

## Testing of Solvent Extraction Process for Recovery and Affining of Fission Palladium from Model Nitrate-Nitrite Solutions

VLADIMIR V. TATARCHUK<sup>1</sup>, IRINA A. DRUZHININA<sup>1</sup>, TAMARA M. KORDA<sup>1</sup>, VALERIY K. VARENTOV<sup>2</sup>, EDOUARD V. RENARD<sup>3</sup> and VLADISLAV G. TORGOV<sup>1</sup>

<sup>1</sup>Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

E-mail: tat@che.nsk.su

<sup>2</sup>Novosibirsk State Technological University, Pr. K. Marxa 20, Novosibirsk 630092 (Russia)

<sup>3</sup>Bochvar All-Russian Research Institute of Inorganic Materials, Ul. Rogova 5, Moscow 123060 (Russia)

(Received April 26, 2002; in revised form June 9, 2002)

### Abstract

In relation to the problem of recovery of fission palladium from highly active liquid wastes from spent nuclear fuel reprocessing, the efficiency of a flow sheet based on solvent extraction and electrochemical processes for palladium purification from a number of accompanying elements (Ag, Te, Se, Sb) was tested using model (in the absence of radiation) nitrate-nitrite solutions. The flow sheet is composed of two extraction cycles which involve solvent extraction of palladium with petroleum sulphides, washing of the extracts with acid solutions, and palladium stripping with aqueous ammonia. In the first cycle imitating recovery from HLW, ~99 % Pd and ~25 % Ag is recovered and separation from other accompanying elements is achieved. High efficiency of palladium separation from silver ( $10^3$ ) is achieved during the second cycle due to solvent extraction affining from hydrochloric solution. For passing from the ammonia strip liquor of palladium and silver, which is the final product of the first cycle, to the starting hydrochloric solution for the second cycle, electrochemical operations are applied, involving co-deposition of these metals on the cathode followed by their anodic dissolution in HCl solution. The efficiency of these operations was also not less than 99 %. At the final stage, purified palladium is recovered from the strip liquor of the second cycle as a difficultly soluble trans-dichlorodiammine (“palladozammine”, PZA). End-to-end palladium fraction extracted with the help of this flow sheet is 97–98 %. No Te, Se or Sb admixtures were detected in the resulting PZA; Ag content is close to the level observed in the reference experiment (mass concentration  $10^{-5}$  %).

### INTRODUCTION

During solvent extraction reprocessing of spent nuclear fuel (SNF), about a half of fission Ru, Rh and Pd contained in it (3–30 kg/t of a heavy metal) remains in high level wastes (HLW) of PUREX process [1, 2]. Ecological aspects of HLW handling are connected with the necessity to recover platinum metals (PM) from a mixture of fission products before or during waste vitrification [2]. Under perspective fractionating of long-lived radionuclides of HLW (for subsequent transmutation of minor acti-

noids), PM can be recovered as a separate fraction along with the fractions containing actinoids, Sr–Cs, etc. [3, 4]. Group extraction of PM can be achieved by reducing with sugar [2] or formic acid [3] during HLW denitration, by fusion with a lead collector [2], by sorption on activated carbon [3]. Methods of PM recovery from the resulting concentrates have not been developed, because an exposure for 30–50 years is necessary in order to decrease the activity of Ru and Rh radionuclides. As far as palladium is concerned, its radioactivity is determined by the long-lived  $^{107}\text{Pd}$  ( $T_{1/2} = 6.5 \cdot 10^6$  years)

isotope, which is a soft  $\beta$ -radiator (35 keV) and is responsible for almost constant radioactivity of fission palladium. So, in the foreseeable future, it is reasonable to develop a technology of recovery and fine purification with the factor of separation from accompanying radionuclides  $10^5$ – $10^7$  [1], which may find limited application in a number of works in nuclear industry excluding any direct contact with man and mixing of the fission palladium with natural one. Development of laser and plasma procedures of isotope separation and reduction of the price of these procedures will allow one to separate  $^{107}\text{Pd}$  in the future and to use stable isotopes of fission palladium without limitations [1, 2]. This problem is urgent because need for palladium on the world market exceeds overall demand for all the other platinum metals, while the cost of palladium is high [5].

Industrial technologies of the recovery of fission palladium are unavailable at present, though works are known which deal with the recovery of fission palladium preparations from actual solutions by means of sorption [6] and solvent extraction [7]. The possibility to achieve the required factor of fission palladium separation from Ag, Ru and Rh radionuclides much higher than the requirement for the conventional affining of natural palladium was not investigated in those works. On the basis of previous investigations [8–10], we proposed a solvent extraction procedure for palladium recovery and affining from acidic nitrate – nitrite systems in application to the recovery of fission palladium from HLW. The procedure consists of two extraction cycles, electrochemical operations providing the transfer from the first cycle to the second one (affining), and the final recovery of purified palladium in the form of difficultly soluble *trans*-dichlorodiammine.

The goal of the present work is laboratory testing of the efficiency of this procedure for the separation of palladium from a series of accompanying elements (Ag, Te, Se and Sb) on the basis of the direct measurement of their content in the intermediate and final products. Admixtures were introduced only into the initial imitates (in the absence of radioactive components) in concentrations close to their calculated concentrations in typical HLW. Such

an approach helps achieving a more adequate correspondence of the stoichiometry and concentrations of element forms to their actual status in the products obtained by the procedure under examination, which varies from one stage of the process to another depending on chemical medium of the liquid products.

## EXPERIMENTAL

We used chemical reagents:  $\text{HNO}_3$ ,  $\text{NH}_4\text{OH}$ ,  $\text{AgNO}_3$  of “kh. ch.” grade (chemically pure), metal Pd (99.9 %), Sb (Su-000), Se (“os. ch.” 22-4 – specially pure), and Te (TV-4). Extractant was concentrate of petroleum sulphides (PS, 10 % sulphide sulphur, distillation range 507–633 K), extracted from sulphurous petroleum with 86 %  $\text{H}_2\text{SO}_4$ . Diluent for PS was technical-grade triethyl benzene (TEB) with isomer mixture content of 99.2 %.

Standard solutions of elements on the basis of 3M  $\text{HNO}_3$  were prepared by dissolving metals in concentrated (Pd and Sb) or 1 : 1 diluted  $\text{HNO}_3$  (Se and Te) followed by dilution with water. Imitate solution obtained by mixing standard solutions was subjected before solvent extraction to nitration with nitrogen oxides until constant effective redox potential of solution was achieved. For the aqueous  $\text{HNO}_2/\text{HNO}_3$  system [1], this means achievement of steady  $\text{HNO}_2$  concentration, which was estimated in agreement with calibration using nitric solutions of  $\text{NaNO}_2$  to be about  $10^{-2}$  M.

Solvent extraction operations (solvent extraction, washing, stripping) were carried out in separating funnels at room temperature (295–298 K) and a given ratio of the volumes of organic and aqueous phases ( $r$ ). The phases were mixed manually for time interval  $\tau$  and separated after emulsion layering as a result of settling. Before analysis, aliquots of phases were additionally centrifuged.

The volumes of imitate (500 ml) and other initial solutions for experiments were chosen taking into account product sampling for analysis, and a minimal amount of solution necessary to fill electrochemical cells (50 ml). Technical difficulties connected with the necessity to process large volumes of solutions in separating funnels did not allow carrying out ex-

traction operations at optimal temperature (in the 2nd cycle, elevated temperature is optimal for solvent extraction), phase volume ratio and duration of mixing. The volume of washing solutions was increased to provide efficient washing of large internal surface of separating funnels; the volume of strip solution in the 1st cycle was increased taking into account minimal volume necessary for filling electrolyzer. To compensate a decrease in the rate of heterogeneous processes due to low temperature (295–298 K) and insufficient intensity of mixing large volumes of phases in separating funnels by manual shaking, mixing time was also increased substantially, though under optimal conditions several seconds and minutes are sufficient for quantitative recovery in the 1st and the 2nd cycles, respectively.

Electroextraction of palladium from ammonia strip liquor of the 1st solvent extraction cycle in experiments B and C (see below) was carried out in two stages. At the first stage, the main amount of palladium was deposited as a metal on a flat titanium cathode without mixing the electrolyte at the current density of  $500 \text{ A/m}^2$ ; at the second stage the residual amount of palladium was recovered on volu-

minous porous carbon fibre cathode (graphitized VINN-250 material) with the solution flowing through it with the help of set-up described in [12]. Overall current density was  $2000 \text{ A/m}^2$ . In experiment A, electroextraction was carried out in one stage using carbon fibre cathode. The anodic dissolution of palladium from titanium and carbon fibre electrode (CFE) was performed in a 4 M HCl aqueous solution at the current density of  $500\text{--}1000 \text{ A/m}^2$ .

Concentrations of elements in solutions were determined by atomic absorption with HITACHI Z-8000 instrument in flame or in graphite atomizer. In order to establish detection limit under the experimental conditions for each operation, blank experiments were carried out using the corresponding solutions in which Pd, Ag, Te, Se and Sb were absent.

## RESULTS AND DISCUSSION

Experiment flow sheet is shown in Fig. 1. The movement of palladium over sequential stages of the process is shown in bold arrows. The products of stages which were analysed are marked with numbers in circles. The flow

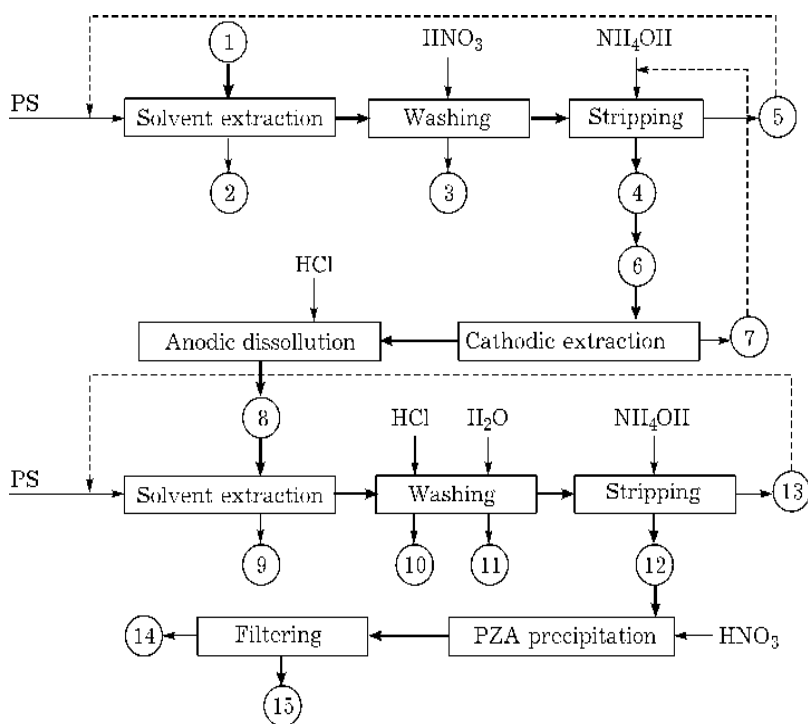


Fig. 1. Flow sheet of the experiment.

sheet includes two solvent extraction cycles. Both cycles include solvent extraction of palladium with petroleum sulphides, washing the extracts with aqueous solutions of acids and palladium stripping with aqueous ammonia solutions. The first cycle imitates palladium recovery from HLW and served to separate palladium from the major part of accompanying elements except silver. The goal of the second cycle is fine separation of palladium from silver. This is achieved by solvent extraction affining of palladium from hydrochloric medium from which silver is not extracted [10]. To pass from the ammonia strip liquor containing palladium with silver admixture, which is the final product of the 1st cycle, to the hydrochloric solution which is initial for the second cycle, electrochemical operations of the joint deposition of palladium and silver in the form of metals on cathode followed by anodic dissolution of these metals in aqueous HCl solution are used. At the final stage, purified palladium is recovered from the strip product of the 2nd cycle in the form of polycrystalline PZA precipitate.

#### *Characteristics of the major operations*

Three experiments (A, B, C) were carried out using different initial model solutions; the experiments included operations of the two solvent extraction cycles, electrochemical cycle and PZA precipitation. The results of experiments are shown in Table 1. Numbers of products in the Table coincide with those in the Fig. 1, while sign "<" (less) indicates that the concentration of an element in the product is below the given value of the blank experiment for this element.

The first solvent extraction cycle consists of solvent extraction, washing and stripping of palladium; these operations are carried out at one step each.

1. Palladium solvent extraction from the model nitrate-nitrite solution with a 0.3 M solution of PS in triethyl benzene at  $r = 0.1$  and  $\tau = 1$  min provides the recovery of 99.8–100 % of palladium, 58–63 % of silver with 10-fold concentrating, and almost complete separation of the admixtures of tellurium, selenium and antimony, which are not detected in all the

subsequent products. A freshly prepared extractant was used in experiment A; extractants regenerated one and two times after A experiment and A, B experiments were used in experiments B and C, respectively.

2. Washing the extract with 0.5 M HNO<sub>3</sub> at  $r = 1$  and  $\tau = 3$  min is accompanied by the removal of 46–52 % of silver without noticeable losses of palladium (<0.01 %).

3. Stripping of 99 % of palladium and 94 % of silver is performed with a 3 M NH<sub>4</sub>OH solution and 10 g/l NH<sub>4</sub>NO<sub>3</sub> at  $r = 1$  and  $\tau = 5$  min. The residual content of these metals in the recovered extractant, taking into account the stoichiometry of extracted complexes of palladium and silver, corresponds to binding not more than 0.001 M of the extractant (0.3 % of the initial PS content). In experiment B, we used stripping solution regenerated once as a result of cathode recovery of palladium in experiment A; freshly prepared stripping solution was used in experiments A and B.

Direct recovery of palladium in the first solvent extraction cycle in experiments A–C was more than 99 % as a mean, according to palladium content in extract, or 99.5–99.7 % according to the total residual content in raffinate, washing water and regenerated extractant.

Electrochemical cycle involves correction of the strip liquor volume to 50 ml, electroextraction of palladium on a flat and /or voluminous porous electrode under cathode polarization from ammonia medium followed by the dissolution of palladium in the aqueous HCl solution under anode polarization of the electrode.

1. In experiments B, C, due to insufficient amount of the strip liquor of the 1st cycle, we added 3 M NH<sub>4</sub>OH and 10 g/l NH<sub>4</sub>NO<sub>3</sub> solutions till the volume of 50 ml, which was necessary to fill the electrolysis cell; this caused dilution of the strip liquor by a factor of 1.1 and 1.7, respectively. The corrected solution is designated as "initial electrolyte".

2. Electroextraction of palladium from the initial electrolyte was carried out in experiments B, C in two stages. At first, the major part of palladium was deposited onto a flat titanium cathode; Pd remaining in solution at a level of 1 g/l was recovered with the help

TABLE 1

The distribution of palladium and accompanying metals over the main products of the flow sheet

No.	Product	Exp.	$C_M$ , mg/l				
			Pd	Ag	Te	Se	Sb
1	Model solution	A	1020	45.5	270	16	14
		B	920	41.6	245	16	12
		C	1070	45.5	—	—	—
2	Raffinate	A	1.7	17	275	16	14
		B	1.0	17.5	245	16	12
		C	0.15	19.2	—	—	—
3	Washing $HNO_3$	A	0.3	110	<0.02	<0.02	<0.02
		B	<0.2	112	<0.02	<0.02	<0.01
		C	<0.1	112	—	—	—
4	Strip liquor	A	9450	94	<0.01	<0.02	<0.02
		B	9500	120	<0.01	<0.02	<0.01
		C	10 600	122	—	—	—
5	Regenerated extractant	A	14	5.5	<0.02	<0.02	<0.02
		B	25	8	<0.02	<0.02	<0.02
		C	32	8	—	—	—
6	Initial electrolyte	A	9450	94	<0.01	<0.02	<0.02
		B	8740	111	<0.01	<0.02	<0.01
		C	6080	70	—	—	—
7	Regenerated strip solution	A	74	1.6	<0.01	<0.02	<0.02
		B	2.3	0.28	<0.01	<0.03	<0.03
		C	32	0.17	<0.01	<0.03	<0.02
8	Initial solution II	A	5200	68	—	<0.04	<0.02
		B	7580	119	—	<0.06	<0.02
		C	5450	74	—	—	—
9	Raffinate	A	103	64	—	—	—
10	Washing HCl	A	0.2	0.5	<0.01	—	—
11	Washing water	A	0.1	0.06	<0.01	—	—
12	Strip liquor	A	42 000	<0.01	<0.05	—	—
13	Regenerated extractant	A	48	<0.02	—	—	—
14	Mother solution	A	80	<0.003	<0.01	—	—
15	PZA precipitate*	A	50.34	$1 \cdot 10^{-3**}$	$<4 \cdot 10^{-4}$	$<4 \cdot 10^{-4}$	$<4 \cdot 10^{-5}$
		B	50.34	$2 \cdot 10^{-5}$	$<4 \cdot 10^{-4}$	$<4 \cdot 10^{-4}$	$<4 \cdot 10^{-5}$
		C	50.34	$1 \cdot 10^{-5}$	$<4 \cdot 10^{-4}$	$<4 \cdot 10^{-4}$	$<4 \cdot 10^{-5}$

\*Content of elements is given in per cent.

\*\*Judging from silver concentration in the ammonia strip liquor No. 12 (&lt;0.01 mg/l), its elevated concentration in PZA precipitate in experiment A can be caused by accidental contamination during the precipitation of PZA and during the preparation of sample for analysis.

of carbon fibre cathode. In experiment A, only CFE was used. The solution obtained as a result of the cathode treatment is designated as “re-generated stripping solution”. The degree of electrochemical recovery of palladium from strip liquor is more than 99 %. Judging from the residual concentration in the regenerated

strip solution (74 (A), 2 (B) and 3 mg/l Pd (C)), two-stage electrolysis is more efficient. This is due to the fact that in the case of high palladium content the pores of CFE get filled with the metal phase, which decreases the working surface area of the electrode and hinders electrolyte circulation through it.

3. Complete dissolution of palladium from titanium and carbon fibre electrodes is achieved under anode polarization in the 4 M HCl aqueous solution resulting in the "initial solution II" for the 2nd solvent extraction cycle. Some decrease in Pd concentration in product No. 8 in comparison with product No. 6 is connected with sampling for analysis and mastering the electrolysis modes, and with subsequent dilution in order to recover the solution volume.

Both electrochemical operations do not involve separation of Pd from Ag.

The second solvent extraction cycle (affining) consists of sequential single-step operations of solvent extraction of palladium, acidic and water washing of the extract, and stripping.

1. Solvent extraction of palladium from the solution based on 4 M HCl is carried out with 0.5 M PS solution in triethyl benzene at  $r = 0.33$  and  $\tau = 1$  h. Extractant regenerated in experiment B was used for experiment C; freshly prepared one was used in experiments A and B. At this stage, 3-fold concentrating and separation of palladium from the major part of silver is achieved. With complete (>98 %) extraction of palladium, more than 94 % of silver remains in raffinate.

2. Washing the extract with 4 M HCl at  $r = 1$  and  $\tau = 10$  min and with water causes the removal of residual silver from the extract; silver content becomes lower than that in the blank experiment.

3. Extraction of more than 99 % of palladium by stripping is performed with 6 M  $\text{NH}_4\text{OH}$  solution at  $r = 3$  and  $\tau = 30$  min. Noticeable residual Pd content (48 mg/l) in the regenerated extractant is due to non-optimal conditions of experiment A, which, however, would not have a decisive importance in multiple cycling use of the extractant.

The precipitation cycle includes obtaining the PZA precipitate, filtering and washing.

1. In order to precipitate palladium in the form of difficultly soluble PZA (*trans*- $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ ), strip liquor from the 2nd cycle is neutralized by 0.5 M  $\text{HNO}_3$  solution to pH 1–2 under moderate cooling (about 283 K). The yield of PZA was measured in experiment A; it was about 98 %.

2. Separation of the precipitate from mother solution was carried out by filtering with a porous glass filter followed by washing with cold water and alcohol. In order to analyse impurities by means of atomic absorption, the mother solution was united with washing water (a 12.5-fold dilution); PZA precipitate dried at a temperature of 373 K was dissolved in HCl under heating. No Te, Se and Sb impurities (less than  $(4-40) \cdot 10^{-5}$  %) were detected in the resulting PZA; Ag content is at the level of  $(1-2) \cdot 10^{-5}$  %.

Mass balance for palladium and silver with respect to all the products of the described flowsheet, calculated for experiment A, agrees at a satisfactory error of 5–7 % with the amount of these metals introduced with the initial imitate solution.

#### *Efficiency of the solvent extraction electrochemical flow sheet*

Laboratory test in three independent experiments provided general confirmation of all the results of preliminary investigations of separate stages [8–10] and showed stable reproducibility of palladium separation factor with respect to the tested impurities. In fact, as early as at the first cycle, at solvent extraction stage Pd is separated from Te, Se and Sb, which remain in raffinate; their content in the products of all subsequent stages is below the level of blank (reference) experiments. As a result, the lower limit of palladium separation factors in the first cycle is estimated as  $S_{\text{Pd,Te}} > 3 \cdot 10^4$ ,  $S_{\text{Pd,Se}} > 2 \cdot 10^3$  and  $S_{\text{Pd,Sb}} > 2 \cdot 10^4$ . After affining solvent extraction cycle, these factors are to increase by several orders of magnitude, but they cannot be measured due to limited sensitivity of the analysis method.

Fine separation of palladium from silver occurs at the 2nd cycle mainly at the solvent extraction stage, as well as during washing. The concentration of Ag in the solutions at all the subsequent stages is lower than that of the blank experiment. As suggested by good reproducibility of results in experiments B and C, mass concentration of Ag in PZA is  $(1-2) \cdot 10^5$  %. In this case, the through separation of palladium from silver starting from the initial mod-

el solution till the PZA precipitate is  $S_{Pd,Ag} \approx (1-2) 10^5$ . On the basis of the data about the composition of strip liquor of the 2nd cycle, the overall separation factor over the two solvent extraction cycles is close to  $S_{Pd,Ag} \approx 2 10^5$ , that is, no additional separation from silver occurs during PZA precipitation, and during electrochemical operations connecting the solvent extraction cycles.

Special experiments and results obtained by us previously [9] show that separation coefficients ( $\beta_{Pd, M}$ ) for palladium and a number of accompanying elements in HLW (Ru, Rh, Mo, Zr, La, Fe, Ni), which were not investigated in the present work, for solvent extraction with PS from nitrate-nitrite solutions are at a level of  $10^6-10^7$ ; for the recovery from hydrochloric media, they are  $10^6-10^7$  for Ru and Rh,  $10^4-10^5$  for Mo, Zr, Se and Cs.

Under the experimental conditions, no negative action of organic substances on palladium electroextraction and no effect of nitrous acid on the stability of extractant were observed. More detailed investigations concerning these problems will be described in separate communications. The applicability of twice and once regenerated extractant solution and strip solution for further use at the corresponding stages of the process is demonstrated. No worsening of recovery characteristics was observed.

For practical implementation of the flow sheet, extraction operations should be performed in phase counter-flow mode. Under optimal modes, it is possible to use centrifugal extractors with phase contact time not more than 10 s in the 1st cycle, in order to minimize radiation chemical action of highly active HLW on the extractant and diluent; in the 2nd cycle under the conditions of substantial decrease in radiation, it is possible to use devices of the mixer-settler type with phase contact time about 10 min at increased temperature (303–308 K). The products No. 2 and 3 (see Fig. 1) are united into highly active liquid wastes; according to the optimal estimation, their volume exceeds the volume of the initial HLW by only 5 %. These wastes do not contain new components and can be processed further according to the existing technology of HLW processing.

A united solution of products No. 9–11 and 14 is a weakly active liquid waste containing HCl, silver, residual palladium and perhaps traces of some accompanying elements. In principle, it is possible to provide electrochemical additional recovery of Pd and Ag from these wastes, with subsequent return for processing according to the flowsheet; partial recovery of HCl by evaporating the waste and utilization of the residue (investigation of the radiation and chemical stability of the components of the organic phase was planned but has not been performed yet).

## CONCLUSION

Laboratory testing of the solvent extraction flow sheet with model solutions confirmed the main parameters obtained at earlier stages of investigation of separate operations involved in the flow sheet. This is true both for the completeness of palladium recovery and concentrating (through recovery is 97–98 % with 40-fold concentrating), and for the quality of the resulting palladium. The content of all impurities in palladium is determined by the reference experiment and is at a level of  $10^{-5}$  %, therefore, it is necessary to apply nuclear-physical methods to obtain more accurate value of palladium separation factor. This question can be answered only with the help of special experiments with imitate solutions containing radionuclides of main impurities (Ag, Ru, Sb, Se, Te, etc.) with high specific activity, in order to reliably estimate separation factors at a level of  $10^6-10^7$  and higher, or experiments with real HLW. In addition, lengthy pilot tests are necessary in order to reveal the stability of separation factors, selectivity of recovered solutions of extractants and strip solutions and their real losses under multiple application.

The investigation is supported by ISTC project No. 1052–98.

## REFERENCES

- 1 Feasibility of Separation and Utilization of Ruthenium, Rhodium and Palladium from High Level

- Wastes, Technical Reports Series No. 308, IAEA, Vienna, 1989.
- 2 V. S. Shaldaev, *Izvlacheniyе platinovykh metallov pri pererabotke obluchennogo topliva za rubezhom*, TsNIIatominform, Moscow, 1990.
  - 3 M. Kubota, Y. Morita, I. Yamaguchi *et al.*, Proc. 5th Int. Inform. Exch. Meeting, Mol, Belgium, 25–27 November 1998, Actinide and Fission Product Partitioning and Transmutation, EUR 18898 EN, OECD Publications, Paris, 1999, p. 131.
  - 4 M. Hugon (Ed.), *Overview of the EU Research Projects on Partitioning and Transmutation of Long-Lived Radionuclides*, Nuclear Science and Technology, EUR 19614 EN, Office for Official Publications of the European Communities, Luxembourg, 2001.
  - 5 *Platinum 2001, Interim Review*, Johnson Matthey, London, 2001.
  - 6 B. N. Zaytsev, V. A. Korolev, V. P. Popik *et al.*, *Radio-khimiya*, 30 (1988) 411.
  - 7 L. V. Arsenkov, B. S. Zakharkin, K. P. Lunichkina *et al.*, *Atom. energiya*, 72 (1992) 462.
  - 8 V. G. Torgov, V. V. Tatarchuk, I. A. Druzhinina *et al.*, *Ibid.*, 76 (1994) 478.
  - 9 V. G. Torgov, V. V. Tatarchuk, I. A. Druzhinina *et al.*, *Ibid.*, 80 (1996) 267.
  - 10 V. G. Torgov, V. V. Tatarchuk, I. A. Druzhinina *et al.*, *Ibid.*, (2000) 358.
  - 11 K. Fetter, *Elektrochimicheskaya kinetika*, Khimiya, Moscow, 1967, p. 526.
  - 12 V. K. Varentsov, *Intensifikatsiya elektrochimicheskikh protsessov*, Nauka, Moscow, 1988, p. 94.