Sorption concentration of ruthenium from sulfuric solutions

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Performed are the studies on sorption concentrating of ruthenium from sulfuric solutions at variant concentrations of sulphuric acid with the use of KU-2 (КУ-2) and EDE-10P (ЭДЭ-1ОП) cation-exchange and anion-exchange resins as well as a CAD (КАД) activated charcoal. It was determined that the highest possible sorption of ruthenium on all the tested sorbents from solutions containing 20 mg/l of ruthenium is observed if concentrations of sulphuric acid are within the range of 80–100 g/l. The EDE-10P sorbent have the most ability to absorb ruthenium; degree of ruthenium extraction by this sorbent doesn't exceed 18% at L : S = 3 : 1. It has been revealed that in the case of three sorbents each contacting with the solution done in turn, the aggregate sorption degree doesn't exceed 43%. At that, changing the order of introducing the sorbents into solution doesn't exert a noticeable influence over the indices of ruthenium extraction into each sorbent type. It is suggested to carry out a preliminary recovery treatment of solutions in order to raise the degree of ruthenium extraction. It is shown that degree of ruthenium sorption by activated charcoal after the preliminary treatment of solutions by sodium sulfite is about four times more, that by anionite is half as much again and practically has not been changed in the case of sulfonic cation-exchange resin usage. A successive sorption by the tested sorbents from the sulfuric solutions treated with sodium sulfite guarantees almost complete extraction of ruthenium.

Key words: sorption processes, sorption concentration, platinum group metals, ruthenium, sodium sulfite, sulfuric solutions.

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Introduction

The recent trend towards enlargement of mineral resource base of platinum group metals (PGM) involves into processing new unconventional ore types (oxidized nickel, chromite, etc.) and man-made materials, stimulating the development of new technologies for PGM concentration. A diversity of material ore composition and customary processing technologies have a substantial effect on the content of PGM, non-ferrous metals, iron and silicates in platinum-bearing products, which determines principles of their further working up. The present-day industrial experience and investigations in the field of processing the sulphide concentrates, containing precious metals, allows noticing that they are mainly directed towards a collective transfer of noble and non-ferrous metals into solution with subsequent extraction of their selective concentrates, including the use of sorption process [1–4].

The methods of sorption concentrating of platinum group metals (PGM) from process solutions during the processing of polytypic mineral raw materials are based on specific peculiarities of the chemistry of these elements, featuring the variety of oxidation levels and forms of coordination compounds, the complexity and ambiguity of transformations in solutions [5–6]. An assortment of the sorbents, which possess the ability to the ion-exchange and donor-acceptor interactions and are recommended for PGM extraction from solutions, is broad enough. By convention the sorbents may be classified into two groups by the matrix type: on the base of organic polymeric matrix and the inorganic one [7–13].

Organopolymers feature high selectivity in reference to platinum metals and provide concentrating of the valuable components against the background of the predominant amounts of non-ferrous and rare metals. As applied to the PGM sorption, the inorganic sorbents (sulphides, oxides, hydroxides, zeolites, activated carbons, etc.) undoubtedly rank below the sorbents on an organic polymeric base in effectiveness and selectivity, though at the same time they surpass the latter in some indicators (by higher sorption rate and an opportunity to realize for them a desorption process) [14].

When separating and concentrating PGM, a growing number of uses are being found for new complexing sorbents based on fibrous materials mainly in ana-

lytical practice [14]. The fibers, constructed on linear or branched macromolecules have essentially much more advanced active surface in comparison with the granulated ones, demonstrates a superior ability to swelling and high selectivity to PGM, especially the complexing sorbents, containing nitrogen and sulfur in the composition of functional groups. Among the nitrogen-containing sorbents of a fiberlike structure, a POLIORGS 4 (6, 10), the sorbent based on polyvinelene carbochain fiber, is widely used in analytics. The sorption is carried out when boiling the solution or in autoclave conditions in the presence of HCl [15].

The sorbents made by Purolite Company (Great Britain) are more and more actively studied and applied. Such resins as S-985 (functional group — polyamine), S-920 (thiourea functional groups), S-108 (functional group — amine), S-930 (aminediacetic chelating functional groups) are the most interesting from the viewpoint of sorption of platinum metals in the form of chloride and sulphate complexes. These sorbents are distinguished by high selectivity for platinum metals and good sorption characteristics. They are recommended for separation of platinoids and non-ferrous metals, abundantly presented in process solutions [16].

Oxidation levels of PGM, duration of solutions storage as well as the processes of aquatation and hydrolysis of complexes exert great influence over sorption of sulphate and chloride complexes by anionites [17—18].

Research on composition and the behaviour peculiarities of platinum metals in sulphate solutions, coordination compounds of which possess a heightened reactionlessness, will allow one to significantly evolve the theory of labilization and inertization of polyvalent polycyclic complexes of platinoids in aqueous systems and to suggest new process techniques for their concentrating during processing of various platinum metal raw material.

Experimental study

Cation-exchange and anion-exchange resins KU-2 (КУ-2) and EDE-10P (ЭДЭ-1ОП) as well as a CAD (КАД) activated charcoal have been used on investigating the ruthenium sorption from sulphate solutions. Preliminary swollen resins have been soaked in a sulphuric acid solution (600 g/l H_2SO_4), then they have been thoroughly washed and finally soaked in the sulphuric acid solution of given concentration. Solutions of brown ruthenium sulfate prepared according to the procedure [17] have served as the initial ones; a part of them have been treated with sodium sulfite (sulphur dioxide). Experiments on ruthenium sorption have been carried out at variant concentrations of sulphuric acid (25—400 g/l). Ruthenium has been detected in solutions by an iCAP 6300 inductively coupled plasma atomic emission spectrometer in accordance with the procedure No. 04-06-145-2011.

Analyzing the data, one can note a uniform nature of ruthenium sorption on all the tested ionites. In all cases

the sorption indices are minimal at the sulphuric acid concentration of about 50 g/l; the peak of the sorption may be observed in the range between 80 and 100 g/l. An insignificant growth of ruthenium extraction into sorbent becomes evident at acidity increase over 200 g/l (Fig. 1, 2).

According to the literary data, the following forms are available for quadrivalent ruthenium in sulphate solutions: a cation (RuO^{2+}) and a neutral ($RuOSO_4$) ones [16]. At the same time, the cation form may be sorbed by cationite, and the neutral one — by activated charcoal. As may be seen from the foregoing, the anionic polymeric forms with oxidation level (3.5), $[Ru_4^{III,IV}O_6(SO_4)_6]^{10-}$, for example, may be present in the solutions under investigation parallel with ruthenium (IV) and ruthenium (III). Moreover, judging from the mode of preparation of the solution, the polymeric forms would be expected to predominate. If we assume that the sorption on anionite is correlated with formation of monomeric anionic complexes, then these latter may have the from for ruthenium (IV): $[RuO(SO_4)_2]^{2-}$, а для Ru(III): $[Ru(SO_4)_2]^-$.
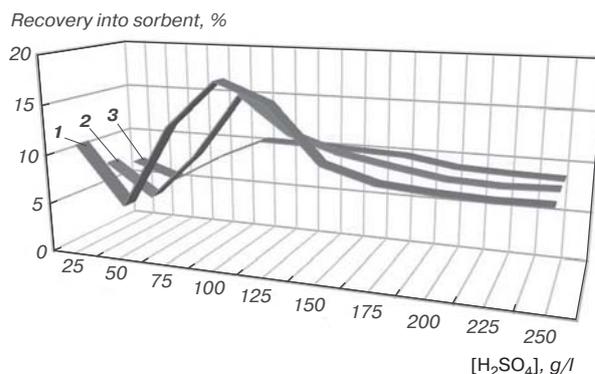

Fig. 1. Sorption of ruthenium on different sorbents from sulfuric solutions of various acidity:
1 — EDE-10P; *2* — KU-2; *3* — CAD.
Conditions: volume of solution — 50 ml, concentration of Ru — 20 mg/l; holding time — 2 hours; sample weight of sorbent — 3 g
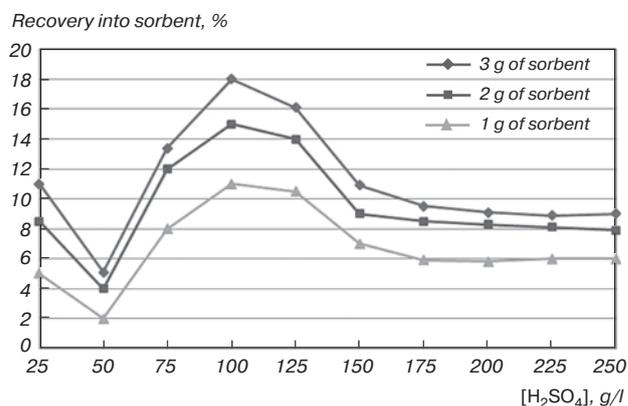

Fig. 2. Sorption of ruthenium on an EDE-10P resin from sulfuric solutions of various acidity
Conditions: volume of solution — 50 ml, concentration of Ru — 20 mg/l; holding time — 2 hours; sample weight of sorbent — 1, 2, 3 g

Table 1
Successive sorption of ruthenium by different sorbents

Order of sorption	Solution					
	1		2		3	
	Sorbent	Extraction into sorbent, %	Sorbent	Extraction into sorbent, %	Sorbent	Extraction into sorbent, %
1	KU-2	16	EDE-10P	18	CAD	10.2
2	EDE-10P	16	CAD	7	KU-2	14.7
3	CAD	9.4	KU-2	10.4	EDE-10P	18
Total		41.4		35.4		42.9

Conditions: volume of solutions — 50 ml; [H_2SO_4] — 100 g/l; successive introduction of sorbents by 3 g. Time of contact — 48 hours.

Availability of interconversion of poly- and monomeric forms of ruthenium in a sorption process has been estimated by the successive sorption method at various order of introducing ionites into solution.
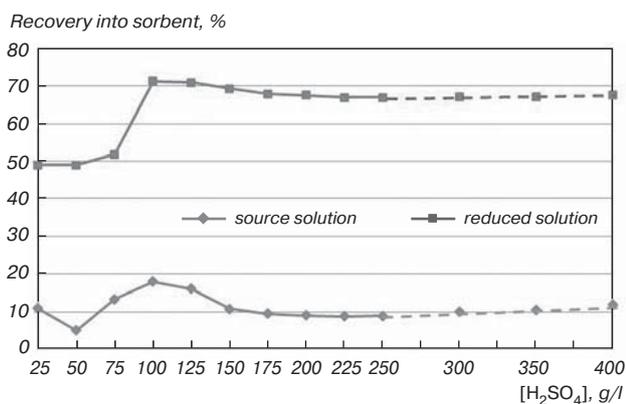

Fig. 3. Sorption of ruthenium on an EDE-10P resin from sulfuric solutions of various acidity: the initial ones and after treatment by sodium sulfite.
Conditions: volume of solution — 50 ml, concentration of Ru — 20 mg/l; holding time — 2 hours; consumption of sodium sulfite — 20 g/l, sample weight of sorbent —3 g
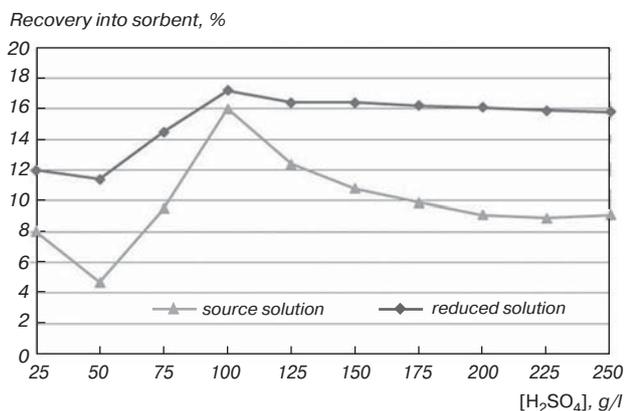
The results of experiments testify that extraction is determined by the type of sorbent, not the order of introducing the sorbents. Since the succession of introducing doesn't affect the function of each sorbent, one can assert that interconversion of different forms of ruthenium doesn't take place during the sorption process. In spite of plethora of sorbents, a significant part of ruthenium is sorbed with none of them. It may be suggested that the monomeric forms are predominantly sorbed. The polymeric forms prevail even at 100 g/l H_2SO_4; their amount rises as concentration of sulphuric acid increases and decreases (Table 1, Fig. 1).

Data on the study of ruthenium sorption from the solutions, processed with sodium sulfite (consumption — 20 g/l), are depicted in Fig. 3, 4, 5. An increase of ruthenium sorption into all the types of sorbents is noticed at predominantly high values for an EDE-10P anionite, which agree with formation of anionic complexes on sulphite treatment of ruthenium sulphate [16].

Change of the order of introducing the sorbents into the "reduced" solutions, processed with sodium sulfite, and doesn't exert some action on ruthenium extraction into each type of sorbent (Table 2).
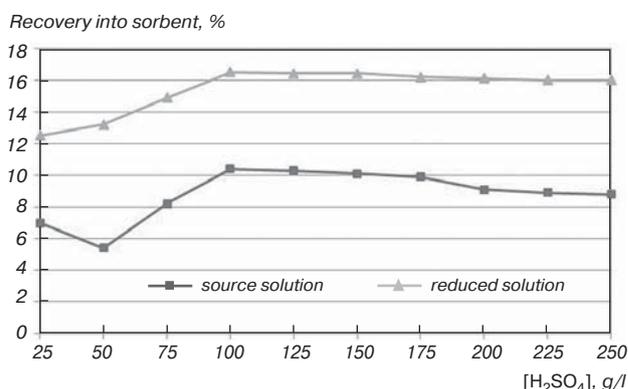

Fig. 4. Sorption of ruthenium on a KU-2 resin from sulfuric solutions of various acidity: the initial ones and after treatment by sulphur dioxide.
Conditions: volume of solution — 50 ml, concentration of Ru — 20 mg/l; holding time — 2 hour

Fig. 5. Sorption of ruthenium on a CAD coal from sulfuric solutions of various acidity: the initial ones and after treatment by sulphur dioxide.
Conditions: volume of solution — 50 ml, concentration of Ru — 20 mg/l; holding time — 2 hours

Table 2
Successive sorption of ruthenium from "reduced" solutions by different sorbents

Order of sorption	Solution					
	1		2		3	
	Sorbent	Extraction into sorbent, %	Sorbent	Extraction into sorbent, %	Sorbent	Extraction into sorbent, %
1	KU-2	17.2	EDE-10P	71.3	CAD	14.2
2	EDE-10P	62.5	CAD	15.9	KU-2	16.6
3	CAD	16.5	KU-2	12.8	EDE-10P	69.1
Total		96.2		100		99.9

Conditions: volume of solutions — 50 ml; [H_2SO_4] — 100 g/l; successive introduction of sorbents by 3 g. Time of contact — 48 hours; consumption of sodium sulfite — 20 g/l.
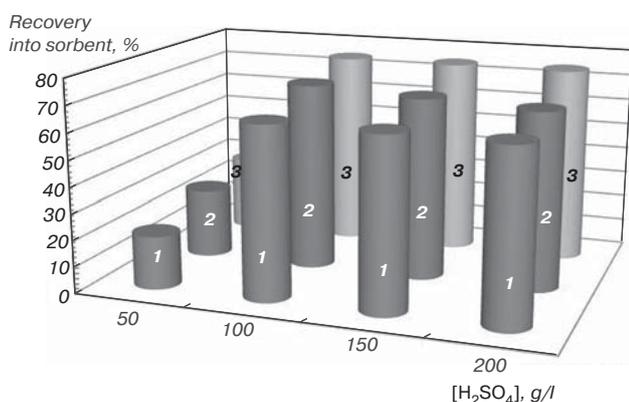

Fig. 6. Impact of the sodium sulfite consumption on sorption of ruthenium on an EDE-10P resin from sulfuric solutions of various acidity.
Conditions: volume of solution — 50 ml, concentration of Ru — 20 mg/l; holding time — 2 hours; consumption of sorbent — 3 g; consumption of sodium sulfite — 20–120 g/l

Fig. 7. A dependence of ruthenium content in an EDE-10P resin upon concentration of ruthenium sulphate complexes in solution.
Conditions: volume of solution — 50 ml, concentration of Ru — 20 mg/l; holding time — 2 hours; [H_2SO_4] — 100 g/l; consumption of sodium sulfite — 60 g/l, consumption of resin — 20–100 g/l

This attests the fact that in the test solution there are three forms of ruthenium complexes, relatively slowly converting into each other. Since total sorption is close to 100%, it is obvious that treatment by sulphur dioxide transforms ruthenium into more easy-to-sorb forms than those in original brown sulphates. Increasing the sodium sulfite consumption from 20 to 120 g/l has a moderate impact upon the indices of ruthenium sorption on the EDE-10P resin at given solution acidity (Fig. 6).

A dependence of ruthenium content in the sorbent of concentration of ruthenium sulfate complexs in the solution (Fig. 7) for an EDE-P10 resin is close to a linear one. The resin capacity is quite sizeable, as even an anionite unsaturated by ruthenium contains 0.13% of the latter at its content in the solution of 50 mg/l.

The authors of [19] have used the method of determining a degree of iridium polymerization in sulfuric solution from the lg $[Ir]_{res}$ graphic dependence of lg $[Ir]_{sol}$. Analysis of a relationship between logarithms of ruthenium concentration in resin and in solution shows its linear character with a slope close to 45°. Taking into consideration
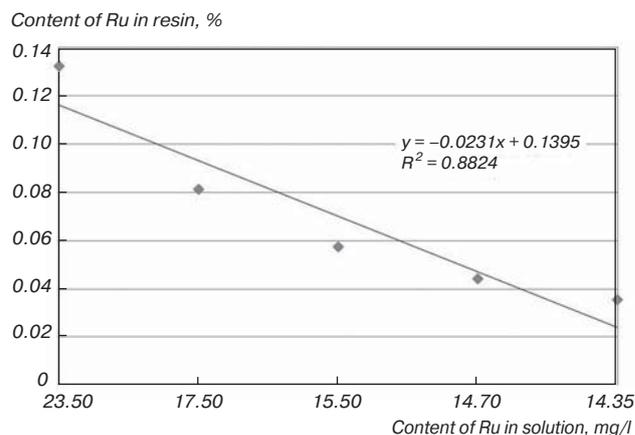
the existing data on depolymerization of ions during the sorption process, the sorbed forms of ruthenium may be assumed to be monomeric, i.e. a treatment by sulfite destroys a framework of the tetracyclic inert complex of ruthenium (III, III, IV, IV).

Conclusion

Specific individual restrictions of the existing hydrometallurgical methods of PGM extraction ride on a variety of PGM forms in different mediums (sulphate, chloride, etc.). Availability of directed managing the behaviour of PGM complexes based on the changes of their reaction activity, in the sorption processes in particular, will allow more justified considering the efficiency of the platinum metals concentrating methods with the use of organic sorbents. The obtained high quantitative indicators of ruthenium sorption from the sulphate solutions preliminary reduced by sodium sulfite create the justified prerequisites for its processing usage in order to obtain a selective concentrate of ruthenium.

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