*Chemistry for Sustainable Development* **11** (2003) 547–555

# Solvent Extraction Concentrating of Palladium by Organic Sulphides from Acidic Nitrate-Nitrite Solutions for Increasing Ecological Safety of the Utilization of Spent Nuclear Fuel

VLADIMIR V. TATARCHUK[1], IRINA A. DRUZHININA[1], TAMARA M. KORDA[1], EDOUARD V. RENARD[2] and VLADISLAV G. TORGOV[1]

[1]*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*

[2]*Bochvar All-Russian Research Institute of Inorganic Materials, Ul. Rogova 5, Moscow 123060 (Russia)*

(Received April 4, 2002; in revised form June 17, 2002)

## Abstract

In connection with search for methods to recover fission palladium from highly active liquid wastes from spent nuclear fuel reprocessing, new results were obtained on palladium solvent extraction by organic sulphides from model (in the absence of radiation) nitrate-nitrite solutions containing also a number of accompanying elements (Ag, Ru, Rh, Te, Se, Sb, Mo, Zr, Fe, Ni). It is shown that within the investigated ranges of the acidity of aqueous phase (0.5–4.5 M $HNO_3$), palladium concentration (0.1–0.7 g/l) and temperature (293–313 K) the recommended petroleum sulphides, dioctyl and dihexyl sulphide allow achieving palladium fraction extracted not less than 99 % within time interval not longer than 10 s with 10-fold concentrating in the extract. The separation factors of palladium from other elements except silver are $10^6$–$10^7$. Additional affining is required in order to separate palladium from silver. For palladium stripping, aqueous solutions of ammonia (1–2 mol/l) are proposed, since they provide 99–99.9 % palladium fraction extracted within 3–4 s under 4-fold concentrating. Good parameters of selectivity, fraction extracted and concentrating are due to high specific affinity of palladium to sulphur- (organic sulphides) and nitrogen-containing (ammonia) reagents, with high lability of Pd(II) complexes and the related irreversibility of coordination chemical processes which occur during extraction and stripping. High rate of the processes is achieved by using optimal excess concentrations of organic sulphides and ammonia.

## INTRODUCTION

Solvent extraction from acidic nitrate-nitrite media is of interest in connection with search for efficient methods to recover the fission palladium which is present in the spent nuclear fuel (SNF), along with other platinoids (Ru, Rh). Urgency of this problem is first of all due to the ecological aspects of handling radioactive wastes (vitrification, disposal), because dispersed phases of platinum metals in glassy matrices produce devitrifying effect [1]. In addition, SNF is a promising man-caused source of palladium and rhodium [2, 3].

During solvent extraction processing of SNF after its dissolution in $HNO_3$ (PUREX process), all the soluble fission products including palladium (with the mean content of 0.2–0.5 g/l), and the products of corrosion of construction materials remain in the aqueous tailing solution (high level waste, HLW). Direct investigation of HLW is hindered because of its high activity. Because of this, model systems based on nitric solutions of palladium (II) are used for investigations [4, 5]. Such an imitation seems inadequate, because HLW contains up to 10 mmol/l of radiolytic $HNO_2$ along with 2–3 M $HNO_3$ [6], and palladium forms stable nitro complexes (the equilibrium formation constant for $[Pd(NO_2)_4]^{2-}$ is lg $\beta_4$ ~ 22 [7]). So, the HLW medium should be considered as nitrate-nitrite.

When choosing solvent extraction systems for the fission palladium, one should take into account a number of specific requirements. The extraction of palladium should be first of all rapid (and complete) in order to decrease radiochemical destruction of the extractant and diluent which are used many times; second, it should be selective to provide deep separation of Pd from radionuclides of the accompanying elements during a minimal number of stages with the enrichment factor $10^6$–$10^7$; third, it should lead to many-times concentrating of Pd at all the operations in order to avoid an increase in the amount of secondary liquid waste. As we have shown in [8, 9], these requirements with respect to acidic nitrate-nitrite solutions are met to a substantial extent by organic sulphides, which are widely used in the technology of reprocessing palladium-containing concentrates from chloride media [10]. Unlike chloride (and to a less extent purely nitrate) solutions, the recovery of palladium from which by organic sulphides is hindered kinetically, in the case of nitrate-nitrite solutions quantitative 10-fold concentrating of palladium is achieved under a short-time contact between the phases (10 s) [9]. The goal of the present work was to optimize the main operations of absolute and relative concentrating of palladium by organic sulphides from the imitate nitrate-nitrite solutions.

## EXPERIMENTAL

Chemical reagents of "kh. ch." grade (chemically pure) were used: $HNO_3$, $NH_4OH$, $AgNO_3$ and $La(NO_3)_2$; $H_2MoO_4 \cdot H_2O$ was obtained from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ [11]; $RhCl_3 \cdot 4H_2O$ and $ZrO_2$ of "ch." grade (pure), metal Pd (99.9 %), Sb (Su-000), Se ("os. ch." 22-4 – specially pure), and Te (TV-4). Extractants were di-*n*-hexyl sulphide (DHS), di-*n*-octyl sulphide (DOS), benzyl-*n*-octyl sulphide (BOS) "ch." (pure) and concentrate of petroleum sulphides (PS), 10 % sulphide sulphur, distillation range 507–633 K, extracted from sulphurous petroleum with 86 % $H_2SO_4$. Diluent for the extractants was technical-grade triethyl benzene (TEB) with isomer mixture content of 98 %.

Standard solutions of elements on the basis of $HNO_3$ were prepared as follows. Weighed portions of metals were dissolved in concentrated (Pd and Sb) or 1 : 1 diluted (Fe, Ni, Se and Te) $HNO_3$. The solution of nitrosoruthenium nitrates was prepared from $Na_2[RuNO(NO_2)_4OH]$ complex (synthesized according to the known procedure [12]) by boiling in 8 M $HNO_3$ for 1 h; the solution was evaporated till humid salts and dissolved in 3 M $HNO_3$. The solution of rhodium was obtained from $RhI_3$ (deposited from rhodium chloride solution by adding NaI) by treating it with a mixture of concentrated $HNO_3$ and $H_2O_2$ under boiling till complete removal of iodine and decomposition of hydrogen peroxide [13], the solution was evaporated and the residue was transferred into 3 M $HNO_3$. In the case of zirconium, $ZrO_2$ powder was alloyed with NaOH in excess, the cake was leached with water, the hydrolytic $Zr(OH)_4$ precipitate was separated, multiply washed with water, and dissolved in 3 M $HNO_3$.

In order to make nitrate-nitrite medium, the aqueous phases prepared on the basis of standard solutions of elements or their mixtures were nitrated before extraction; nitration was performed with nitrogen oxides till the establishment of constant efficient redox potential of the solution ($E_{\text{eff}}$). This meant achievement of steady $HNO_2$ concentration, which was estimated, on the basis of calibration for $E_{\text{eff}}$ with nitric solutions of $NaNO_2$ [14], to be at the level of $10^{-2}$ mol/l for the solutions based on 3 M $HNO_3$. Concentrations of elements in the initial aqueous phases were close to their calculated concentrations in typical HLW.

Solvent extraction was performed in tubes mixing phases due to intensive hand agitation during the time t at the given phase volume ratio (*r*). The dynamics of extraction and stripping was investigated using a glass thermostated cylindrical reactor equipped with a turbine mixer ($\omega$ ~ 40 $s^{-1}$) and reflective edges to prevent the formation of hydrodynamic cone. Concentration of the major part of elements in phases was determined by atomic absorption with HITACHI Z-8000 instrument in flame

TABLE 1

Dynamics of palladium solvent extraction with DOS and PS solutions in triethyl benzene from nitrate-nitrite solutions based on 3 M $HNO_3$ ($T$ = 298 K, $r$ = 0.1)

| $\tau$, s | $[Pd]_w^\tau$, mg/l | $E_{Pd}$, % | $\tau$, s | , mg/l | $E_{Pd}$, % |
|---|---|---|---|---|---|
| *0.1 M DOS,* $C_{Pd}$ *= 95 mg/l* | | | | | |
| 6 | 0.28 | 99.7 | 80 | 0.03 | 99.97 |
| 14 | 0.23 | 99.8 | 600 | 0.03 | 99.97 |
| 31 | 0.04 | 99.96 | | | |
| *0.1 M DOS,* $C_{Pd}$ *= 200 mg/l* | | | | | |
| 4 | 9.3 | 95.4 | 61 | <0.01 | 100 |
| 11 | 0.27 | 99.9 | 600 | <0.01 | 100 |
| 25 | 0.01 | 100 | 780 | <0.01 | 100 |
| *0.1 M DOS,* $C_{Pd}$ *= 418 mg/l* | | | | | |
| 4 | 63 | 84.9 | 72 | 0.08 | 99.98 |
| 12 | 20 | 99.5 | 420 | 0.04 | 99.99 |
| 25 | 0.80 | 99.8 | 600 | 0.08 | 99.99 |
| *0.1 M DOS,* $C_{Pd}$ *= 628 mg/l* | | | | | |
| 4 | 176 | 72.0 | 60 | 64 | 89.8 |
| 12 | 110 | 82.5 | 300 | 66 | 89.5 |
| 24 | 72 | 88.5 | 600 | 64 | 89.8 |
| *0.3 M DOS,* $C_{Pd}$ *= 207 mg/l* | | | | | |
| 3 | 0.1 | 99.95 | 77 | 0.1 | 99.95 |
| 11 | 0.1 | 99.95 | 300 | 0.08 | 99.96 |
| 26 | 0.1 | 99.95 | 480 | 0.09 | 99.96 |
| *0.3 M DOS,* $C_{Pd}$ *= 398 mg/l* | | | | | |
| 5 | 0.15 | 99.96 | 62 | 0.07 | 99.98 |
| 13 | 0.10 | 99.97 | 300 | 0.08 | 99.98 |
| 26 | 0.08 | 99.98 | 480 | 0.06 | 99.98 |
| *0.3 M DOS,* $C_{Pd}$ *= 656 mg/l* | | | | | |
| 4 | 11.5 | 98.2 | 60 | 0.04 | 99.99 |
| 10 | 0.05 | 99.99 | 300 | 0.06 | 99.99 |
| 22 | 0.05 | 99.99 | 600 | 0.04 | 99.99 |
| *0.3 M PS,* $C_{Pd}$ *= 218 mg/l* | | | | | |
| 4 | 3.4 | 98.4 | 55 | 1.7 | 99.2 |
| 11 | 2.1 | 99.0 | 300 | 1.5 | 99.3 |
| 28 | 2.0 | 99.1 | | | |
| *0.3 M PS,* $C_{Pd}$ *= 425 mg/l* | | | | | |
| 5 | 3.0 | 99.3 | 72 | 2.0 | 99.5 |
| 13 | 2.1 | 99.5 | 303 | 2.2 | 99.5 |
| 28 | 2.0 | 99.5 | 480 | 2.0 | 99.5 |
| *0.3 M PS,* $C_{Pd}$ *= 662 mg/l* | | | | | |
| 4 | 2.5 | 99.6 | 59 | 1.8 | 99.7 |
| 12 | 1.8 | 99.7 | 300 | 2.4 | 99.6 |
| 23 | 1.8 | 99.7 | 480 | 2.0 | 99.7 |

$[Pd]_w^\tau$

or in graphite atomizer, low Zr and La content in organic phase was determined using photometry [15, pp. 148 and 177] after their stripping by arsenazo III solution.

## OPTIMIZATION OF PALLADIUM SOLVENT EXTRACTION CONDITIONS

In order to determine minimal necessary time of contact between the phases for quantitative extraction of palladium, we investigated the dynamics of its solvent extraction using the above-described reactor, which provided the best reproducible results, for DOS and PS solutions as examples within extractant concentration range 0.1–0.3 mol/l in triethyl benzene, palladium concentration 100–700 mg/l and phases contact time 3–600 s. It turned out that 0.3 mol/l solutions of both PS and DOS allow quantitative extraction (>99 %) of palladium for 10-fold concentrating in extract within as short time as 4–6 s (Table 1). Because of this, further investigations were performed with short-time contact ($\tau$ = 10 s) and 10-fold palladium concentrating in extract ($r$ = 0.1). These rapid solvent extraction processes can be conducted in centrifugal extractors applied in atomic industry.

We performed comparison of extractabilities for organic sulphides: DOS, DHS and PS, which are most suitable for the technology from the viewpoint of their physicochemical properties. DOS and DHS, as technical products based on individual dialkyl sylphides, are already used as extractants in the production of palladium from natural raw material. Unlike them, PS is new for technology as an extractant, though it has won wide application in solvent extraction instrumental methods of determination of gold and platinum metals in natural and technological samples [16]. Petroleum sulphides are a concentrate of mixture of natural organic sulphides isolated from medium distillation fractions of high-sulphur petroleum, which include mainly alkylthia cyclanes (of mono-, di- and tricyclic structure) and dialkyl sulphides [17].

Preliminary experiments demonstrated that the solvent extraction of Pd(II) from nitrate-nitrite solutions in the case of excess of extractant (L) proceeds in fact irreversibly (the fraction extracted $E_{\mathrm{Pd}} \to 100$ %), so it is impossible to determine equilibrium palladium distribution ratio ($D_{\mathrm{Pd}}$). Comparison between non-equilibrium ($\tau$ = 10 s) data on palladium solvent extraction, obtained within a wide range of the concentrations of $HNO_3$ (0.5–4.5 mol/l) and extractants (0.1–0.6 mol/l), allows us to conclude that generally the nature of L does not play any substantial role in achieving completeness of palladium extraction (Figs. 1 and 2). In spite of some differences in extraction with changed conditions for dialkyl sulphides and PS with $C_{\mathrm{L}} \geq 0.3$ mol/l, efficient $^*$ is at a level of $10^3$ and higher.

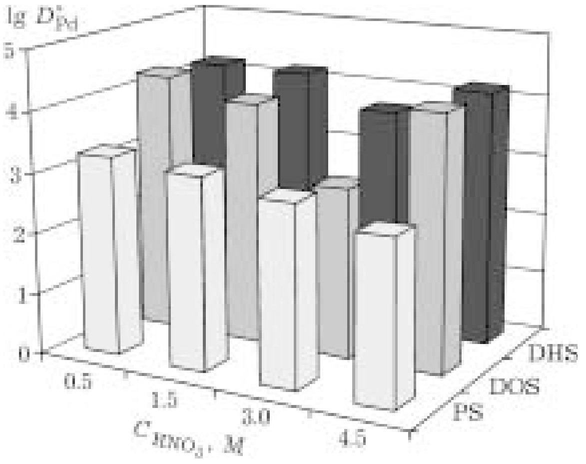

Fig. 1. Effect of acidity of nitrate-nitrite solution on the solvent extraction of Pd(II) with the solutions (0.3 mol/l) of DOS, DHS and PS in triethyl benzene. $C_{\mathrm{Pd}}$ ~ 0.2 g/l, $T$ ~ 298 K, $\tau$ = 10 s, $r$ = 0.1.

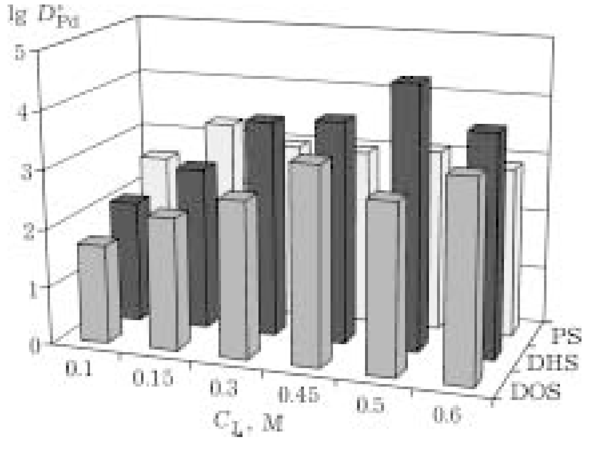

Fig. 2. Effect of extractant concentration on Pd(II) extraction from nitrate-nitrite solutions, based on 3 M $HNO_3$, with the solutions of DOS, DHS and PS in triethyl benzene. $C_{\mathrm{Pd}}$ ~ 0.2 g/l, $T$ ~ 298 K, $\tau$ = 10 s, $r$ = 0.1.

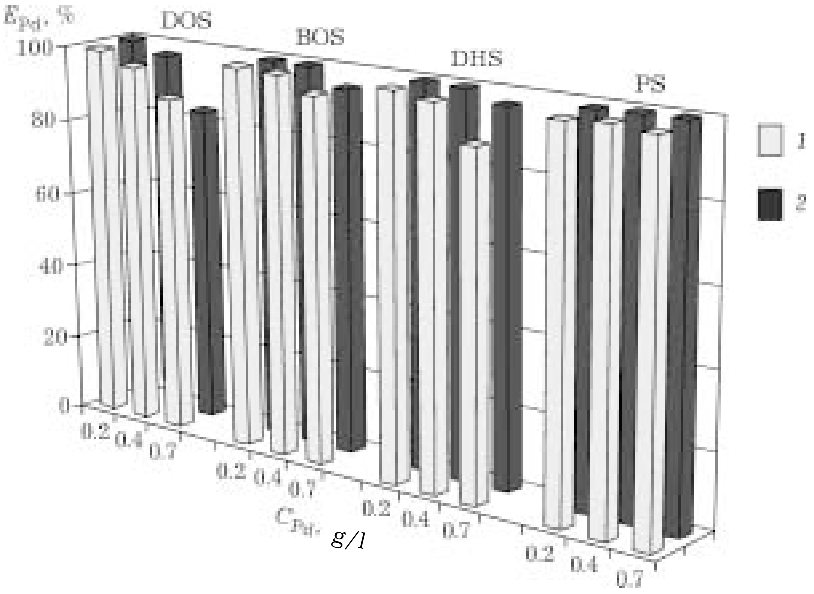

Fig. 3. Solvent extraction of palladium with 0.3 mol/l solutions of DOS, BOS, DHS and PS in triethyl benzene from nitrate-nitrite solutions based on 3 M $HNO_3$. *T*, K: ~ 298 (*1*) and 313 (*2*); $\tau$ = 10 s, *r* = 0.1.

It is evident that high fraction extracted within a short time of phases contact requires relatively high rate of extraction. With other conditions kept constant, a definite excess of extractant is necessary to provide such a rate: $C_L r > C_{Pd}$ ($C_L$ and $C_{Pd}$ are analytical concentrations of extractant and palladium). The data shown in Fig. 2 provide an evidence that for $C_{Pd}$ ~ 2 mmol/l optimal result is achieved when extractant concentration $C_L$ = 0.3 mol/l is used (approximately seven-fold excess over stoichiometry), because its further increase does not cause any substantial increase of extraction. However, with a decrease in the excess of extractant due to an increase of $C_{Pd}$ > 5 mmol/l, a trend for decrease in fraction extracted is observed (Fig. 3). This effect is most vividly expressed for dialkyl sulphides, especially for DOS, and is likely to be due to higher solvation extent for sulphides with large hydrocarbon radicals. Petroleum sulphides in all the cases extract palladium not less than by 99 %. Variation of temperature (298 and 313 K) has no substantial effect on palladium extraction within 10 s (see Fig. 3), since this time is sufficient for equally high fraction extracted at both temperature. In general, palladium solvent extraction with sulphides from nitrate-nitrite solutions occurs more rapidly than from nitrate [18] and chloride [19] media.

## SELECTIVITY OF PALLADIUM SOLVENT EXTRACTION

High selectivity of dialkyl sulphides and PS with respect to palladium and a limited number of other precious metals is well known for the case of extraction from chloride and nitrate media [20]. In particular, only Ag(I) is extracted together with palladium from nitric solutions. However, the data on solvent extraction of metals, except Ag, Rh, Ru and Sb [8, 9] from nitrate-nitrite media are absent from literature. Because of the complicated elemental composition of HLW, we chose several groups of elements most unfavourable for selective concentrating of palladium and its deep purification. The first group includes precious metals (Ag is extracted with organic sulphides from nitric media together with Pd, whereas Ru and Rh are group analogs in the Periodic Table and are poorly extracted from chloride media due to inertness of their complexes). The second group is represented by the elements which are fission products (Mo, Zr, Sb, lanthanoids) and products of corrosion of construction materials (Fe, Ni). These macrocomponents of HLW (about 1 g/l and more) can affect the degree of palladium extraction. The possibility of contamination of extracts by the salts of these metals also cannot be excluded, along with precipitation, resulting from hydrolysis

TABLE 2

Distribution ratios and separation factors for metals solvent extraction from individual nitrate-nitrite solutions based on 3 M $HNO_3$ (I) and from model mixtures (II)

| M | $C_M$, mg/l | | lg $D^*_M$ | | lg $\beta_{Pd,M}$ | |
|---|---|---|---|---|---|---|
| | I | II | I | II | I | II |
| Pd | 176 | 178 | 3.0 | 2.9 | – | – |
| Ag | 100 | 148 | 1.8 | 1.8 | 1.1 | 1.1 |
| Ru | 161 | 165 | −3.5 | <−2.4 | 6.5 | >5.3 |
| Rh | 230 | 195 | −3.4 | <−3.5 | 6.3 | >6.4 |
| Pd | 195 | 189 | 3.0(2.8)$^a$ | 2.9(3.2)$^a$ | – | – |
| Sb | – | 12.5 | – | <−3.2(<−3.2)$^a$ | – | >6.1(>6.3)$^a$ |
| Pd | – | 920 | – | 3.96 | – | – |
| Te | – | 245 | – | <−4.1 | – | >8.0 |
| Se | – | 16 | – | <−2.9 | – | >6.9 |
| Sb | – | 12 | – | <−3.1 | – | >7.0 |
| Pd | – | 200 | – | 2.9(3.2)$^a$ | – | – |
| Fe | – | 1400 | – | −4.5(−4.7)$^a$ | – | 7.4(7.9)$^a$ |
| Pd | – | 200 | – | 3.0(3.2)$^a$ | – | – |
| Ni | – | 230 | – | <−4.0(<−4.0)$^a$ | – | >7.1(7.2)$^a$ |
| Pd | 440 | 440 | 3.4 | 3.4 | – | – |
| Mo | 1500 | 1500 | −3.0 | – | 6.4 | – |
| Zr | 2200 | 2200 | <−4.0 | – | >7.3 | – |
| La | 2500 | 2500 | <−3.3 | – | >6.7 | – |

*Note.* Diluent was TEB, L = PS, $C_L$ = 0.3 mol/l, $T \approx 293$ K, $\tau = 10$ s, $r = 0.1$.
$^a$Extraction with 0.3 M DOS.

and polymerization in the organic phase, for example in the case of antimony. The third group includes Se and Te which are not extracted from chloride media with organic sulphides but generally can be extracted with aromatic and unsaturated components of technological diluents and extractants (PS) in the form of molecular and organometallic compounds.

Efficient metal distribution ratio for the cases of separate and joint presence of palladium and other elements are compared in Table 2. On this basis, we estimated separation factors $\beta_{Pd,M} = {}^{*} / {}^{*}$. The results confirm high selectivity of organic sulphides for the solvent extraction of Pd from nitrate-nitrite media. The separation factors for palladium from all the elements except silver are $10^6$–$10^7$. The mutual effect of elements on extraction and separation are absent. Petroleum sulphides do not differ from DOS in the selectivity of palladium extraction. As we have shown previously, deep purification from silver is achieved by additional solvent extraction affining of palladium, which is performed in chloride medium using the same dialkyl sulphides and PS [21].

## PALLADIUM STRIPPING

For palladium stripping in different systems, aqueous solutions of ammonia, ammonium thiocyanate and thiocarbamide are recommended [5, 22, 23]. Tests of the indicated solutions and some other (NaOH, $Na_2CO_3$, $NH_4HCO_3$, $(NH_4)_2C_2O_4$, $(NH_2)_2CO$) demonstrated that in nitrate-nitrite system the recovery of palladium into strip liquor above 99 % is achieved by using 1 mol/l solutions of $NH_4OH$, $NH_4HCO_3$ and $(NH_2)_2CS$. In the case of thiocarbamide strip liquor and weak acidity (0.1 M $HNO_3$), instability of the solution was observed; precipitate was gradually formed. Low stability of palladium complexes with thiocarbamide in aque-

TABLE 3

Dynamics of palladium stripping with aqueous solutions of reagents (Z) from sulphide extracts (diluent: TEB, $C_L$ = 0.3 mol/l, $T \approx 298$ K)

| L | Z | $C_Z$, mol/l | $r$ | $C_{Pd}$, g/l | $\tau$, s | , mg/l | $E_{Pd}$, % |
|---|---|---|---|---|---|---|---|
| DOS | $NH_4OH$ | 1 | 4 | 5.40 | 4 | 5.5 | 99.9 |
| | | | | | 12 | 5.5 | 99.9 |
| | | | | | 23 | 6.0 | 99.9 |
| | | | | | 60 | 4.2 | 99.9 |
| | | | | | 300 | 4.3 | 99.9 |
| DOS | $NH_4OH$ | 2 | 8 | 5.40 | 3 | 6.2 | 99.9 |
| | | | | | 11 | 5.0 | 99.9 |
| | | | | | 24 | 6.5 | 99.9 |
| | | | | | 60 | 4.8 | 99.9 |
| | | | | | 300 | 5.6 | 99.9 |
| PS | $NH_4OH$ | 1 | 4 | 4.96 | 4 | 45 | 99.1 |
| | | | | | 17 | 34 | 99.3 |
| | | | | | 33 | 33 | 99.3 |
| | | | | | 58 | 34 | 99.3 |
| | | | | | 300 | 35 | 99.3 |
| PS | $NH_4OH$ | 2 | 8 | 4.38 | 4 | 40 | 99.1 |
| | | | | | 12 | 34 | 99.2 |
| | | | | | 24 | 34 | 99.2 |
| | | | | | 64 | 47 | 98.9 |
| | | | | | 310 | 48 | 98.9 |
| PS | $NH_4HCO_3$ | 1 | 4 | 5.44 | 5 | 2220 | 59.2 |
| | | | | | 16 | 2120 | 61.0 |
| | | | | | 38 | 1600 | 70.6 |
| | | | | | 62 | 1100 | 79.8 |
| | | | | | 300 | 112 | 97.9 |
| PS | $NH_4HCO_3$ | 2 | 8 | 5.34 | 4 | 1700 | 68.2 |
| | | | | | 13 | 1120 | 79.0 |
| | | | | | 26 | 925 | 82.7 |
| | | | | | 62 | 260 | 95.1 |
| | | | | | 330 | 70 | 98.7 |

$[Pd(NH_3)_4]^{+}$

ous solutions has been known long ago [24]. Stripping with other reagents changes from 4 ($(NH_2)_2CO$) to 28 % ($Na_2CO_3$). So, among the investigated stripping agents, the most suitable ones were aqueous solutions of ammonia and ammonium bicarbonate. It should be noted that $NH_4HCO_3$ solutions have not been previously used for palladium stripping.

In order to provide technological compatibility of continuous extraction operations, palladium stripping rate should be not lower than the rate of its preceding solvent extraction. We did not find any data on palladium stripping kinetics in literature. Under the condition of 10-fold palladium concentrating at the stage of its solvent extraction, its concentration in the extract is up to 5 g/l (0.05 M). Since Pd(II) forms with ammonia strong complex cations of composition [25], stripping does not require large excess of the stripping agent. It turned out that diluted 1–2 mol/l solutions of $NH_4OH$ stripp palladium rapidly and efficiently both from DOS and from PS: as early as after 3–4 s fraction extracted is $E_{Pd} > 99$ % (Table 3). Absolute 4–8-fold palladium concentrating in strip liquor is achieved. At the same time, stripping with ammonium bicarbonate proceeds much slower, though for long-time

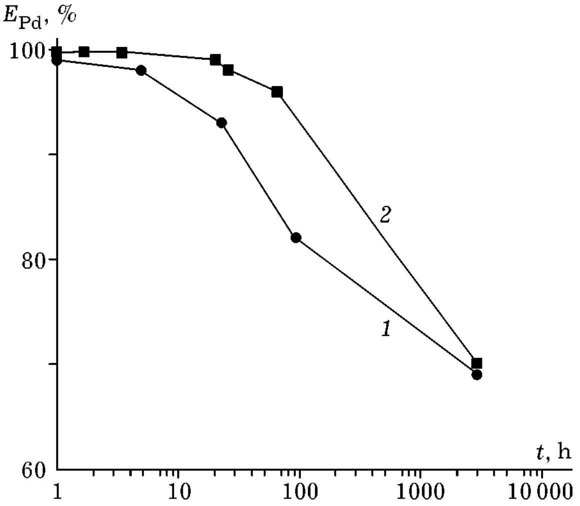

Fig. 4. Effect of ageing of extracts in nitrate (*1*) and nitrate-nitrite (*2*) systems on palladium stripping with the aqueous solution of 6 M $NH_4OH$. Diluent is TEB, L = DOS, $C_L$ = 0.1 mol/l, $T \approx 298$ K, $\tau$ = 1 h, $r$ = 0.5.

phases contact ($\tau > 5$ min) the fraction extracted approaches 99 %. Because of low rate of palladium stripping, the use of $NH_4HCO_3$ is unreasonable in the systems under consideration.

Similarly to palladium, silver forms stable ammines, therefore it is stripped from sulphide extracts together with palladium [9].

It is known that in some cases extracts are prone to ageing, which involves side processes in the organic phase: hydrolysis and polymerization of the compounds to be extracted, as well as reduction-oxidation interactions which decrease the efficiency of stripping. As a rule, ageing occurs relatively slowly and manifests itself during lengthy exposure (for time $t$) of the extracts before stripping, for example, in case of emergency conditions. Tests showed (Fig. 4) that extracts are more stable in nitrate-nitrite systems, since the ageing effect is exhibited for $t > 1$ day, while in nitrate systems stripping decreases as early as for $t > 5$ h. This is the indirect evidence that the composition of extracted compounds is different in the indicated systems.

## EXTRACTED AND STRIPPED PALLADIUM COMPOUNDS

Stoichiometric L/Pd and $NH_3$/Pd ratios for extracted and stripped complexes were determined by means of saturation method after lengthy contact of the organic solutions of extractants and aqueous ammonia solutions with the aqueous solutions and extracts, respectively, which contained obvious excess of palladium. The data presented in Table 4 indicate that these ratios are: L/Pd ≈ 2 and $NH_3$/Pd ≈ 3.8–4. In this case, taking into account the state of palladium in the initial aqueous phase [14] and electroneutrality requirement for the compounds extracted into weakly polar media, Pd(II) is extracted from acidic nitrate-nitrite media most likely in the form of a mixture of complexes $[PdL_2(NO_3)_2]$, $[PdL_2(NO_2)_2]$ and $[PdL_2(NO_2)(NO_3)]$. It is known that $[PdL_2(NO_3)_2]$ [18] (see also Table 4) and $[PdL_2Cl_2]$ [26] are extracted from nitrate and chloride media. For stripping, judging from the fact that $NH_3/Pd \le 4$,

TABLE 4

Loading capacity of the solutions of sulphides and $NH_4OH$ with respect to palladium for its solvent extraction and stripping in nitrate (I) and nitrate-nitrite systems (II)

| System | L | $[Pd]_o$, mol/l | L/Pd | $C_{NH_3}$, mol/l | $[Pd]_w$, mol/l | $NH_3$/Pd |
|---|---|---|---|---|---|---|
| I | DOS | 0.142 ± 0.004 | 2.11 ± 0.06 | – | – | – |
| | PS | 0.150 ± 0.008 | 2.0 ± 0.1 | – | – | – |
| II | DOS | 0.138 ± 0.005 | 2.17 ± 0.09 | 1 | 0.26 ± 0.01 | 3.8 ± 0.2 |
| | | | | 2 | 0.53 ± 0.03 | 3.8 ± 0.2 |
| | | | | 4 | 1.06 ± 0.02 | 3.8 ± 0.1 |
| II | PS | 0.150 ± 0.002 | 2.00 ± 0.02 | 1 | 0.26 ± 0.01 | 3.8 ± 0.1 |
| | | | | 2 | 0.51 ± 0.04 | 3.9 ± 0.3 |
| | | | | 4 | 1.0 ± 0.1 | 4.0 ± 0.5 |

*Note.* Diluent is TEB, $C_L$ = 0.3 mol/l, $T \approx 293$ K (errors were estimated on the basis of variation ranges when determining palladium concentrations in 2–3 parallel samples of the solutions to be analyzed).

along with the basic $[Pd(NH_3)_4]^{2+}$ form, the formation of $[Pd(NH_3)_3H_2O)]^{2+}$ or $[Pd(NH_3)_3X]^+$ where X = is possible under the conditions of saturation (low equilibrium concentration of $NH_3$), because is a stronger ligand for $Pd^{2+}$ than [7, 14, 27].

## CONCLUSIONS

The described results comprise the scientific basis for substantiation of the technological operations for solvent extraction concentrating of palladium from HLW. The entire set of operations is likely to include solvent extraction, scrubbing the extract with diluted $HNO_3$ and stripping of palladium with aqueous solution of ammonia. High efficiency of solvent extraction and stripping, from the viewpoint of both the fraction extracted and selectivity, is provided by irreversibility of the coordination chemical processes involving high specific affinity of palladium to sulphur- (organic sulphides) and nitrogen-containing (ammonia) reagents at high lability of Pd(II) complexes, compared to kinetically inert compounds of other chalco- and nitrophilic platinum metals: Rh(III) and Ru(III, IV). At the stages of solvent extraction and scrubbing, high degree of palladium separation from all the accompanying non-precious elements and platinum metals (Rh and Ru), as well as from the major part of silver can be achieved [9]. The product of this extraction cycle is the ammonia solution of palladium with silver admixture, in which the 40-fold concentrating of palladium is possible (10-fold during solvent extraction and 4-fold during stripping). A through recovery of palladium into the product of extraction cycle is not less than 98 % (for solvent extraction and stripping, 99 % each). Under optimal conditions, in order to achieve quantitative recovery of palladium at all the operations of the cycle, it is sufficient to use one step with phase contact time of several seconds. To perform these operations, we may recommend centrifugal extractors which are standard in radiochemical technology. Additional palladium affining is necessary for deep purification from silver.

$NO_2^-$

## Acknowledgement

The work has been performed within the ISTC 1052–98 project.

## REFERENCES

1 A. V. Demin, M. I. Fedorova, Yu. I. Matyunin, *Atom. energiya,* 80 (1996) 179.

2 Feasibility of Separation and Utilization of Ruthenium, Rhodium and Palladium from High Level Wastes, Technical Reports Series No. 308, IAEA, Vienna, 1989.

3 V. S. Shaldaev, Izvlecheniye platinovykh metallov pri pererabotke obluchennogo topliva za rubezhom, TsNII Atominform, Moscow, 1990.

4 L. V. Arseenkov, B. S. Zakharkin, K. P. Lunichkina *et al.*, *Atom. energiya,* 72 (1992) 462.

5 G. H. Rizvi, J. N. Mathur, M. S. Murali, R. H. Iyer, *Sep. Sci. Technol.*, 31 (1996) 1805.

6 M. V. Vladimirova, S. V. Kalinina, Yu. I. Savelyev, *Khimiya vysokikh energiy,* 6 (1969) 526.

7 I. P. Alimarin, V. I. Shlenskaya, A. A. Biryukov *et al., Izv. SO AN SSSR. Ser. khim. nauk,* 4 (1970) 3.

8 V. G. Torgov, V. V. Tatarchuk, I. A. Druzhinina *et al.*, *Atom. energiya,* 76 (1994) 478.

9 V. G. Torgov, V. V. Tatarchuk, I. A. Druzhinina *et al.*, *Ibid.,* 80 (1996) 267.

10 M. A. Meretukov, A. M. Orlov, Metallurgiya blagorodnykh metallov (zarubezhny opyt), Metallurgiya, Moscow, 1991, p. 360.

11 N. G. Klyuchnikov, Rukovodstvo po neorganicheskomu sintezu, Khimiya, Moscow, 1965, p. 251.

12 N. M. Sinitsyn, V. N. Pichkov, O. E. Zvyagintsev, *Radiokhimiya,* 8 (1966) 545.

13 W. C. Brienza, Pat. 4983372 USA.

14 V. V. Tatarchuk, V. I. Belevantsev, I. A. Druzhinina, *Zhurn. neorgan. khimii,* 47 (2002) 1209.

15 S. B. Savvin, Arsenazo III, Atomizdat, Moscow, 1966.

16 V. G. Torgov, T. M. Korda, L. A. Terentyeva, in: Blagorodnye metally: khimiya i analiz, in V. G. Torgov, F. A. Kuznetsov (Eds.), izd. INKh SO AN SSSR, Novosibirsk, 1989, p. 4.

17 Ya. B. Chertkov, V. G. Spirkin, Sernistye i kislorodnye soyedineniya neftyanykh distillatov, Khimiya, Moscow, 1971.

18 V. S. Shmidt, N. A. Shorokhov, S. D. Nikitin, *Zhurn. neorgan. khimii,* 31 (1986) 998.

19 S. J. Al-Bazi, H. Freiser, *Solv. Extr. Ion Exch.*, 5 (1987) 265.

20 V. G. Torgov, *Isotopenpraxis*, 20 (1984) 352.

21 V. G. Torgov, V. V. Tatarchuk, I. A. Druzhinina *et al.*, *Atom. energiya,* 88 (2000) 358.

22 K. Kirishima, H. Shibayama, H. Nakahira, *et al.*, Proc. Intern. Conf. Nucl. Waste Manag. Envir. Rem., vol. 1, Prague, 1983, p. 667.

23 J. Prihoda, M. Kyrs, *Jad. Energ.*, 28 (1982) 127.

24 S. I. Ginzburg, I. L. Ezerskaya, I. V. Prokofyeva *et al.*, Analiticheskaya khimiya platinovykh metallov, Nauka, Moscow, 1972.

25 L. Rasmussen, K. Jorgensen, *Acta Chem. Scand.*, 22 (1968) 2313.

26 V. G. Torgov, V. V. Tatarchuk, *Zhurn. neorgan. khimii,* 41 (1996) 1402.

27 V. S. Shmidt, N. A. Shorokhov, *Atom. energiya,* 64 (1988) 103.