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Extraction of Fission Ruthenium in the Form of Heterometallic Complexes from Nitrate-Nitrite Solutions

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Abstract

The effects of nonferrous metals on extraction of the ruthenium form $[RuNO(NO_2)_4OH]^{2-}$ (An^{2-}), prevailing in weak acid solutions, by mixed-radical phosphine oxide (L) are investigated from the viewpoint of extraction of fission ruthenium. The syneric effect has been found to be high ($n \cdot 10^3$) because $[RuNO(NO_2)_4OHML_m]$ heterometallic complexes are formed (M = Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}; $m = 1–3$). Extraction constants have been determined for the complexes, and conditions of their formation and extraction from nitrate solutions have been optimized. An approach to ruthenium extraction by nitration the starting solution to convert various forms of ruthenium into the An^{2-} form and by extracting Ru in the form of Ru/M complexes has been verified experimentally. The suggested method for extracting ruthenium was tested on real high-level waste.

INTRODUCTION

Fission ruthenium belongs to the group of the most radiation-hazardous fission products of nuclear fuel wastes. When major actinides are separated from nitric acid solutions of nuclear fuel wastes [1] or when minor actinides are extracted from aqueous tail solutions using trialkyl and carbamoyl phosphine oxides [2, 3], ruthenium is almost completely preserved in the high-level wastes (HLW). Meanwhile, the ecological aspects of high-level waste management necessitate preliminary separation of ruthenium in order to avoid radioactive release of volatile RuO_4 in the course of HLW vitrification [1] and decomposition of the glass-like matrix in the presence of disperse phases of fission platinides (Ru, Rh, Pd) [4]. The difficulties of ruthenium separation from HLW by extraction or by other methods (sorption, coprecipitation) are explained by the numerous forms in which ruthenium is distributed in nitric acid solutions and also by the kinetic inertness of these forms. According to [1], HLW solutions are nitrate (2–3 M HNO_3) and nitrite (0.01 M HNO_2) solutions where nitrosonitrate and nitrosonitro forms, as well as mixed forms, are the major groups of ruthenium complexes [5, 6]. Therefore, conversion of various ruthenium forms into the most stable form, prevailing (over 90 % Ru) in weak acid solutions $[RuNO(NO_2)_4OH]^{2-}$ (An^{2-}) by nitration of the starting solution and selective extraction of this form seems to be a promising new approach to ruthenium separation. In particular, this kind of process is generation of heterometallic complexes of An^{2-} with nonferrous metals during Ru extraction with neutral organophosphorus compounds from the series of alkylphosphates – trialkyl phosphine oxides [7, 8].

For this process, we discovered a high synergic effect for ruthenium, which can be of interest from the viewpoint of coextraction of actinides and ruthenium from HLW [9, 10].

The aim of the present work is to develop an extraction procedure for separating fission ruthenium using mixed-radical phosphine oxide based on the novel synergic effect and to verify this procedure on solutions of real HLW.

EXPERIMENTAL

The copper, cobalt, nickel, zinc, and sodium nitrates used in this work were of analytical grade. The ruthenium complex $Na_2[RuNO(NO_2)_4OH] \cdot 2H_2O$ was synthesized by the procedure of [11]. Solutions of commercial mixed-radical phosphine oxide $(C_5H_{11})(C_{7-9}H_{15-19})_2PO$ (POR) in 1,2-dichloroethane (DCE), *n*-hexane (HX), and *m*-nitro-(trifluoromethylbenzene) (F_3) were prepared by the exact weight. DCE was preliminarily washed with a 5 % NaOH solution and distilled; HX was treated with concentrated H_2SO_4, washed with water, dried, and distilled. The commercial F_3 solvent (Rhodia, France) was treated with 5 % NaOH, 5 % HNO_3, and water and dried (three such sequences). The solid extractant (solex) based on POR was obtained by impregnating the granular divinylbenzene-styrene matrix with an extractant at 50 °C. The matrix was preliminarily kept in vacuum to remove air, the mass fraction of POR being 50 % after impregnation.

Extraction was carried out from the freshly prepared solutions of $Na_2[RuNO(NO_2)_4OH] \cdot 2H_2O$ in 2 M $NaNO_3$ (to imitate the macro composition after neutralization of the model solution with 2 M $NaNO_3$). Equal volumes of the aqueous and organic phases were stirred at room temperature for 30 min in the presence of nonferrous metals (to avoid the lowering effect of An^{2-} aquation processes) until the maximal values of D_{Ru} were reached. The ruthenium content was determined by analyzing the alkylaniline extract by the atomic absorption method on a Hitachi Z-8000 spectrometer with Zeeman correction of background in flame or in an graphite atomizer. The nitric acid solutions and the re-extracts (obtained after re-extraction of Ru with a NaOH solution) were previously transformed into chlorides, and ruthenium was extracted with a toluene solution of alkylaniline. The balance error was up to ±5 % for ruthenium. In both phases, the contents of nonferrous metals were determined trilonometrically using murexide and eriochrome black T as indicators. For processing the extraction data, the initial concentrations of the components C_0^i and their equilibrium concentrations in the organic $\bar{C}_i$ and aqueous C_i phases were evaluated. The approximate values of extraction constants were estimated graphically and refined by iteration.

For test experiments in a solution – solex system, we used a HLW sample (Mayak concern, Ozersk, Russia) that contained a solution of 1.8 M HNO_3, 160 mg/l Pd, 50 mg/l Rh, 200 mg/l Ru, and radionuclides (Bq/l): ^{241}Am ($4.0 \cdot 10^9$), $^{154,155}Eu$ ($6.8 \cdot 10^9$), ^{125}Sb ($4.0 \cdot 10^8$), ^{106}Ru ($9.0 \cdot 10^8$), as well as Cs and Sr isotopes, corrosion products (Fe, Cr, Ni), and some other metals [9]. The HLW sample was preliminarily treated by adding the calculated amount of a 2 M $NaNO_2$ solution until solution coloring ceased, and zinc nitrate was added. Ruthenium was extracted under static conditions: solex : HLW = 1 : (10–20), contact time 1 day. For test experiments in a solution-extractant system (40 % POR in F_3), we used a sample (Mining and Chemical Plant, Zheleznogorsk, Russia) [10] containing 1.2 M HNO_3, 50 mg/l Am, and radionuclides (Bq/l): ^{106}Ru ($3.0 \cdot 10^9$), ^{154}Eu ($6.0 \cdot 10^7$), ^{125}Sb ($8.0 \cdot 10^7$), ^{90}Sr ($4.0 \cdot 10^{10}$), ^{137}Cs ($6.0 \cdot 10^8$), *etc.* Before Ru extraction, ZnO (0.106 g) and $NaNO_2$ (0.3 g) were added in sequence to the starting solution (8 ml). The mixture was heated for 10 min on a boiling water bath. An idle run was performed using previously neutralized HLW by adding Na_2CO_3 (0.26 g) to the solution (8 ml). The content of radionuclides in the starting and end solutions was monitored radiometrically (by α- and γ-radiation of the corresponding elements).

RESULTS AND DISCUSSION

Separate extraction of the An^{2-} form and nonferrous metals

During ruthenium extraction with mixed-radical phosphine oxide, which is a coordination

TABLE 1

Synergic effects (S_{Ru}) during An^{2-} extraction with POR solutions in F_3 in the presence of nonferrous metals. Aqueous phase: $NaNO_3$ 2 M, $M(NO_3)_2$ 0.25 M, Ru 6–8 mM

$\bar{C}_{POR}$, mol/l	$D^0_{Ru} \cdot 10$	D^0_{Zn}	$D^0_{Cu} \cdot 10$	$D^0_{Co} \cdot 10^2$	$D^0_{Ni} \cdot 10^2$	$S_{Ru} = D_{Ru}/(D^0_{Ru} + D^0_M)$			
						Zn^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}
0.05	0.0052	0.016	0.0485	0.083	0.018	670	1200	2150	~1000
0.10	0.0244	0.045	0.155	0.228	0.056	1110	890	4200	1100
0.15	0.0393	0.080	0.310	0.364	0.099	1080	860	6140	2640
0.20	0.061	0.116	0.492	0.639	0.148	1200	770	5600	2600
0.30	0.24	0.202	0.811	1.34	0.310	1110	1140	4240	1640

type extractant, the high inertness of the An^{2-} form in ligand substitution reactions showed itself as low values of D^0_{Ru} (Table 1). According to the data of [12], replacement of two NO_2 groups in An^{2-} by two $(C_4H_9)_3PO$ molecules occurs if the extract is heated for prolonged time. The complex of the An^{2-} form being extracted probably also contains two POR molecules, as can be judged from the slope of the bilogarithmic curve $\lg D^0_{Ru} = 1.971 \lg C_{POR} - 0.724$ (Fig. 1). The mononuclear state of the ruthenium complex in the conjugate phases is confirmed by the constancy of $D^0_{Ru} = 0.024 \pm 0.004$ ($P = 0.95$, $f = 8$) at various concentrations of An^{2-} (from 0.001 to 0.04 M) for the 0.3 M POR solution in F_3. The concentration constants of extraction ($K_{0,2} = D^0_{Ru} / C^2_{POR}$) for the 2 M $NaNO_3$ solution are listed in Table 2. The one-charged form, $[RuNO(NO_2)_3(H_2O)OH]^-$ (An^{1-}) [13], is in equilibrium with An^{2-}. After 5 days, accumulation of the former in time due to aquation of An^{2-} leads to D^0_{Ru} which is an order of magnitude higher than that of the freshly prepared solution of An^{2-}. For $(C_8H_{17})_3PO$ (TOPO), it was found that the Na^+ concentration in the organic phase increases symbatically with the ruthenium content in the extract in view of the formation of a solvated ion pair (Na^+An^-). The higher extractability of the An^{1-} form compared to An^{2-} was reported in [7] for TBP, and the presence of an ion pair of this kind in the TBP phase was detected by NMR [13].

The distribution coefficients of nonferrous metals in the absence of ruthenium D^0_M vary from 10^{-3} to 10^{-1} for Zn and Cu and from 10^{-4} to 10^{-2} for Co and Ni (see Table 1) and are

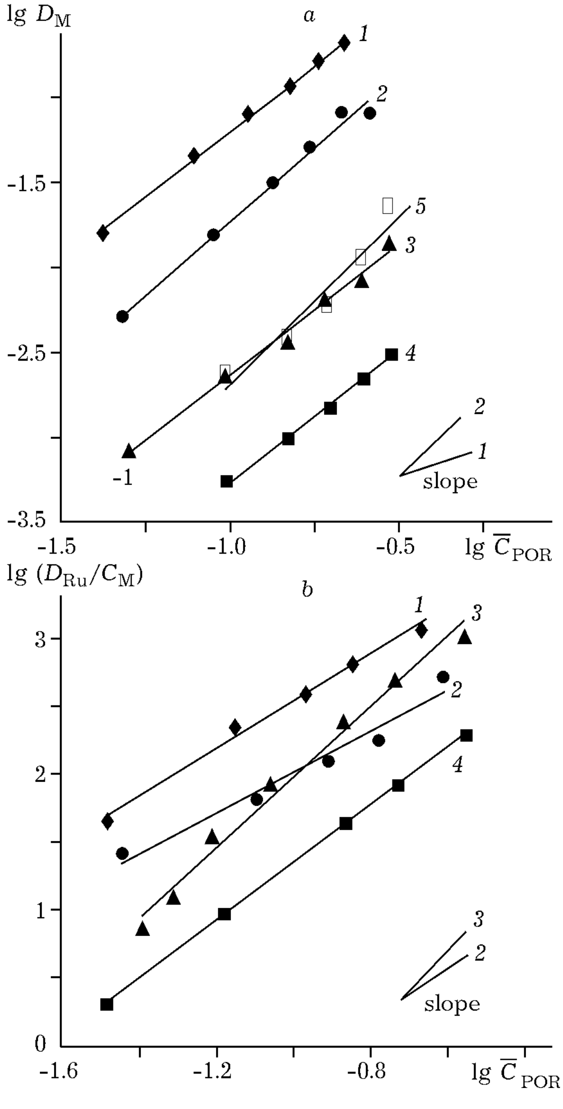

Fig. 1. Determination of the composition of the extracted $M(NO_3)_2$ and An^{2-} (*a*) and Ru/M (*b*) complexes with POR: *1* – Zn^{2+}, *2* – Cu^{2+}, *3* – Co^{2+}, *4* – Ni^{2+}, *5* – An^{2-}. The composition of the aqueous phase: 2 M $NaNO_3$, 0.25 M $M(NO_3)_2$, and 7 mM Ru.

TABLE 2

Composition and extraction constants for nonferrous metal complexes and heterometallic Ru/M complexes with POR in F_3

M^{2+}	$[ML_n(NO_3)_2]$				$[RuNO(NO_2)_4(OH)ML_m]$				
	n	lg $K_{0,1}$	lg $K_{0,2}$	$\sigma_{\pm}^{*}$	m	lg $K_{1,1}$	lg $K_{1,2}$	lg $K_{1,3}$	$\sigma_{\pm}^{*}$
Ni^{2+}	1.57	−3.32	−2.44	0.032	2.12	–	3.22	3.70	0.08
Co^{2+}	1.53	−2.74	−1.78	0.072	2.58	–	3.53	4.88	0.15
Cu^{2+}	1.75	−2.04	−0.84	0.074	1.50	2.47	3.81	–	0.13
Zn^{2+}	1.55	−1.42	−0.35	0.078	1.75	3.01	4.30	–	0.07
Ан^{2-}	1.97	–	−0.56	–	–	–	–	–	–

$^{*}\sigma_{\pm} = \sqrt{U/k-2}$, where $U = \Sigma(C^{exp}/C^{calc} - 1)^2$; k is the number of experimental points.

comparable to D^0_{Ru}. For all metals, the slopes of the corresponding bilogarithmic dependences (see Fig. 1, *a*) are <2, which can be attributed to the presence of complex species with $n = 1$ and 2 in the extract. Table 2 presents the concentration constants of extraction

$$M^{2+} + 2NO_3^- + nL \rightleftarrows \overline{ML_n(NO_3)_2} \qquad (1)$$

for both forms ($K_{0,n} = D^0_M / C^2_{NO_3} C^n_{POR}$). The scatter of the experimental values of D^0_M relative to the values calculated using the above constants was 3–8 %. The dominant forms in the extract (more than 0.1 M POR) are complexes with $n = 2$ (60–80 %), in which, like in TOPO [8], the M^{2+} cations have tetrahedral oxygen surroundings. The values of $K_{0,1}$ and $K_{0,2}$ decrease in the series $Zn^{2+} \geq Cu^{2+} > Co^{2+} > Ni^{2+}$, which coincides with the Irwing – Williams series for the stability constants of metal complexes with oxygen-containing ligands in aqueous solutions [14].

Co-extraction of the An^{2-} form with nonferrous metals

When ruthenium is present together with nonferrous metals (in particular, Zn^{2+}), one can observe a relative increase in D^0_{Ru} for both forms, An^{1-} (by a factor of 7) and An^{2-} (440), which reverses the extractability series: $An^{2-} > An^{1-}$. As can be seen from Table 3, when the concentration of M^{2+} increases from 0 to 0.25 mol/l, D_{Ru} increases from 0.02 to 700 depending on the nature of the solvent for POR (0.3 mol/l). Other conditions being equal, D_{Ru} decreases in the series HX > F_3 > DCE, thus changing antibatically with the solvating ability of the diluent. The sequence showing the effect of nonferrous metals on ruthenium extraction, $Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$, does not coincide with the sequence of M^{2+} hydration energy variation, as was in the case with extraction of ion pairs. Thus under optimum conditions of ruthenium extraction ($C^0_M >> C^0_{Ru}$), the synergic effect (S_{Ru}) is high (n 10^3) for all metals (see Table 1). The value of S_{Ru} is almost independent of POR concentration and is markedly higher for Co^{2+} and Ni^{2+} compared to Zn^{2+} and Cu^{2+} because of the low extractability of Co^{2+} and Ni^{2+} nitrates (see Table 1).

The equilibrium between the mixed Ru/M complexes formed

$$An^{2-} + M^{2+}\ \overline{mL} \rightleftarrows \overline{[AnML_m]} \qquad (2)$$

with an equilibrium constant

$$K_{1,m} = \bar{C}_{Ru}\bar{C}_M/(C_{Ru}C_M C^m_{POR}) \qquad (3)$$

is the key process responsible for the synergic effect.

According to eq. (3), during the formation of Ru/M (1 : 1) complexes, $D_{Ru}/C_M = D_M/C_{Ru}$. As can be seen in Fig. 2, for all nonferrous metals, experimental data fit a single curve with a slope of 1.00 ($r = 0.998$). Furthermore, additional evidence in favor of the formation of the 1 : 1 complexes is provided by D_M, which increases with ruthenium concentration, and by the linear dependence of lg D_M on lg C^0_{Ru} (Fig. 3) with slopes of 0.964 and 1.072 for nickel and zinc, respectively. In the presence

TABLE 3

Extraction of An^{2-} with POR solutions in diluents of nitrate solutions in the presence of nonferrous metals. Concentrations: POR 0.3 M, $NaNO_3$ 2 M, Ru 7–14 mM

M^{2+}	ΔG_{hydr}, kcal/mol	Diluent	D_{Ru} at different metal concentrations, mol/l			
			0.03	0.06	0.12	0.25
Ni^{2+}	−491	F_3	13	20	29	45
		DCE	2.5	4.5	8.8	16
Co^{2+}	−480	F_3	4.0	54	77	97
		DCE	10	21	43	86
Cu^{2+}	−491	F_3	–	86	104	122
		DCE	57	83	102	132
Zn^{2+}	−479	HX	163	300	380	680
		F_3	76	160*	200**	250
		DCE	67	114	180	250

*Zn^{2+} concentration is 0.1 mol/l.
** Zn^{2+} concentration is 0.15 mol/l.

of Zn and Ni, D_{Ru} remains constant (210 ± 30 and 42 ± 7, respectively) in the concentration range 2.5–20 mmol/l Ru, which confirms that the Ru/M complexes (like the starting An^{2-} form) are monomers.

The number of coordinated POR molecules was determined by the dilution method (see Fig. 1, *b*). It was found that the slope of the bilogarithmic dependence (Table 2) are ~2 for Zn^{2+} and Cu^{2+}, and higher than 2 for Co^{2+} and Ni^{2+}; that is, equilibrium takes place for complexes with 1–3 POR molecules. The extraction constants of the Ru/M complexes (see Table 2) determined with allowance for reaction (1) adequately reproduce the phase distribution of ruthenium. The scatter of the experimental values of C_{Ru} relative to the calculated values is 7–15 % for all systems. The contributions of various Ru/M complexes ($\alpha_{1,m}$) and the average number of POR molecules in the complexes $\bar{m} = \sum_{m=1}^{m=3} m\alpha_{1,m}$ were

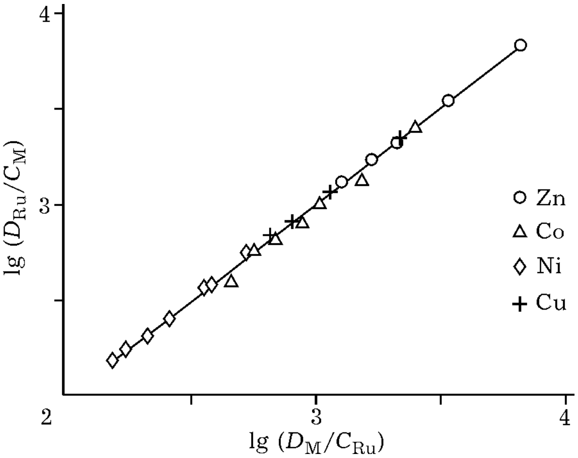

Fig. 2. Determination of the Ru : M ratio in the complexes during ruthenium extraction with a 0.3 M POR solution in F_3. The composition of the aqueous phase: 2 M $NaNO_3$, 0.03–0.25 M $M(NO_3)_2$.

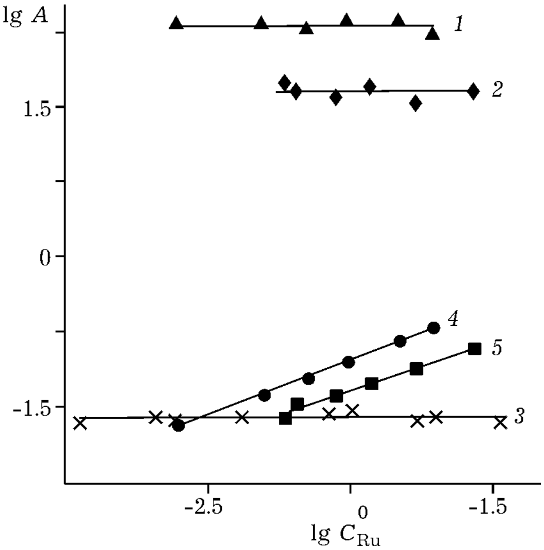

Fig. 3. Effect of An^{2-} concentration in the aqueous phase on extraction of Ru, Zn^{2+}, and Ni^{2+} from nitrate media using the 0.3 M POR solution in F_3 when the elements are present simultaneously (*1*, *2*, *4*, *5*) and when ruthenium is present alone (*3*). lg A: *1* – lg D_{Ru} (Zn); *2* – lg D_{Ru} (Ni); *3* – lg D^0_{Ru} ; *4* – lg D_{Zn}; *5* – lg D_{Ni}. The composition of the aqueous phase: 2 M $NaNO_3$ and 0.25 M $M(NO_3)_2$.

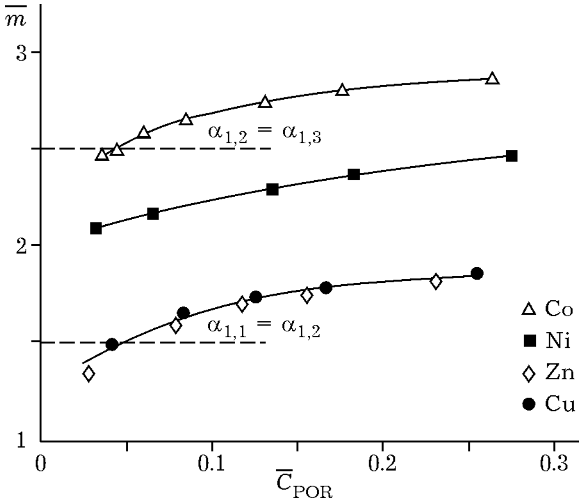

Fig. 4. Dependence of $\overline{m}$ during the formation of Ru/M complexes on the equilibrium concentration of POR in extracts. Concentration: 7 mM Ru, 0.25 M $M(NO_3)_2$.

calculated as functions of POR concentration using the values of $K_{1,m}$ (Fig. 4). Complexes with $m = 2$ were found to be the dominant (more than 50 %) forms for Zn^{2+} and Cu^{2+} ($\alpha_{1,1} + \alpha_{1,2} > 1.5$) , as well as Ni^{2+} ($2.0 < \alpha_{1,2} < 2.5$). As in the case of TOPO [8, 15], the M^{2+} cations are tetrahedrally surrounded by the oxygen atoms of the PO groups of two POR molecules and the oxygen atoms of the OH group and one of the NO_2 groups in An^{2-}. For cobalt, the complex with $m = 3$ prevails (see Fig. 4) and possibly has an octahedral environment of Co^{2+} with an additionally coordinated H_2O molecule. As in the case of $K_{0,n}$, the sequence of $K_{1,m}$ values coincides with the Irwing – Williams series, indicating that the extraction constants of nonferrous metals increased four or five orders of magnitude when the NO_3^- anion surrounded by M^{2+} was replaced by An^{2-}.

Thus generation of the Ru/Zn complex may be conveniently used in developing of a ruthenium extraction procedure because addition of zinc salts in solution provides the highest values of D_{Ru} (Table 4).

Ruthenium extraction from nitric acid solutions

For nitric acid solutions (2 M HNO_3), optimum conditions of ruthenium extraction were chosen by analyzing the effect of HNO_3 concentration on extraction of the freshly prepared An^{2-} form. In the presence of nitric acid, ruthenium extraction decreases abruptly (see Table 4) because of the competing extraction of HNO_3 and possible conversion of An^{2-} to other forms. When the acidity is low (0.3 and 0.5 HNO_3), the dominant tendency is a decrease in the equilibrium concentration of POR because acid binds 60–75 % of POR. Judging from the Ru extraction percent, E = 77–94 %, the An^{2-} form is preserved in solutions with these acidities. Conversion of An^{2-} to mixed forms, in particular, to the dominant $[RuNO(NO_2)_2NO_3(H_2O)_2]^0$ form occurs when $C^0_{HNO_3}$ is higher than 1 mol/l. Therefore, to preserve high values of D_{Ru} demands neutralization of the starting solution (2–3 M HNO_3) with concomitant nitration by adding $NaNO_2$ for generating and stabilizing the An^{2-} form. In the course of neutralization, $C^0_{NaNO_3}$,

TABLE 4

Effect of HNO_3 concentration on An^{2-} extraction with POR solutions in diluents of nitric acid solutions in the presence of zinc. Concentrations: POR 0.3 M, $Zn(NO_3)_2$ 0.15 M, $NaNO_3$ 2 M, Ru 8–10 mM

$C^0_{HNO_3}$, mol/l	POR in HX		POR in F_3	
	$\overline{C}_{HNO_3}$, mol/l	D_{Ru}	$\overline{C}_{HNO_3}$, mol/l	D_{Ru}
0	–	380	0	222
0.13	0.104	114	0.102	43.7
0.30	0.176	15.2	0.196	7.1
0.5	0.222	3.3	0.211	1.85
1.0	0.262	0.46	0.239	0.30
1.5	0.287	0.050	0.265	0.14
2.0	0.300	0.035	–	–
2.5	0.306	0.018	–	–

TABLE 5

Effects of $NaNO_3$ concentration and ionic strength of solution (I) on ruthenium extraction. Concentrations: POR 0.3 M, $Zn(NO_3)_2$ 0.155 M, Ru 9.8 mM

$C^0_{NaNO_3}$, mol/l	$\overline{C}_{Ru}\cdot 10^3$, mol/l	D_{Ru}	$\overline{C}_{Zn}\cdot 10^2$, mol/l	D_{Zn}	$\overline{C}_{Zn}/\overline{C}_{Ru}$	I
0	9.8	200	1.4	0.10	1.43	0.42
0.5	9.8	220	1.9	0.14	1.94	0.91
1.0	9.8	230	2.4	0.18	2.45	1.39
1.5	9.8	240	2.8	0.22	2.86	1.88
2.0	9.8	250	3.3	0.27	3.37	2.37
2.5	9.8	270	3.7	0.31	3.78	2.85
3.0	9.8	280	4.0	0.35	4.08	3.34

TABLE 6

Results of test experiments on extraction of fission elements from real HLW with solid extractants based on POR

Element	Content in sample, Bq/l	Solex/HLW = 1/20		Solex/HLW = 1/10	
		D_M	E, %	D_M	E, %
^{106}Ru	$9\cdot 10^8$	45	70	35	78
^{241}Am	$4\cdot 10^9$	16	44	18	64
$^{154+155}$Eu	$6.8\cdot 10^9$	35	64	38	79
Pd	160 (mg/l)	18	47	43	81
Rh	200 (mg/l)	0	0	0	0

increases, which does not affect D_{Ru}, but increases D_{Zn} considerably due to the common ion effect during co-extraction of the $[ZnL_m(NO_3)_2]$ complex nonelectrolyte and the Ru/M complex (Table 5). The minor increase in D_{Ru} in this case results from the salt effect of the medium ($D_{Ru} = 23.9I + 198$).

CONCLUSIONS

Thus our results permit us to recommend the following sequence of operations for extracting Ru from real solutions: neutralization (to 0.3 M HNO_3) and nitration by treating the starting solutions with sodium nitrite, addition of zinc salts (10 g/l), and finally extraction. For the 40 % POR solution in F_3, the Ru distribution coefficient increased from 0.64 in the idle run to 24 after treatment; after three contacts, the extraction amounted to 98 %. For solex based on POR (Table 6), Ru extraction is 70–80 % for 10- to 20-fold concentrating. In both cases, REE, actinide, and palladium radionuclides are quantitatively extracted together with Ru. Previously, it was also found [10] that cesium is co-extracted with ruthenium, possibly due to extraction of An^-. These results validate the approach proposed in this work and show that ruthenium may be extracted in the form of Ru/M complexes from real HLW. Because of some technical difficulties in monitoring the equilibrium composition of real HLW (according to acidity and Ru forms) after neutralization and nitration, there is still much to be done to create optimum conditions for Ru extraction. To optimize the procedure of HLW preparation for extraction it seems promising to lower the acidity and to perform denitration by treating HLW with formic acid.

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