl, 2-ethylhexyl or 2,4,4-trimethylpentyl), do not show any noteworthy ability to extract Pd(II) (15).

Dialkyl sulfoxides extract Pd(II) nitrate more effectively than other oxygen donor extractants. A distribution ratio of 16.5 is attained in extracting Pd(II) by a 0.05 M solution of dioctyl sulfoxide in Solvesso 100 from simulated HLLW containing 3.1 M nitric acid (16). Di(2-ethylbexyl) sulfoxide appears to extract Pd(II) nitrate less effectively. A 0.05 M solution in toluene — a diluent with similar properties to Solvesso 100 — gives a distribution ratio of 3.55 in extracting Pd(II) from 3.0 M HNO<sub>3</sub>, while a 0.2 M solution in Solvesso 100 gives a distribution ratio of 10.0 (17).

Results of counter-current experiments indicate that N,N'-dimethyl-N,N'-dibutyl-2-tetradecylmalon-amide in a branched alkane is also able to extract Pd(II) nitrate. A non-uniform distribution ratio of Pd(II), namely 3.5 or 11, has been observed in extraction by a 0.51 M solution of the extractant from simulated HLLW at 3.5 M nitric acid (18).

Pd(II) nitrate is also effectively extracted by less common mixed nitrogen/oxygen donor pyridine-based extractants, such as 2,6-bis(diphenylphosphinyl-2-oxabutyl)-pyridine, 2,6-bis[2-(diphenylphosphinyl)phenoxymethyl]-pyridine and 2,6-bis[2-(diphenylphosphinylmethyl)phenoxymethyl]pyridine. The extracting power of the compounds slightly increases in the given order. In extraction by a 0.002 M solution of the second of the above extractants in 1,2-dichloroethane from

0.01–6 M HNO<sub>3</sub>, the distribution ratio of Pd(II) reaches a maximum of  $\sim 90$  at 0.5 M HNO<sub>3</sub>. Useful distribution ratios are attainable at  $\leq 4$  M HNO<sub>3</sub>, and Pd(II) is extracted selectively over U(VI) and Th(IV) (19).

The above <u>pyridine-based extractants</u> seem to be applicable only in halogenated diluents, where the extraction efficiency slightly decreases in the order: 1,2-dichloroethane > dichloromethane > 1,2-dichlorobenzene > chloroform. The extraction efficiency is markedly lower in a toluene diluent. As might be expected, similar but <u>pure oxygen donors</u> in 1,2-dichloroethane extract Pd(II) nitrate very weakly. These are 1,5-diphenylphosphinyl-3-oxapentane, 1,5-bis-[(2-diphenylphosphinyl)phenoxy]-3-oxapentane, 1,5-bis-[(2-diphenylphosphinylmethyl)phenoxy]-3-oxapentane and 1,5-diphenylphosphinyl-3,6,9-trioxaundecane (19).

The extraction of Pd(II) nitrate by dialkyl sulfides is very effective. For example, 0.25 M diheptyl sulfide in benzene extracts Pd(II) with distribution ratios of several hundreds from ≥ 1 M HNO<sub>3</sub>. It is not too serious a drawback that the distribution equilibrium is attained slowly after a phase contact of 8–10 hours. Sufficiently high (even if non-equilibrium) distribution ratios (> 10) can be attained after ~ 5 minutes if the extractant concentration is high enough, for instance 0.67 M (20). Even a very dilute solution of diheptyl sulfide (0.002 M) in chloroform extracts initially 0.001 M Pd(II) from 2 M HNO<sub>3</sub> with a distribution ratio of 6.1 (21).

Dihexyl sulfide, at a concentration of 10 vol.% in dodecane, gives distribution ratios for Pd(II), after a 30 minute phase contact, of 1000–5000 at 0.1–6 M HNO<sub>3</sub>. The separation factor from Pb(II) and Mo(VI) is extremely high at ~ 10<sup>6</sup> (22). Finally, a distribution ratio of 13.7 is attained after a 45 minute phase contact of simulated HLLW containing 3.1 M HNO<sub>3</sub> with 0.0005 M dioctyl sulfoxide in Solvesso 100 (16).

Two possible ways of accelerating the extraction rate of Pd(II) chloride have been described, and should also be investigated in nitrate media. One of them uses <u>fluorinated asymmetrical sulfides</u> as extractants, such as 5-(chlorodifluoromethyl)-3,3,4,4,5,-6,6,6-octafluorohexyl 2-hydroxyethyl sulfide or 6-(chlorodifluoromethyl)-3,3,4,4,5,5,6,6,7,8,8,8-dodecafluorooctyl-

2-hydroxyethyl sulfide. Extraction of initially 0.005 M Pd(II) by a 0.005 M solution of one of these extractants in toluene from 3 M HCl reaches an equilibrium after 20–30 minutes, compared with the 1 to 3 hours needed with simple dialkyl sulfides (23). The other way is to add alkylammonium salts as phase transfer catalysts. These can shorten the approach to an equilibrium from > 30 minutes to 5–12 minutes. At a concentration of 0.0017 M they accelerate the extraction of Pd(II) by 0.1 M dihexyl sulfide in kerosene from 2 M HCl, with accelerating efficiency increasing in chloride order: dioctylammonium < Aliquat 336 < triisooctylammonium (24).

Diesel fuel is perhaps the cheapest source of sulfide extractant - with some of the sulfides still not being fully identified. The diesel fuel contains, besides sulfides and strong reductants, organic nitrogen and oxygen compounds which can also extract Pd(II) nitrate. The N and O compounds can be removed by contacting the fuel with a HNO<sub>3</sub>/K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution followed by washes with NaOH and NaNO3 solutions or, alternatively, by a wash with 57% H<sub>2</sub>SO<sub>4</sub>. After this either the sulfides can be separated by extraction into 86% sulfuric acid or the treated fuel can be used as an intrinsically ready-to-use solvent, that is, a solution of sulfide compounds in a mixed paraffin, aromatic and naphthene diluent (25). This solvent extracts Pd(II) from 2-3 M HNO3 with a distribution ratio of 10-100, and with a high selectivity over actinides(III-VI), Ru(III)NO, Cs(I), Sr(II), Ce(III) and Zr(IV) (26).

Triisobutylphosphine sulfide is even more effective than di-n-alkyl sulfides. A solution as dilute as 0.0001 M in Solvesso 100 extracts Pd(II) with distribution ratios of 0.64, 0.96, 1.40 and 1.60 at 0.1, 1.0, 3.0 and 6.0 M HNO<sub>3</sub>, respectively. A distribution equilibrium is attained after 45 minutes (16).

Straight chain and macrocyclic thioether: exhibit a very high extraction efficiency for Pd(II). This is illustrated by data on Pd(II) extraction from initially 2 M HNO<sub>3</sub> + 0.001 M Pd(NO<sub>3</sub>)<sub>2</sub> by 0.0005–0.002 M extractants in chloroform. The bidentate extractants: 6,9-dithiatetradecane, 6,10-dithiapentadecane, 9,13-dithiauncosane and 6,11-dithiahexadecane (all 0.001 M) give distribution ratios of 7.1, 39, 29.3 and 42, respectively. The tridentate extractant

6,9,12-trithiaheptadecane (0.0005 M) gives a value of 1.1. The macrocyclic extractants 1-octyl-2,5,8-trithia-cyclononane (0.002 M) and 1-octyl-3,7,11,15-tetrathia-cyclohexadecane (0.001) M give values of 1.08 and 5.8, respectively. In extraction from a real dissolver solution (a solution obtained from irradiated nuclear fuel in contrast to a simulated solution prepared from non-radioactive chemicals and labelled with radioactive tracers) 6,9,12-trithiaheptadecane proved to be very selective for Pd(II) (21).

Examples of some less common sulfur donor extractants are alkylenebis(O-butylxanthate) or alkylenebis(O-isobutylxanthate) with alkylene being methylene to butylene. These are able to extract Pd(II) nitrate at a low concentration (0.0025 M) in dichloroethane, but again the distribution equilibrium is only slowly established in 1 hour and there are some solubility problems (27). A nitrogen donor extractant, namely 01-benzoin oxime (as dilute as 0.0001 M in Solvesso 100) extracts Pd(II) nitrate from 2 M HNO3 with a distribution ratio of 1.7 (16).

Rhodium Extraction – The extractability of Rh(III) nitrate by *phosphoryl extractants* is even weaker than that of Pd(II). Thus, unaliluted *TBP* yields, at 1–15 M HNO<sub>3</sub>, distribution ratios of 0.1–0.01 (28), but these ratios were found after a phase contact time of 2 minutes and are possibly non-equilibrium values.

Diisoamyl methylphosphonate in diethylbenzene extracts Rh(III) nitrate from < 5 M nitric acid under harsh conditions, that is, at a high concentration of the extractant (50%) and of salting-out agents (1.6 M Al(NO<sub>3</sub>)<sub>3</sub> + 1 M NH<sub>4</sub>NO<sub>3</sub>) (29).

Trioctylphosphine oxide in xylene, unfortunately studied at a phase contact time of 2 minutes, extracts Rh(III) nitrate very weakly (28), to a similar extent as alkyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxides (alkyl = octyl, 2-ethylhexyl or 2,4,4-trimethylpentyl) (15).

It is unfortunate that Rh(III) nitrate is not extracted by dialkyl sulfides, which are so effective for Pd(II). After a phase contact time of 30 minutes, a 10 vol.% solution of dibecyl sulfide in dodecane yields distribution ratios for Rh(III) as low as 0.001–0.002 (22).

Ruthenium Extraction – Nitrosylruthenium(III) is well extracted by TBP, especially in the form of the trinitrate RuNO(NO<sub>3</sub>)<sub>3</sub>, but nitric acid suppresses the extraction. For example, when the trinitrate is extracted by 30% TBP in dodecane the distribution ratio decreases from 63 at 0.1 M HNO<sub>3</sub> to 0.9 at 4 M HNO<sub>3</sub>. This happens after a phase contact time of 30 seconds; after longer contact times (≥ 5 minutes) the distribution ratio decreases due to conversion of the trinitrate to less extractable nitrate complexes (30). With ø-dichlorobenzene as diluent, the extractability of the whole Ru(III)NO from 1–8 M HNO<sub>3</sub> increases in order: TBP < trioctylphosphine oxide < di-(p-tolyl)-N,N-dibutylcarbamoylmethylphosphine oxide < ditolyldiphenylmethylenediphosphine dioxide (31).

#### Acidic Extractants

Palladium Extraction – An extractant as common and generally efficient as di(2-ethylhexyl)phosphoric acid extracts Pd(II) very weakly. This is clearly shown by data obtained in a chloride system (32). A chloroform solution of a less common oxygen donor extractant, 5-methyl-2,3-hexanedione dioxime, extracts Pd(II) at pH 0.5–1.5 (33). This compound is limited to the laboratory scale.

A surprising ability to extract Pd(II) is exhibited by a mixed nitrogen/oxygen donor extractant, N,N'-bis[\alpha-(1-phenyl-3-methyl-5-bydroxy-4-pyrazolyl)benzylidene]-1,3-diaminopropane, the enol form of a Schiff base. In toluene diluent it extracts > 50% Pd(II) from 1 M nitric acid even at an initial concentration as low as 0.0004M. The distribution equilibrium is attained in < 20 minutes (34).

Pd(II) is also rather effectively extracted from a nitrate solution by a sulfur donor extractant, bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301). The distribution of Pd(II) was measured only down to pH 0.8 where, at a phase contact time of 30 minutes, a phase volume ratio organic:aqueous of 0.5 and 0.2 M extractant in kerosene, the extracted percentage of Pd(II) is practically 100% (35). It is quite possible that Pd(II) may also be extracted well at nitric acid concentrations typical of HLLW. Difficulties can arise due to limited stability of the extractant toward oxidation.

Bis (2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) can extract Pd(II) from 1 M HCl (36). As the anion of this mineral acid does not participate in the formation of the extracted complex, Cyanex 302 should also be able to extract Pd(II) from nitric acid solutions.

To study the extraction chromatography (mentioned earlier) of Pd(II), bis(2,4,4-trimethylpentyl)-dithiophosphinic acid was encapsulated into capsules of Ca alginate gel. The uptake of Pd(II) from 0.13 M HNO<sub>3</sub> is so slow that a distribution equilibrium is only attained after 3 days, but it is selective with regard to Ru(III)NO and Rh(III). In spite of the slow uptake rate, column operation was shown to be possible (37).

Also usable as an extractant for Pd(II) is 2-hydroxy-5-nonylbenzophenone (LIX65N). A 0.01 M solution of it in a 9:1 ratio in heptane:chloroform extracts Pd(II) from 1 M HCl at a distribution ratio of  $\sim$  40. Unfortunately, the extraction rate is slow, requiring a contact time as long as 25 hours to attain distribution equilibrium. Adding Aliquat 336 as a phase transfer catalyst shortens the equilibration time, but to no better than 4 hours (38). Since chloride ions do not participate in the formation of the extracted complex, it can be expected that LIX65N will also extract Pd(II) from solutions of nitric acid. Still to be found are the extraction rate in the absence of chloride ions and the chemical stability of LIX65N.

Rhodium Extraction – Rh(III) is extractable by dinonylnaphthalenesulfonic acid in kerosene, but only at low concentrations of nitric acid (0.1–1.0 M). The Rh<sup>3+</sup> ion is incorporated into an inverted micelle of the extractant, and a distribution equilibrium is reached in < 15 minutes. At 2 M HNO<sub>3</sub> and 0.2 M extractant the Rh(III) distribution ratio is low (39).

Ruthenium Extraction – Nitrosylruthenium is extracted by a 0.2 M solution of bis(2,4,4-trimethylpentyl)dithiophosphinic acid in kerosene with low efficiency. The distribution ratio decreases from 4 at pH 4.0 to 0.2 at pH 1.1 (35).

#### Basic Extractants

Palladium Extraction – As with solvating extractants, it is desirable to extract platinoids in a nitrate or nitrite form. *Amines* extract Pd(II) nitrate

complexes only moderately. For example, when 0.33 M trioctylamine (TOA) is used as extractant in benzene, the distribution ratio reaches a maximum value of 1.6 at ~ 1.2 M HNO<sub>3</sub> (40). Tridecylamine and tridodecylamine in benzene give a similar result, indeed, seeming to be slightly less effective than TOA (41), while dioctylamine, octylamine and dodecylamine extract Pd(II) markedly less efficiently that TOA (40). When the organic phase is 10 vol.% TOA in dodecane modified with 5 vol.% dodecanol, the distribution ratio of Pd(II) decreases monotonously with increasing acid concentration from ~ 15 at 0.1 M HNO<sub>3</sub> to ~ 0.6 at 3 M HNO<sub>3</sub> and ~ 0.2 at 6 M HNO<sub>3</sub> (22).

At < 1.5 M HNO<sub>3</sub> the extraction by TOA in benzene is supported by nitrite ions which exhibit a visible effect at a concentration as low as 0.005 M (40).

Quaternary ammonium bases are powerful extractants for Pd(II) nitrate complexes. As with TOA, the distribution ratio reaches its maximum value at a rather low concentration of nitric acid. However, at an appropriate extractant concentration the distribution ratio could be high enough to extract Pd(II) at nitric acid concentrations typical of HLLW.

As an example, 0.042 M solutions of trioctyl-methylammonium and tetraoctylammonium nitrates in benzene yield for Pd(II), maximum distribution ratios of  $\sim 20$  and  $\sim 4.5$ , respectively, at 0.5 M HNO<sub>3</sub>. With the former extractant the ratio is still  $\sim 1.3$  for 3 M HNO<sub>3</sub> (42).

Rhodium Extraction – Rh(III) nitrate complexes appear to be very weakly extractable by Amberlite LA-1 and triisooctylamine in xylene from 1–14 M HNO<sub>3</sub>. Distribution ratios of < 0.01 have been found, unfortunately after a short phase contact time of 2 minutes (28). With 10 vol.% TOA in dodecane modified with 5 vol.% dodecanol and at a 30 minute phase contact time, the distribution ratio of Rh(III) decreases monotonously from  $\sim$  0.06 at 0.1 M HNO<sub>3</sub> to  $\sim$  0.001 at 6 M HNO<sub>3</sub> (22).

Rh(III) is efficiently extractable as a nitrite complex by *trioctylamine*. Unfortunately, with 0.5 M extractant in xylene, appreciable distribution ratios of Rh(III) are attained only at pH > 2 (43). It must

be noted that Aliquat 336 in benzene extracts Rh(III) with moderate efficiency in an undefined, possibly sulfate form at pH 0.3–9.5 (44).

#### Ion Exchange and Sorption

Ion exchange has been applied to radiochemical processes to treat highly radioactive solutions. However, it is less useful than solvent extraction because it is discontinuous and has a limited throughput, even when a quasi-continuous operation mode is possible. The contact time between the exchanger and the radioactive solution is rather long, and operational difficulties, such as plugging the column, cannot be completely eliminated. On the other hand, one advantage is that platinoids can be sorbed from strongly acidic solutions. The distribution coefficient,  $K_d$  used here is defined as:

$$K_d = N_{M,e} \cdot V/N_{M,s} \cdot m$$

 $N_{M,e}$  and  $N_{M,s}$  are the metal amounts in a particular valence state in the ion exchanger and solution, respectively, V is the volume (in ml) of the solution and m is the mass (in g) of the ion exchanger.

#### Anion Exchangers

Palladium(II) - can be sorbed from solutions containing several moles of nitric acid per litre. A comparison of data from (45) with previously published data (see references therein) shows that at 6 M HNO3 the strongest affinity to Pd(II) is exhibited by a tertiary/quaternary type exchanger: 4-(N,N-dimethylbenzimidazole)phenyl (AR-01). The exchange rate, however, is so slow that no distribution equilibrium is attained even after 20 hours of contact at 60°C. Common commercial anion exchangers from the U.S.A., such as tertiary Amberlite IRA-93ZU and quaternary Amberlite IRA-900, Amberlite IRN-78, Dowex 1X8-400 and Dowex 2X8-400 sorb Pd(II) from 6 M HNO3 much less efficiently, but a distribution equilibrium is attained after 1 hour at 60°C. When Pd(II) is sorbed on Dowex 1X8 and Amberlite INR-78 from 0.1 M HNO<sub>3</sub>, an equilibrium is attained after 0.5-1 hours both at 20 and 60°C. However, the distribution coefficient at 60°C is higher by a factor of 1.2-1.5. The dependence of the distribution coefficient of Pd(II) on the nitric acid concentration is

nonmonotonous; the maximum distribution coefficients at 2–2.5 M HNO<sub>3</sub> and 20°C are ~ 35 with *Dowex 1X8* and ~ 95 with *Amberlite INR-78*. Thiourea is effective in the elution of Pd(II) (45).

The strongly basic resin AV-17X8 from Russia, comparable with, for example, Dowex 1X8, gives distribution coefficients for Pd(II) of 64, 56 and 200 at acidities of 0.5, 3.0 and 8.0 M HNO<sub>3</sub>, respectively. Similarly, a strongly basic pyridinium anion exchanger (VP-1AP) gives, for the same acidities,  $K_d$  values of 64, 77 and 35, respectively. A stronger affinity to Pd(II) is exhibited by a weakly basic anion exchanger (AN-104), which yields  $K_d = 475$ , 350 and 120, respectively, and, especially, by a strongly basic phosphonium anion exchanger (KbFO) which yields  $K_d = 900$ , 500 and 200, respectively (46).

Rhodium(III) – is generally less efficiently sorbed by anion exchangers than Pd(II). In sorption on Dowex 1X8 and Amberlite INR-78 from 0.5 M HNO<sub>3</sub>, a distribution equilibrium is attained after 1 hour both at 20 and 60°C, but the distribution coefficients are higher at 60°C. As a function of the nitric acid concentration, the distribution coefficient reaches maximum values of ~ 13 with Dowex 1X8 and ~ 8 with Amberlite INR-78 at 20°C and 2–3 M HNO<sub>3</sub> (45). The Russian quaternary ammonium (AV-17X8), weak basic ammonium (AN1-4), pyridinium (VP-1AP) and phosphonium (KbFO) resins sorb Rh(III) from 3 M HNO<sub>3</sub> with a distribution coefficient of < 5 (46).

Nitrosylruthenium(III) – is sorbed by the quaternary ammonium (AV-17X8), pyridinium (VP-1AP) and phosphonium (KbFO) resins from 3 M HNO<sub>3</sub> with distribution coefficients as low as 1.3, 6 and 11, respectively (46).

The strongly basic resin Amberlite IRA-401 sorbs both Pd(II) and Rh(III) efficiently enough from aged alkaline supernatant solutions, obtained by the alkalisation of Purex process wastes (12).

#### Cation Exchangers

Using cation exchangers is hardly applicable to the uptake of platinoids from strongly acidic solutions. The adsorption of Rh(III) on *Dowex 50W* at 20°C is strongly suppressed by nitric acid, the distribution coefficients being ~ 55, 9 and 1 at 0.5, 1

and 3 M HNO<sub>3</sub>, respectively (45). Similarly, platinoids are weakly sorbed on Russian cation exchangers. In 3.0 M HNO<sub>3</sub> the sulfonic acid resin *KU-2X8* gives K<sub>d</sub> values for Pd(II), Rh(III) and Ru(III)NO of 9, 0.5 and 5, respectively, and the phosphoric acid resin *KRF-20t-60* gives the K<sub>d</sub> values 9, < 5 and 3, respectively (46).

Four Russian aminocarboxylic resins (trade names VPK, ANKB-2, ANKB-35 and MS-50) sorb Pd(II) effectively from 3 M HNO<sub>3</sub>, yielding K<sub>d</sub> values of 850, 350, 150 and 160, respectively. Ru(III)NO is moderately sorbed, with K<sub>d</sub> being 51, 45, 43 and 55, respectively, for the resins. The VPK, ANKB-35 and MS-50 resins sorb Rh(III); K<sub>d</sub> is 230, 24 and 5, respectively (46).

Semiquantitative data on the chelating amide oxime exchanger CS-346 show that Pd(II) is sorbed well from 0.5–6 M HNO<sub>3</sub>, while Ru in an unspecified chemical state is sorbed rather weakly and Rh(III) is sorbed very weakly (22).

The affinity of inorganic sorbents for Pd(II), again in sorption from 3 M HNO<sub>3</sub>, decreases as: Cu hexacyanoferrate/silica gel (FS-15,  $K_d = 100$ ) > Ni hexacyanoferrate/silica gel (FS-14,  $K_d = 74$ ) > CuS (GSM,  $K_d = 36$ ) > hydrous  $TiO_2$ :ZrO<sub>2</sub> (12:1 to 25:1,  $K_d = 9$ ). The weak sorption of Rh(III) is characterised by  $K_d = 10$  on FS-14 and FS-15 and  $K_d < 5$  on GSM and  $TiO_2$ :ZrO<sub>2</sub>. Ru(III)NO is sorbed very weakly on FS-14 ( $K_d \sim 4$ ), FS-15 ( $K_d \sim 2$ ) and  $TiO_2$ :ZrO<sub>2</sub> ( $K_d \sim 0.5$ ) (46).

#### Other Sorbents

Pd(II) is strongly sorbed from 0.5 M nitric acid solutions on active carbon. As break-through curves indicate, Tc(VII) is sorbed with a comparable efficiency, and Rh(III) is weakly sorbed. Various complex forms of Ru(III)NO appear to exhibit different affinities for active carbon, so the observed sorption of Ru(III)NO ranges from as weak as that of Rh(III) to stronger than that of Pd(II) (47, 48). Pd is also sorbed from alkaline Purex wastes on active carbon more strongly than Rh (49).

#### Precipitation

Precipitation is a discontinuous process and is possibly difficult to perform on a large scale, especially in treating amorphous precipitates like hydroxides. The liquid/solid phase separation is much less complete than, for example, in ion exchange, and is still much less clean than the liquid/liquid phase separation in solvent extraction. A considerable amount of the liquid phase may be occluded by the precipitate, and this makes it difficult to wash out solutes that are required to remain in the supernatant. These disadvantages can be compensated by the high selectivity of some precipitation reactions.

#### Precipitation of Platinoid Compounds

Pd(II) is precipitated as Pd<sub>1.1</sub>C<sub>2.1</sub>H<sub>4.1</sub>N<sub>2</sub>O in the partial denitration of the HLLW by sucrose at reflux temperature (50). Some precipitation methods require chloride ions to be added to the HLLW, but nowadays this is considered unacceptable. The methods are mentioned here only because they have been suggested as a way of separating platinoids from the HLLW. Thus, Cs<sub>2</sub>PdCl<sub>6</sub> can be precipitated, if the Pd(II) in the HLLW is oxidised to Pd(IV) either electrochemically or by NaClO, and a source of chloride ions is added (51).

Hardly applicable to HLLW is precipitation of salts of the type Cs<sub>2</sub>[MCl<sub>2</sub>(SnCl<sub>3</sub>)<sub>2</sub>] where M is a platinoid (52). The addition of HCl and SnCl<sub>2</sub> up to concentrations as high as > 2 M and ~ 0.1 M, respectively, is required. Pd(II), Rh(III) and Ru(III)NO are precipitated with efficiencies of 97 to 100%.

A Rh(III) fraction of 94–96% is precipitated as hydroxide from simulated radioactive waste containing 20 wt.% acetate at pH 8–12. More than 90% Pb(II) remains in the supernatant solution. Rh(III) can be separated from Mo(VI), particularly at pH 12, where 87% Mo(VI) is not precipitated (22).

Precipitation of platinoids in metal form is dealt with below as a redox reaction.

#### **Electrochemical and Chemical Redox Reactions**

Although in many systems electrolytic deposition is a discontinuous and time consuming operation, it is still a prospective method for isolating platinoids — mainly due to the easy and selective reduction of Pd(II) to metal. Also advantageous are: ease of scale-up and simplicity of the

equipment, the potentially clean separation of deposited metal from the solution and the limited production of secondary wastes.

#### Electrochemical Reduction

Pd(II) is deposited from a simulated HLLW onto a Pt cathode at a potential of -0.2 to 0.1 V (vs. SCE) and a current density of 8-70 mA cm<sup>-2</sup> (53). The deposition rate on a tantalum electrode at -0.1 V (vs. SCE) and 40°C decreases in the order of Pd > Rh > Ru (the original source does not specify the initial chemical form), and the deposition rate also decreases when the concentration of nitric acid is increased from 0.5 to 5 M. Uranium(VI), even at concentrations as  $\geq 0.001$  M, strongly decelerates the deposition of Pd (54). The effect of U(VI) might be a hindrance if Pd is to be deposited directly from a dissolver solution. According to present knowledge, Pd appears to be the only fission platinoid deposited at a rate suitable for a separation process.

At 100 ppm levels, Pd(II) and Ru(III)NO mutually influence their deposition rates from 3 M HNO<sub>3</sub>. The deposition of Pd(II) is slightly slowed by the presence of Ru(III)NO, while the presence of Pd(II) markedly accelerates the deposition of Ru(III)NO (55).

#### Chemical Reduction and Photoreduction

Pd(II) is reduced to metal by ascorbic acid, and the precipitation yield from simulated HLLW decreases with increasing nitric acid concentration. The reported concentration of ascorbic acid needed to precipitate > 99% Pd is 0.03–0.06 M at 0.5–4 M HNO<sub>3</sub> (56) or 0.04 M at 2 M HNO<sub>3</sub> (57). The precipitation is selective with respect to Rh(III) and Ru(IV) (56, 57) and also Mo(VI), Fe(III), Nd(III), Sr(II) and Cs(I) (57). The precipitation of Pd(II) as metal is practically complete after 20 minutes (57), but Pd redissolves as the solid/liquid system ages. Redissolving starts after 14 hours and is complete after 18 hours; it is ascribed to oxidation of ascorbic acid by HNO<sub>3</sub> mediated by the Pd(II)/Pd(0) and Fe(II)/Fe(III) couples (57).

The precipitation of Pd(II) from simulated HLLW is effective even in the presence of 0.5 M oxalic acid. At 0.25 M ascorbic acid and 0.4–2 M

HNO<sub>3</sub> the precipitated fraction of Pd is 98–99%; this decreases to ~ 10% at 4 M HNO<sub>3</sub> (58). Both Pd(II) and Rh(III) are reduced to metallic form in the denitration of HLLW by refluxing with formic acid, when the nitric acid concentration is reduced from an initial 3.5 M HNO<sub>3</sub> to pH 2 (59). The platinoid metals are obtained in a mixture with other solids, mainly hydroxide precipitates.

The photoreduction of the platinoids to metals is possible in the presence of  $TiO_2$  powder as photocatalyst. With a 2 kW xenon lamp as a light source and in 3 M HNO<sub>3</sub> containing 20% ethanol, 100% Pd and  $\sim$  90% Rh are reduced after 60 minutes. The reduction of the initial Ru(III) is slower at  $\sim$  60 and  $\sim$  80% after 60 and 90 minutes, respectively; the reduction of initial Ru(III)NO is quite inefficient (2–3% after 60–90 minutes) (60).

#### Oxidation of Ruthenium

Ru(III)NO can be electrooxidised in synthetic HLLW to RuO<sub>4</sub> at  $30^{\circ}\text{C}$ ,  $\geq 2\text{ V}$  (vs. SCE),  $\geq 12\text{ mA}$  cm<sup>-2</sup> and at air flow 0.4–1 l m<sup>-1</sup>. RuO<sub>4</sub> gas is formed at a Pt anode, and transferred with the air stream into an absorbing solution containing, for example, HCl and ethanol (53). During the oxidation to RuO<sub>4</sub> by bubbling ozone, more than 98% Ru can be recovered from a solution that is obtained by dissolving a Pb phase button (see below) in boiling 3 M nitric acid (61). It should be mentioned that large-scale operation would probably be fundamentally disturbed by the easy reduction of RuO<sub>4</sub> to the almost insoluble solid RuO<sub>2</sub>, which deposits on the walls of reaction vessels and pipe connections.

#### **Pyrochemistry**

The advantages of this method are due to the nature of the materials handled, namely molten inorganic salts, metals and/or alloys, or solids. These display higher radiation stability than aqueous solutions or organic compounds in hydrometallurgical processes. Since the process streams have smaller volume than in hydrometallurgy, the operations can be performed in compact equipment. The discontinuous nature of many of the operations and the difficulty in achieving continuous operations are disadvantages. The

counter-current contact of two immiscible molten phases is much less easy than in solvent extraction. A further disadvantage is in partitioning the HLLW, namely the need to convert an acidic nitrate solution to an oxide or chloride solid. It is a common feature that platinoids are not mutually separated in pyrochemical procedures and a mixture of two or all three fission platinoids is the resulting product. Thus, further separation is needed and is conveniently achieved in a hydrometallurgical procedure after dissolving the product in nitric acid.

#### Extraction by Molten Metals and Salts

Pd and Rh are extractable into some molten metals from a LiCl:KCl (50:50 mol%) melt. Both are quantitatively extracted (~ 100%) into Zn at 800°C, into Cd at 500 and 650°C, and into Pb and Bi at 600 and 800°C, respectively. A 70 to ~ 100% fraction of Ru is extracted at 600 and 800°C into Zn, while Cd, Pb and Bi extract ~ 5 to ~ 40% of Ru at 500–800°C (62).

One variation of the molten salt/metal extraction involves melting a particular salt/metal system. After cooling a metal button containing the platinoids and a glass phase containing other fission products are formed. To achieve this, glass (borosilicate type, developed for the vitrification of radioactive wastes), a metal oxide scavenger and a reductant are added to fission product oxides, and the mixture is melted at 1100°C. A comparative study (63) has shown that Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and PbO scavengers can be reduced to metals by graphite, charcoal, flour, corn starch, sugar and silicon, but SnO and CuO are reduced only by graphite. A 30-100% fraction of Pd or Rh and a 20-100% fraction of Ru are found in the metal button. Both the yield to the button and the quality of the glass phase are dependent on the nature of the scavenger and the reductant. The quality of the glass phase is best when the scavenger is PbO and poorest when the reductant is charcoal.

In a simpler form of the method the scavenger is added as a metal, and no reductant is needed. Thus, platinoids are extracted into molten Pb after it is added in metallic form (61, 64). Platinoid recovery is 85–100% in melting Pb with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>

or B<sub>2</sub>O<sub>3</sub> both in an argon atmosphere and under bubbling air, and independent of temperature at 750–1100°C. Using Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> as the glass-forming material allows somewhat higher recoveries than achieved with B<sub>2</sub>O<sub>3</sub> (64).

High selectivity for Ru over Pd has been observed in systems where molten magnesium and uranium:chromium eutectic (weight ratio 19:1) form two separate phases. At 900–950°C Pd and Ru distribute themselves in favour of the magnesium and eutectic phases, respectively, giving a separation factor of 10°. A similar picture has been found at 750–850°C in a system with magnesium and uranium:iron eutectic (weight ratio 89:11) phases. There is no separation in the molten aluminium:bismuth system at 700–900°C, where both the Pd and Ru much prefer the aluminium phase (3).

#### Reactions Involving Solids

A super-high-temperature reduction of the platinoids in a calcined radioactive waste proceeds under an Ar atmosphere at 1800°C. As the original source can be understood, the platinoids are reduced without adding a reductant. They separate, together with Mo as a metal phase, from the rest of the solid which mainly consists of lanthanide oxides (65). Elsewhere, platinoids have been reported to be reduced at ≥ 1600°C in the presence of AlN, BN, TiN or Si<sub>3</sub>N<sub>4</sub> as reductants (66). A metal phase and an oxide phase are formed, the former containing the bulk of platinoids and the Mo.

#### **Conclusions**

- [1] Fission platinoids (Pd, Rh and Ru) are distributed between two fractions of wastes that result from reprocessing spent nuclear fuel, namely radioactive high-level liquid waste (HLLW) and the undissolved fuel residue.
- [2] The platinoids of main interest (Pd and Rh) are preferably recovered from the HLLW by a hydrometallurgical process. Solvent extraction and electrolytic deposition are the preferred methods, while precipitation and ion exchange or extraction chromatography are less favoured.
- [3] Numerous extractants (mainly S donors) are

known to extract Pd efficiently from nitric acid solutions and can be used for extraction from HLLW. The chemistry of Pd in nitrate-based solvent extraction systems is known. Searching for new extractants and more detailed investigation of the basic chemistry of Pd may be useful but unnecessary.

- [4] Rh is generally less extractable by known extractants than Pd, and knowledge of its basic chemistry in nitrate solutions is insufficient. Further investigations are needed, aimed at improving the efficiency and selectivity of Rh solvent extraction.
- [5] Conditions for the satisfactory electrolytic deposition of Pd from nitrate solutions are largely known, and the method can be adapted to recover Pd from HLLW. The deposition of Rh is slow for practical application and further investigations are necessary.
- [6] Pyrometallurgical treatment appears to be the only feasible option to separate the platinoids from the dissolver residue. The treatment can convert the residue to a form that is soluble in dilute nitric acid. However, with the present state of knowledge, the platinoids are not mutually separated and are contaminated by some fission products. Subsequent hydrometallurgical separation is needed after dissolving the product of the pyrochemical procedure in a mineral acid. The possibility of combining the obtained solution with the HLLW instead of treating it separately should be checked.

Separation processes will be looked at in Part II of this paper, to be published later.

#### References

- 1 "Feasibility of Separation and Utilization of Ruthenium, Rhodium and Palladium from High-Level Wastes", IAEA Technical Report Series, No. 308, IAEA, Vienna, 1989
- 2 B. N. Zaitsev, V. A. Korolev, V. P. Popik, Yu. Z. Prokopchuk and M. N. Chubarov, *Radiokhimiya*, 1988, 30, (3), 411; Sov. Radiochem., 1988, 30, (3), 387
- 3 F. J. Smith and H. F. McDuffie, Sep. Sci. Technol., 1981, 16, (9), 1071
- 4 R. J. Newman and F. J. Smith, *Platinum Metals Rev.*, 1970, 14, (3), 88
- 5 H. Koch and A. Schober, *Isotopenpraxis*, 1976, 12, (2), 49
- 6 R. Thompson, Report AERE-R-11966, U.K. At. Energy Res. Establ., Harwell Lab., 1986

- 7 R. P. Bush, Platinum Metals Rev., 1991, 35, (4), 202
- V. S. Schmidt and N. A. Shorokhov, At. Energya, 1988, 64, (2), 103; Sov. At. Energy, 1988, 64, (2), 119
- W. A. Hoffman, Jr., Report ARH-732, Atlantic Richfield Hanford Co., Richland, WA, U.S.A., 1968
- E. Blasius, J.-P. Glatz and W. Neumann, *Radiochim. Acta*, 1981, 29, 159
- 11 E. Blasius, H. J. Luxenburger and W. Neumann, Radiochim. Acta, 1984, 36, 149
- 12 J. V. Panesko, Report ARH-733, Atlantic Richfield Hanford Co., Richland, WA, U.S.A., 1968
- 13 K. P. Lunichkina, E. V. Renard and V. B. Shevchenko, Zb. Neorg. Khim., 1974, 19, (1), 205; Russ. J. Inorg. Chem., 1974, 19, (1), 110
- 14 V. S. Shmidt, N. A. Shorokhov, S. S. Novikova, E. G. Teterin and A. N. Panteleeva, Radiokhimiya, 1983, 25, (2), 202; Sov. Radiochem., 1983, 25, (2), 189
- 15 E. P. Horwitz, D. G. Kalina, H. Diamond, G. F. Vandegrift and W. W. Schulz, Solvent Extr. Ion Exch., 1985, 3, (1-2), 75
- 16 G. H. Rizvi, J. N. Mathur, M. S. Murali and R. H. Iyer, Sep. Sci. Technol., 1996, 31, (13), 1805
- 17 J. P. Shukla, R. K. Singh, S. R. Sawant and N. Varadarajan, Anal. Chim. Acta, 1993, 276, 181
- 18 O. Courson, M. Lebrun, R. Malmbeck, G. Pagliosa, K. Römer, B. Sätmark and J.-P. Glatz, Radiochim. Acta, 2000, 88, 857
- A. N. Turanov, V. K. Karandashev and V. E. Baulin, Zh. Neorg. Khim., 2000, 45, (7), 1259; Russ. J. Inorg. Chem., 2000, 45, (7), 1145
- V. S. Shmidt, N. A. Shorokhov and S. D. Nikitin, *Zh. Neorg. Khim.*, 1986, 31, (4), 998; Russ. J. Inorg. *Chem.*, 1986, 31, (4), 568
- 21 V. Guyon, J. Foos, A. Guy, T. Moutarde, R. Chomel, M. Draye and M. Lemaire, Sep. Sci. Technol., 1995, 30, (7-9), 1961
- 22 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 Rep., ASME, New York, NY, U.S.A., 1993, Vol. 1, p. 667
- 23 M. Wisniewski, J. Szymanowski, G. Cote and E. Meissner, J. Chem. Tech. Biotechnol., 1994, 60, 31
- 24 G. Cote, D. Bauer and S. Daamach, C. R. Acad. Sci. Paris, Sér. II, 1988, 306, 571
- V. G. Torgov, V. V. Tatarchuk, I. A. Druzhinina, T. M. Korda, A. N. Tatarchuk and E. V. Renard, At. Energya, 1994, 76, (6), 478; Sov. At. Energy, 1994, 76, (6), 442
- L. V. Arseenkov, B. S. Zakharkin, K. P. Lunichkina,
  E. V. Renard, V. Yu. Rogozhkin and N. A. Shorokhov, At. Energiy, 1992, 72, (5), 462; Sov. At. Energy, 1992, 72, (5), 411
- 27 D. A. Chowdhury, C. S. Mendoza and S. Kamata, Solvent Extr. Ion Exch., 1994, 12, (5), 1051
- 28 T. Ishimori, Y. Kobayashi and Y. Usuba, Bull. Chem. Soc. Jpn., 1968, 41, (6), 1458
- 29 K. P. Lunichkina and E. V. Renard, Radiokhimiya, 1974, 16, (2), 268; Sov. Radiochem., 1974, 16, (2), 269

- 30 A. M. Rozen, N. A. Kartasheva and Z. N. Nikolotova, Radiokhimiya, 1995, 37, (3), 232; Sov. Radiochem., 1995, 37, (3), 213
- 31 A. M. Rozen, Z. N. Nikolotova and N. A. Kartasheva, Radiokhimiya, 1995, 37, (3), 239; Sov. Radiochem., 1995, 37, (3), 220
- 32 K. Kimura, Bull. Chem. Soc. Jpn., 1960, 33, (8), 1038
- 33 S. P. Tandel, S. B. Jadhav and S. P. Malve, Indian J. Chem., Sect. A, Inorg., Bioinorg., Phys. Theor. Anal. Chem., 2001, 40, (10), 1128
- 34 Jian-Ming Ouyang, Solvent Extr. Ion Excb., 1999, 17, (5), 1255
- 35 Jing Chen, Rongzhou Jiao and Yongjun Zhu, Radiochim. Acta, 1999, 86, 151
- 36 S. G. Sarkar and P. M. Dhadke, *Indian J. Chem. Technol.*, 2000, 3, (7), 109
- 37 H. Mimura, H. Ohta, H. Hoshi, K. Akiba and Y. Onodera, Sep. Sci. Technol., 2001, 36, (1), 31
- 38 Qingxin Rong and H. Freiser, Solvent Extr. Ion Exch., 1987, 5, (5), 923
- 39 N. M. Patel, J. R. Thornback and J. H. Miles, Proc. Symp. Extraction '87: Recovery High Value Metals (EFCE Event No. 347), 23–26 June, 1987, Dounreay, U.K. Symp. Series No. 103, Inst. Chem. Eng., Rugby, U.K., 1987, p. 163
- 40 V. S. Shmidt, N. A. Shorokhov and S. S. Novikova, Zb. Neorg. Khim., 1984, 29, (3), 773; Russ. J. Inorg. Chem., 1984, 29, (3), 445
- 41 V. S. Shmidt, E. A. Mezhov, V. N. Rubisov, L. V. Troyanovskii and N. A. Shorokhov, *Radiokhimiya*, 1986, 28, (3), 345; Sov. Radiochem., 1986, 28, (3), 311
- 42 V. S. Shmidt, N. A. Shorokhov and S. S. Novikova, Radiokhimiya, 1984, 26, (4), 445; Sov. Radiochem., 1984, 26, (4), 426
- 43 B. Gorski, M. Beer and L. Russ, *Isotopenprascis*, 1988, 24, (5), 200
- 44 M. H. Campbell, Anal. Chem., 1968, 40, (1), 6
- 45 S. H. Lee and H. Chung, J. Nucl. Sci. Technol., 2000, 37, (3), 281
- 46 V. V. Milyutin, S. B. Peshkishev and V. M. Gelis, Radiokhimiya, 1994, 36, (1), 25; Sov. Radiochem., 1994, 36, (1), 26
- 47 M. Kubota, Radiochim. Acta, 1993, 63, 91
- 48 Y. Yamagishi and M. Kubota, J. Nucl. Sci. Technol., 1993, 30, (7), 717
- 49 J. V. Panesko, Report ARH-1552, Atlantic Richfield Hanford Co., Richland, WA, U.S.A., 1970
- D. O. Campbell and S. R. Buxton, U.S. Patent 4,290,967; 1981
- 51 D. O. Campbell, U.S. Patent 3,979,498; 1976
- 52 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
- 53 M. Yoneya, Y. Hanamoto, K. Kawamura, H. Igarashi and Y. Miyamoto, Proc. Int. Conf. Future Nucl. Systems: Challenge Towards 2nd Nucl. Era Advanced Fuel Cycles (Global '97), 5–10 Oct., 1997, Yokohama, Japan, p. 1501

- 54 K. Koizumi, M. Ozawa and T. Kawata, J. Nucl. Sci. Technol., 1993, 30, (11), 1195
- 55 M. Ozawa, Y. Tanaka, C. Oohara and H. Tanuma, Proc. Int. Conf. Future Nucl. Systems: Challenge Towards 2nd Nucl. Era Advanced Fuel Cycles (Global '97), 5–10 Oct., 1997, Yokohama, Japan, p. 1232
- 56 S. H. Lee, C. H. Jung, J. S. Shon and H. Chung, Sep. Sci. Technol., 2000, 35, (3), 411
- 57 E.-H. Kim, J.-H. Yoo and C.-S. Choi, Radiochim. Acta, 1998, 80, 53
- 58 E.-H. Kim, D.-Y. Chung, W.-H. Kim, Y.-J. Shin, E. H. Lee and J.-H. Yoo, J. Nucl. Sci. Technol., 1997, 34, (3), 283
- 59 Wu Chuanchu, Liu Yuanfang and Jiang Lingen, J. Nucl. Radiochem. (Chin.), 1986, 8, (3), 147
- 60 T. Nishi, N. Uetake, F. Kawamura and H. Yusa, Trans. Am. Nucl. Soc., 1987, 55, 242
- 61 M. Myochin, K. Kawase, Y. Wada, Y. Kishimoto, M. Ayabe, M. Hatta and K. Arita, Proc. Int. Conf. Nucl. Waste Management Environ. Remed., 5-11 Sept., 1993, Prague, Czech Rep., ASME, New York, U.S.A., 1993, Vol. 1, p. 663
- 62 H. Moriyama, K. Kinoshita, T. Seshimo, Y. Asaoka, K. Moritani and Y. Ito, Proc. 3rd Int. Conf. Nucl. Fuel Reprocessing Waste Management (RECOD '91), 14–18 Apr., 1991, Sendai, Japan, Vol. II, p. 639

- 63 G. A. Jensen, A. M. Platt, G. B. Mellinger and W. J. Bjorklund, Nucl. Technol., 1984, 65, 305
- 64 K. Naito, T. Matsui, H. Nakahira, M. Kitagawa and H. Okada, I. Nucl. Mater., 1991, 184, 30
- 65 M. Horie, Trans. ENS/ANS-Foratom Conf. (ENC '90), 23–28 Sept., 1990, Lyon, France. Verlag TÜV Rheinland, Köln, Germany, 1990, Vol. IV, p. 2281
- 66 M. Uno, Y. Kadotani, H. Kinoshita and C. Miyake, J. Nucl. Sci. Technol., 1996, 33, (12), 973

#### The Authors

Zdenek Kolarik retired from the Forshungszentrum 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 platinoids from radioactive high-level liquid wastes.

### Ruthenium Complexes Aimed at Chagas' Disease

The parasite Trypanosoma cruzi causes Chagas' disease, a major health problem in Latin America. The disease is transmitted by insects, blood transfusion and maternal infection to the foetus. The poorest environments suffer most. Debilitating illness leads to later death. Transmission is attacked by vector insect control and blood screening. Drug treatment (usually Nifurtimox™ and benznidazole) is used for acute, early, indeterminate and congenital cases. As T. cruzi antigens can stimulate autoimmunity, immunisation is not possible.

Nifurtimox<sup>TM</sup> is inefficient at treating the chronic stage of the disease and has undesirable side effects. To counter this, semicarbazones derived from 5-nitrofurfural have been synthesised and show activity against T. cruzi. The compounds generate nitro anion radicals, which may be the cause of their activity.

Earlier work has shown metal complexes of some antitrypanosomal drugs (imidazole and thiazole derivatives) are more active against *T. cruzi* than the free ligands. As there are similarities between metal drugs displaying antitumour and trypanocide activity, ruthenium complexes with antitrypanosomal ligands have been synthesised. However, ruthenium semicarbazones have received less attention for this use (1).

Now, in a further attempt to produce complexes that combine the antitrypanosomal activities of both the metal and ligand, researchers at the Universidade de São Paulo, Brazil, Universidad de la República, Uruguay, and Universidad Nacional de La Plata and Instituto IFLP, Argentina, have synthesised new Ru(II) complexes (2). The complexes have general formula, [Ru<sup>II</sup>Cl<sub>2</sub>(DMSO)<sub>2</sub>L] (DMSO = dimethylsulfoxide; L = 5-nitro-2-furaldehyde semicarbazone (L1), N<sup>4</sup>-n-butyl-5-nitro-2-furaldehyde semicarbazone (L2) and 3-(5-nitrofuryl)acroleine semicarbazone (L3)). The complexes have been characterised and crystal and molecular structures of the L1 and L2 complexes determined. The Ru atom in both crystals is in a similar octahedral environment, equatorially coordinated to the semicarbazone molecule, acting as a bidentate ligand through the N and O atoms. Work to evaluate the activity of these Ru complexes on the proliferation of in vitro T. Cruzi cultures is underway.

#### References

- C. S. Allardyce and P. J. Dyson, *Platinum Metals Rev.*, 2001, 45, (2), 62
- L. Otero, P. Noblia, D. Gambino, H. Cerecetto, M. González, J. A. Ellena and O. E. Piro, *Inorg. Chim. Acta*, 2003, 344, 85