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Choice of Sorbent for Selective Recovery of Palladium from Electrolytes of Silver Refining

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Abstract

Selective sorption and desorption of the complex compounds of palladium from nitric solutions of silver on the ionites of different kinds was studied. Anionite VP-1P is recommended for the purification of electrolyte solutions from palladium in silver refining.

Key words: palladium, silver, ionite, electrolyte, sorption, desorption

INTRODUCTION

Solutions of leaching the gold-silver alloy (GSA) formed in the production of refined gold and silver have the following composition, g/dm³: HNO₃ 5–10, NH₄⁺ 3–4, Ag 150–190, Cu 5–7, Pd 0.4–0.6, Pt 0.04–0.06, Te 0.03–0.06. As a consequence, the necessity of selective sorption purification of these solutions from platinum group metals (PGM) including palladium arises, to be performed before silver electroextraction [1, 2]. Sorbents to be used for this purpose should be selective to PGM in the presence of silver and copper as macrocomponents; they should also possess chemical and mechanical stability in aggressive media, and easily desorb palladium and platinum.

EXPERIMENTAL

The object of studies was cation-exchange sorbents KU-2, KB-2, KFP-12; highly basic anion-exchange sorbents AV-(17,29), AMP, VP-1AP; low-basic anion-exchange sorbents AN-(18,20,21,22,511,61,31); ampholytes ANKB-(1,2,35,50); vinyl pyridine anion-exchange sorbents VP-1P, SN-3, AN-61 (Table 1). Sorption

isolation of palladium micro-impurity from model solutions was carried out under static conditions until the equilibrium in the system was established. Model solutions had the following composition, g/dm³: Pd 0.53, HNO₃ 6–500.

The studied sorbents are characterized by the structure of functional groups, as well as the value of total exchange capacity. The following parameters are the criteria of the interaction of the sorbent with palladium ions: the static exchange capacity with respect to palladium (SEC_{Pd}), the coefficient of palladium ion distribution between the solution and the sorbent K_d (Table 1), desorption of palladium by water, including the static exchange capacity with respect to nitric acid SEC_{ac} and metal concentration in the eluate (Table 2).

RESULTS AND DISCUSSION

It is known [3–7] that palladium and platinum in nitrate solutions form complexes with a charge from +2 to –2: [Me(H₂O)₄]²⁺, [Me(H₂O)₃NO₃]⁺, [Me(H₂O)₃OH]⁺, [Me(H₂O)₂(OH)₂]⁰, [Me(H₂O)₂NO₃OH]⁰, [Me(H₂O)(OH)₃][–], [Me(H₂O)(NO₃)₃][–] etc. Complexing of PGM with NO₂[–], NO[–] ions and NH₃ possessing the high trans-effect can-

TABLE 1

Characteristics of palladium (II) ion sorption at different concentrations of nitric acid (0.15/1.5/3 mol/dm³, respectively)

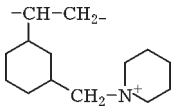
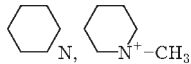
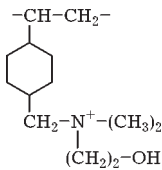
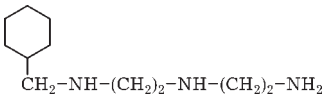
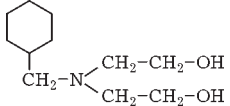
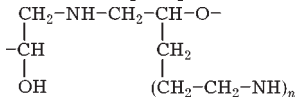
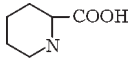
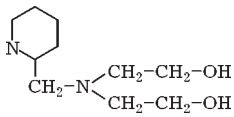
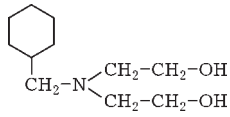
Ionites	Structure of functional groups	TEC _{HNO₃} , mmol/g	Sorption parameters	
			COE _{Pd} , mmol/g	K _d
KU-2×8	-SO ₃ H	2.164	0.7/0.005/<0.01	140.6/0.44/-
KB-2×7II	-COOH	5.512	1.4/<0.01/<0.01	83.6/0.84/-
KFP-12	-PO(OH) ₂	3.505	0.67/0.03/<0.01	52.4/1.46/-
AV-17	(H ₃ C) ₃ N-	0.829	0.53/0.29/0.32	149/129/124
AMP		0.728	0.074/0.13/0.15	23.6/50.5/58.9
VP-1AP		1.15	0.38/0.37/0.39	150/156/153
AV-29		1.125	0.14/0.08/0.085	31/15.5/16.5
AN-18	-CH ₂ -N(CH ₃) ₂	2.151	0.35/0.12/0.02	39.8/11.3/1.5
AN-20	-CH ₂ -NH ₂	1.875	0.51/0.31/0.1	88.3/38.6/9.4
AN-21	-CH ₂ -NH-(CH ₂) ₆ -NH ₂	1.593	0.22/0.06/0.014	33.1/7.3/1.5 ×
AN-22	-CH ₂ -NH-(CH ₂) ₂ -NH ₂	1.707	0.32/0.46/0.4	48.6/84.1/57.5
AN-511		3.664	1.02/0.85/0.72	86.4/66.1/45.9
AN-61		2.89	0.83/0.35/0.17	119/30.5/11.7
AN-31		6.03	2.34/1.5/1.81	148.6/76.3/74
ANKB-1	-N-CH ₂ -COOH	5.265	1.09/1.04/0.65	64.9/69.8/54.35
ANKB-2		4.688	1.59/1.55/1.12	157.6/371.6/262.9
ANKB-35	R-N-CH ₂ -COOH	2.603	0.99/0.74/0.5	218.1/161.3/132.1
ANKB-50	R-N-CH ₂ -COOH	1.05	0.53/0.37/0.24	841.6/596.5/226.8
VP-1P		2.224	0.73/0.67/0.63	151.6/139.5/99.1
SN-3		3.764	1.53/1.25/1.27	273.4/176.3/146.9
AN-61		2.89	0.83/0.35/0.17	119.1/30.5/11.7

TABLE 2

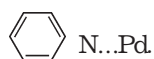
Water washing of ionites from solutions with nitric acid concentration 0.15/1.5/3 mol/dm³

Ionites	Desorption parameters		Ionites	Desorption parameters	
	SEC _{HNO₃} , mmol/g	Pd, mg/dm ³		SEC _{HNO₃} , mmol/g	Pd, mg/dm ³
KU-2×8	0.04/0.24/0.64	<0.01/<0.01/<0.01	AN-511	0.59/1.59/2.7	0.83/0.71/0.92
KB-2×7II	0.28/1.69/3.42		AN-61	0.47/1.27/2.46	<0.01/0.22/0.46
KFP-12	0.21/1.58/3.11	<0.01/<0.01/0.093	AN-31	1.27/2.69/2.81	0.05/<0.01/<0.01
AV-17	0.17/1.39/3.25	26.45/47.4/53.99	ANKB-1	1.46/2.68/3.78	0.19/<0.01/<0.01
AMP	0.15/1.34/2.53	153.3/68.95/122.3	ANKB-2	0.88/2.83/4.85	0.82/<0.01/<0.01
VP-1AP	0.4/23/4.14	3.37/14/13.8	ANKB-35	0.46/2.36/4.22	0.69/0.24/<0.01
AV-29	0.17/1.34/2.82	0.14/0.08/0.084	ANKB-50	0.47/1.81/2.68	0.045/0.053/<0.01
AN-18	0.21/1.9/3.71	0.56/3.68/9.31	VP-1II	0.6/248.5/4.06	1.78/1.52/1.18
AN-20	0.36/0.98/1.59	0.15/0.16/0.06	CN-3	1.28/20.5/5.1	1.23/0.29/0.09
AN-21	0.3/1.22/2.45	0.85/2.71/3.52	AN-61	0.47/1.27/2.46	<0.01/0.22/0.46
AN-22	0.37/0.76/1.92	0.045/0.028/0.062			

not be excluded [8–10]; these species are able to participate in ligand substitution and exchange processes, for example, $[\text{Me}(\text{NH}_3)_4]^{2+}$, $[\text{Me}(\text{NH}_3)_3\text{NO}_2]^+$, $[\text{Me}(\text{NH}_3)_2(\text{NO}_2)_2]^0$, $[\text{Me}(\text{NH}_3)_3\text{NO}_2]\text{NO}_2$, where Me = Pd, Pt [11].

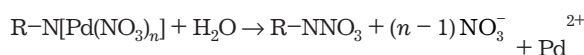
Cation-exchange sorbents quantitatively sorb ($\text{SEC}_{\text{Pd}} = 0.7\text{--}1.4$ mmol/g, $K_d = 52.4\text{--}140.6$) positively charged or neutral palladium complexes from weakly acidic diluted electrolytes ($\text{pH} \geq 3$, $[\text{NO}_3^-] \leq 120$ g-ion/dm³), which is confirmed by the data on the desorption of palladium cations with water when the maximal metal concentration in the eluate does not exceed 0.093 mg/dm³ for the phosphoric cation-exchange sorbent KFP-12.

Highly basic anion-exchange sorbents sorb palladium within the entire studied range of nitric acid concentrations. Pyridine-containing sorbents possess higher capacity with respect to the metal and form a covalent bond:



The maximal capacity was revealed for the sorbents containing pyridine nitrogen and other heteroatoms. Macrocomponents (silver, copper) in acid media are unable to enter the coordination interaction with the functional groups of anion-exchange sorbents, which allows selective recovery of palladium from highly mineralised solutions. The high degree of palladium desorption, decreasing from AMP to VP-1P, points to the low stability of the nitrate

complexes of the metal, destroying with a decrease in the concentration of nitric acid during washing with water:



It was established that anionite AV-17 absorbs complex palladium (II) anions within a broad range of nitric acid concentrations with the maximum within the range 1–3 M HNO₃ (Fig. 1). At higher acidity, the competitive effect of nitrate ion for binding ionogenic groups of the sorbent increases, and the parameters of sorption process SEC_{Pd} and K_d decrease.

The results of the IR spectroscopic examination confirmed the presence of nitrate complexes, including unsaturated ones, in the phase of ion-exchange sorbent, without the formation of covalent bonds with functional groups of AV-17, as well as their destruction with

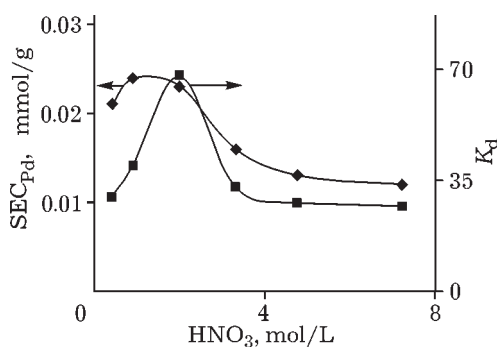
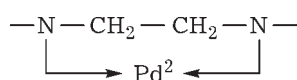


Fig. 1. Dependence of palladium (II) ion sorption parameters on the concentration of nitric acid.

the formation of low-basic amino groups and dehydration.

Low-basic anion-exchange sorbents with aliphatic nitrogen (AN-18, AN-20, AN-61) can form only one coordination bond with metal ion. The functional groups of anion-exchange sorbent AN-21 containing two nitrogen atoms through six methyl radicals do not form a chelate complex with one metal ion. The highest capacity with respect to palladium ions within a broad range of HNO_3 concentrations is exhibited by polyfunctional cation-exchange sorbents AN-22, AN-511, AN-31 containing ethylenediamine fragment and forming a strong chelate complex (according to the IR spectroscopic data):



The formation of the chelate complex is indirectly confirmed by the insignificant degree of palladium desorption during water washing of saturated ion-exchange sorbents (see Table 2).

Due to bonding between the metal and the cation-exchange group and nitrogen, amphoteric ion-exchange sorbents form chelate complexes with palladium ions; the strength of these complexes increases in the sequence: ANKB-1 < ANKB-35 < ANKB-50. This is indicated by the change of the phase composition of ANKB-35 resin during palladium sorption from nitrate solutions. Thus, in comparison with hydrochloric solutions, the amount of water molecules are the volume of ion-exchange sorbent decrease substantially, similarly to the case of the chelate-forming anion-exchange sorbent AN-31 (Table 3).

Complex-forming properties of sorbents are enhanced if pyridine is used as the amination agent. It is characteristic that the maximum of palladium sorption on ANKB-2 is observed from the solution with nitric acid concentration 1.5 g-equiv./dm³ and is due to the mechanisms of both complex formation and ion exchange.

During water washing of ampholytes, palladium is not desorbed similarly to the case of low-basic anion-exchange sorbents.

For ionites synthesized on the basis of vinyl pyridine, a dependence between the capacity of sorbents with respect to palladium ions and their ability to form complexes can be revealed: SN-3 > VP-1P > VP-1AP > AMP. The degree of palladium removal into the aqueous phase increases in the same sequence; for highly basic VP-1P and AMP this is connected with the ion-exchange mechanism of palladium sorption.

Anion-exchange sorbents based on vinyl pyridine absorb palladium ions in much larger amount than the low-basic ionites containing aliphatic nitrogen do. This is connected with the stronger coordination bonding between palladium ions and pyridine nitrogen. The addition of amino groups into the structure of the ionite containing pyridine nitrogen increases the strength of coordination bonds, due to which CN-3 anion exchange sorbent possesses the highest capacity with respect to palladium ions.

With the monofunctional anion-exchange sorbent VP-1P, we studied the change of the phase composition during palladium sorption (Table 4). Unlike chelate-forming ionites, no large differences were revealed between palladium sorption from nitrate and chloride media.

TABLE 3

Changes of the composition of ANKB-35 phase depending on Pd (II) sorption

SEC _{Pd} , mmol/g	Specific volume of ionite, cm ³	SEC _{HNO₃} , mmol/g	Ionite capacity, mmol/g	
			for water	total
0.74678	2.60	0.818	42.6704	44.23486
0.71732	2.60	1.221	41.10848	43.04721
0.50551	2.65	2.497	40.62793	43.63009
0.45949	2.65	2.607	41.57287	44.63979
0.15339	2.80	5.927	42.00274	48.083
0.05137	2.95	8.587	41.40814	50.04623

TABLE 4

Changes of the composition of VP-1P phase depending on Pd (II) sorption

SEC _{Pd} , mmol/g	Specific volume of ionite, cm ³	SEC _{HNO₃} , mmol/g	Ionite capacity, mmol/g	
			for water	total
0.672	~2.8	0.894	48.071	49.637
0.621	~2.8	1.426	48.662	50.710
0.290	~2.8	2.906	49.540	52.740
0.120	~2.9	4.606	49.070	53.797
0.065	~3.0	6.360	49.955	56.379
0.032	~3.0	6.533	55.522	62.087

Analysis of the IR spectra of VP-1P samples allows us to conclude that palladium is sorbed from nitric solutions due to complex formation. In this process, the internal sphere of the ionite complex contains a smaller amount of nitrogen-containing anions in comparison with the sorbents containing aliphatic nitrogen.

The spectral analysis of SN-3 samples containing amino alcohol groups along with pyridine revealed the formation of chelate complexes of palladium with pyridine and aliphatic nitrogen. Nitrogen-containing anions, hydroxyl ions and water molecules can enter either the internal of the external sphere of the formed complex to compensate for the positive charge.

The character of the interaction of palladium (II) ions with ionites does not change in the solutions of ammonium nitrate with small addition of 0.03 M HNO₃, which is the evidence of the secondary role of macro cation in the equilibrium solution (Fig. 2). Sorption of palladium (II) ions is determined by the structure

of the functional groups of sorbents and the concentration of nitrate ions.

CONCLUSIONS

1. Investigation of palladium sorption on cation-exchange and highly basic anion-exchange sorbents revealed the presence of low-stable nitrate complexes of the metal in nitric solutions. In weakly acidic solutions [Pd(H₂O)₄]²⁺, [Pd(H₂O)₃NO₃]⁺ ions are quantitatively sorbed on cation-exchange sorbents. With an increase in the concentration of nitric acid, the fraction of anion complexes Pd(NO₃)_n increases, reaching the maximum within concentration range 1–3 M HNO₃, which increases the sorption of palladium on highly basic anion-exchange sorbents.

2. Among low-basic anion-exchange sorbents, the highest capacity with respect to palladium ions within a broad range of HNO₃ concentrations is exhibited by polyfunctional AN-22, AN-511, AN-31 containing ethylenediamine fragment and forming a strong chelate complex.

3. Due to metal bonding with the cation-exchange group and nitrogen, amphoteric ionites form chelate complexes with palladium ions; the strength of these complexes increases in the sequence ANKB-1 < ANKB-35 < ANKB-50.

4. For ionites synthesized on the basis of vinyl pyridine, a dependence between the sorbent capacity with respect to palladium ions and their ability to form complexes is observed in the following row: SN-3 > VP-1P > VP-1AP > AMP.

5. Sorbents containing aliphatic and pyridine nitrogen with unshared electron pair, in addition to ion exchange, are able to hold palladi-

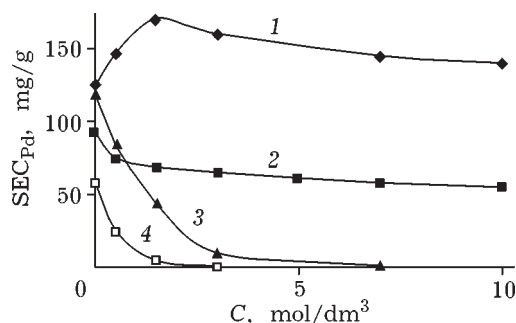


Fig. 2. Dependence of palladium (II) ion sorption on the concentration of ammonium nitrate: 1 – AN-31, 2 – ANKB-35, 3 – KU-2, 4 – KB-2.

um due to the formation of complexes. In acidic solutions with HNO_3 concentration not less than 3 mol/L, for the sorbents with monofunctional groups the sorption of palladium according to both mechanisms decreases substantially in comparison with the chelate sorbents. The latter can be used for selective sorption of palladium (II) ions and their separation from accompanying elements, in particular copper and silver those are unable to form complexes in acidic media.

6. Vinyl pyridinic anion-exchange sorbent VP-1P possessing the maximal sorption with respect to palladium and chemical stability in acid media among all the studied sorbents is recommended for use in conditioning the electrolyte for silver electroextraction.

REFERENCES

- 1 Plekhanov K. A., Lebed A. B., Naboychenko S. S., Skopin D. Yu., *Tsv. Metally*, 5 (1999) 27.
- 2 RU Pat. No. 2100484, 1998.
- 3 Anpilogova G. R., Kondratieva E. V., Afzaletdinova N. G., *Zh. Neorg. Khim.*, 41, 3 (1996) 429.
- 4 Shorokhov N. A., Vashman A. A., Samsonov V. E., *Zh. Neorg. Khim.*, 27, 12 (1982) 3137.
- 5 Lidin R. A., Molochko V. A., Andreev L. A., *Khimicheskiye Svoystva Neorganicheskikh Veshchestv* (High School Book), Khimiya, Moscow, 1997.
- 6 Naboychenko S. S. (Ed.), *Poroshki Tsvetnykh Metallov* (Handbook), Metallurgiya, Moscow, 1997.
- 7 Skorokhodov V. I., Volkova N. A., Goryaeva O. Yu., Rychkov D. M., 2 Mezhdunar. Konf. "Blagorodnye i Redkiye Metally. BRM-97" (Proceedings), Donetsk, 1997, part I, p. 149.
- 8 Chugaev L. A., *Khimiya Kompleksnykh Soyedineniy. Stat'i 1907-1927*, in N. M. Zhavoronkov, Yu. N. Solov'yev (Eds.), Nauka, Leningrad, 1979.
- 9 Grinberg A. A., *Fizicheskaya Khimiya Kompleksnykh Soyedineniy. Izbrannye Trudy*, Nauka, Leningrad, 1972.
- 10 Kukushkin Yu. N., *Khimiya Koordinatsionnykh Soyedineniy* (High School Book), Vysshaya Shkola, Moscow, 1985.