

## NEW TECHNOLOGIES FOR PROCESSING TAILINGS OF A COPPER PROCESSING PLANT FOR THE EXTRACTION OF PLATINOIDS

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### Highlight

Copper processing plant for the extraction of platinoids.

### Abstract

The most important task of the mining and metallurgical industry in the world is the development of technology for the processing of industrial waste from metallurgical industries. In the world, balance ores of precious metals are practically available. This issue develops the processing of man-made waste, refractory ores, off-balance and low-grade dumps.

The article considers studies of the material and rational compositions of the tailings of a copper concentrating plant in the conditions of JSC Almalyk MMC, determines the optimal method for tailings enrichment with an increase in the content of precious metals in the concentrate, and enhances an unconventional new scheme for processing platinum group concentrates with the extraction of platinum, palladium, silver and high recovery gold. Based on the learned subjects and analysis of studies results, the authors concluded that the centrifugal concentration of platinoids from the composition of the tailings was achieved due to accurate determinations of the particle size in the tailings with the selection of intense gravity modes. Combined hydrometallurgical methods for purifying platinoids and gold from impurities using combinations of chemical solvents have been developed. As a result, the developed technologies have achieved the possibility of complex extraction of platinum group metals from the tailings of concentrating plants of copper production with high degrees, through extraction of all precious metals.

### Keywords

platinum metals, platinum; rhodium; copper processing plant waste; selective phosphatia; aqua regia dissolution; industrial waste; washing; centrifugal concentration; knelson.

## Introduction

In the Republic of Uzbekistan, special attention is paid to the mining and metallurgical industry, the development of advanced technologies for the processing of mineral and man-made raw materials, in particular polymetallic ores and tailings of processing plants, with the aim of complex extraction of all valuable components [17]. Platinum group metals are found in associated methods in magmatic deposits that accumulate precious components together with sulfide minerals of polymetallic ores. They are extracted only in passing, during the extraction of other non-ferrous metals, such as copper and nickel. In the Ores, the birthplace of Kalmakkir was found, as well as Palladium telluride with an admixture of platinum–mereskite - (Pd,Pt)Te<sub>2</sub> [3][23].

Sulfide polymetallic copper ores in the conditions of Almalyk MMC JSC are enriched, flotation method and later copper is extracted according to the pyrometallurgical scheme, while technogenic waste within 1.3 billion tons is formed. The composition of these technogenic wastes mainly includes the tailings of a copper processing plant (CPP-1, CPP-2). The presence of precious metals such as platinum, palladium and rhodium in the composition of technogenic waste of AMMC JSC indicates that the plant can conduct a production industry for processing these wastes without involving ores for several years [20]. Processing and neutralization of technogenic waste from the metallurgical industry is one of the urgent problems of Russia, the USA, Chile and South Africa, and the extraction of precious metals based on their complex processing is one of the new directions of the future [18]. Purpose of the work: development and improvement of the technology of extraction of precious metals from the tailings of copper processing plants [7][19].

## Experimental Methods

We have studied the chemical, mineralogical and rational composition of the objects of research, and based on this, the number of precious metals in the tailings of the processing plant has been determined and optimal technologies for their extraction have been developed. Samples from the waste of the copper processing plant (CPP-1, CPP-2) of JSC "AMMC" were selected as objects of research.

In order to study the material and mineralogical composition of the tailings of processing plants (CPP-1, CPP-2), samples were obtained, which were subjected to analysis in the Central Analytical Laboratory using an energy-dispersive X-ray fluorescence spectrometer of the NEX CG RIGAKU brand. Also, to study the phase composition of the tailings of the copper processing plant, all samples were analyzed using a scanning electron microscope JSM-IT200 [2][4] [6][22]. Studying the volume of storage No.1 (CPP-1), 546.2 million were determined. tons of tailings of flotation enrichment, they contain a copper content of 0.112%, gold with a content of 0.21 g/t with a total weight of 114.0 tons, silver – 577.8 tons with a content of 1.06 g/t [4]. There are 775.3 million tons of enrichment tailings in tailings No.2 (CPP-2), including 801.6 thousand tons of copper with a content of 0.103%, 156.5 tons of gold with a content of 0.20 g/t, and 800.9 tons of silver with a content of 1.03 g/t. The number of elements contained in the tails of CPP-1, 2 is given in Table 1.

As a result of studying the mineralogical composition of the tailings, it can be said that the main elements of the platinum group after enrichment are mainly found in oxidized minerals and sulfide minerals that do not transition to the concentrate phase in combination with pure minerals of copper, mereskiite, chalcopyrite, and their quantity is constantly changing, which is shown in Figure 1.

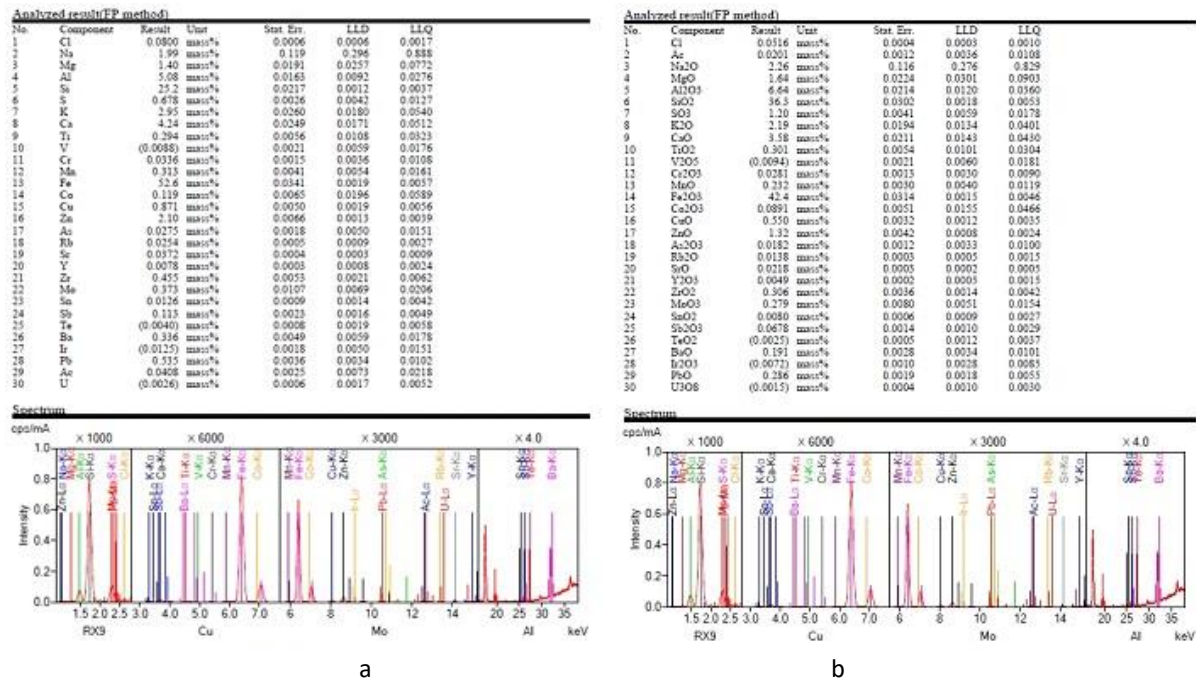


Figure 1. The material composition of waste of JSC "AMMC": a-CPP-1; b- CPP-2

According to chemical analysis, in the average sample of mos tails -2 is contained, %: SiO<sub>2</sub> – 36,3; Al<sub>2</sub>O<sub>3</sub> -6,64; MgO – 1,64; SO<sub>3</sub> – 1,20; K<sub>2</sub>O – 2,19; CaO – 3,58; Fe<sub>2</sub>O<sub>3</sub> – 42,4; CuO – 0,55; ZnO – 1,32; As<sub>2</sub>O<sub>3</sub> – 0,0182; SnO<sub>2</sub> – 0,008; Rb<sub>2</sub>O – 0,0138; ZrO – 0,0218; Au – 0,0002; Ag – 0,001; Pd – 0,000001; Pt – 0,00041; PbO -0,286; MnO – 0,232; TiO<sub>2</sub> – 0,301; Ac – 0,0201; Cl – 0,0516; Sb<sub>2</sub>O<sub>3</sub> – 0,00678; U<sub>3</sub>O<sub>8</sub> – 0,0015; Ir<sub>2</sub>O<sub>3</sub> – 0,0072; BaO – 0,191; Co<sub>2</sub>O<sub>3</sub> – 0,0891; V<sub>2</sub>O<sub>3</sub> – 0,0094.

Table 1. Number of elements contained in CEP-1 and CEP-2 tailings (1353.1 million tons)

No	Metal	Clark Metal	The content of precious metals in tailings, g/t	Number of lu in tails, t
1	Au (Gold)	4,3·10 <sup>-7</sup> %	0,21	277,51
2	Ag (Silver)	7·10 <sup>-6</sup> %	1,06	1400,79
3	Se (selenium)	500 mg/t	5,0	6607,5
4	Pt (Platinum)	5·10 <sup>-7</sup> %	0,001	1,32
5	Pd (Palladium)	1·10 <sup>-6</sup> %	0,410	541,81
6	Re (Rhenium)	7·10 <sup>-8</sup> %	0,038	50,21
7	Os (Osmium)	5·10 <sup>-6</sup> %	0,0018	2,37
8	In (indium)	10 <sup>-5</sup> %	0,042	55,50
9	Ru (ruthenium)	5·10 <sup>-7</sup> %	0,091	120,25
10	Te (Tellurium)	1·10 <sup>-6</sup> %	0,007	9,25
11	Mo (molybdenum)	3·10 <sup>-4</sup> %	49,0	64753,5
12	W (tungsten)	1,3 g/t	4,50	5946,75
13	Rh (rhodium)	1·10 <sup>-7</sup> %	0,039	51,53
14	Ir (iridium)	10 <sup>-7</sup> %	0,0084	11,10
15	Be (beryllium)	3,8 g/t	0,370	488,95
16	Ga (gallium)	19 g/t	6,80	8986,2
17	Nb (niobium)	18 g/t	0,200	264,3

To determine the phase composition of the enrichment tailings and to clarify the sizes of the available platinoids, the samples were additionally analyzed using a scanning electron microscope JSM-IT200 [4]. The results of the analyses show that platinum metals, mainly after flotation enrichment of copper, remained only in the crystal lattice of the iron oxide compound.

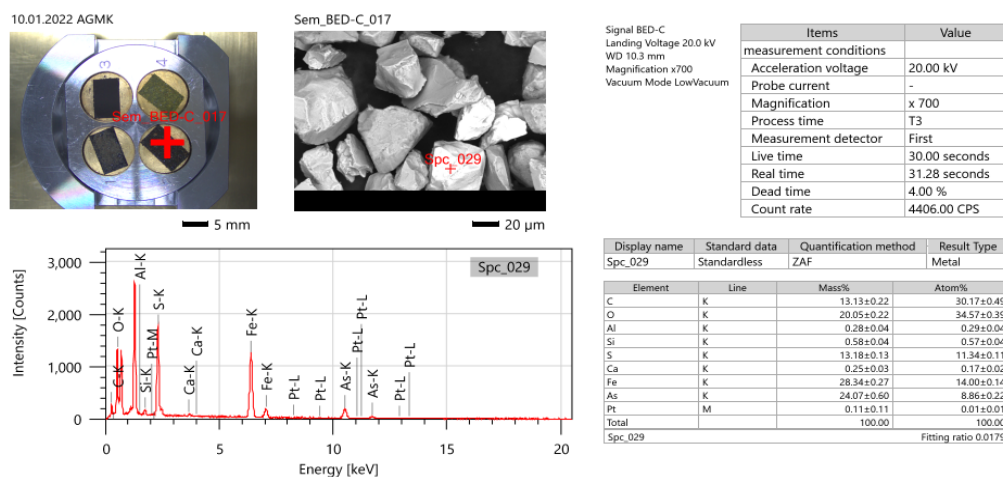


Figure 2. CPP-1 images studied with the JSM-IT 200 electron microscope in 110 times the size by definition of platinum

In Figure 2, the average platinum content of the sample under study was detected in the 029 spectrum with a bright white color, from the analysis results it can be seen that the platinum content in individual particles is 0.11%, respectively, and other samples also showed a low amount of platinum up to 0.01%. For the reliability of the data obtained, analyses were carried out with an energy-dispersive spectrometer in a Scanning electron microscope (SEM-EDX brand Zeiss EVOMA 10/Aztec Energy Advanced X-Act, Zeiss SMT LTD/Oxford Instruments) to study a complete surface map.

This method determines which part of the sample contains the constituent elements. Figure 3 states that the sample mainly contains oxygen, and where there is oxygen, Fe and Si signals shine through. Palladium and oxygen signals are very close, so the patterns of palladium L-line and oxygen K-line are almost the same. The energy resolution of the energy dispersion spectrometer is 130 eV. But the difference between the palladium  $L\alpha$ -line and the oxygen  $K\alpha$ -line is almost 14 eV.

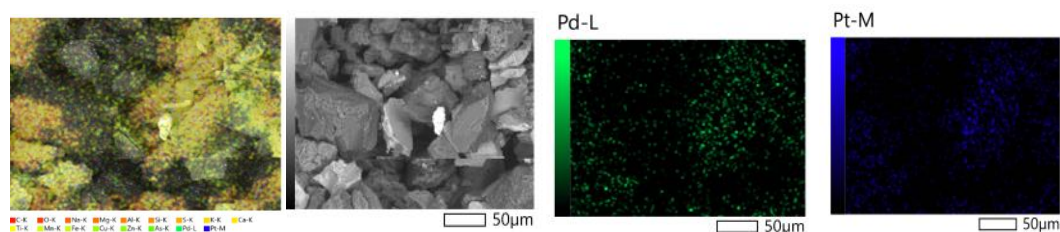


Figure 3. General elemental analysis of the CPP-1 sample

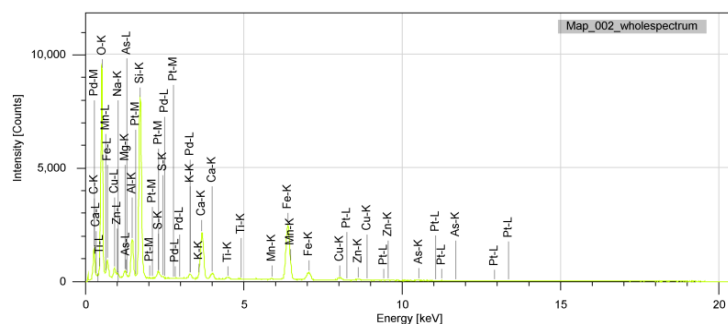


Figure 4. General elemental analysis of the CEP-1 sample (EMF analyses – platinum and palladium compounds with hydrogen were determined)

The palladium content in the studied samples is 0.02-0.25% and, accordingly, with impurities, the increased content of iron and oxygen is explained by iron oxide. Therefore, when analyzing the energy-dispersive spectrometer, palladium and oxygen are shown in the same peak, which are clearly shown in Figure 4. The above-studied elementary and mineralogical analyses of CPP-1 and CPP-2 tails show platinoids in the tails in sufficient quantities and their main method of enrichment can be carried out by the gravitational method and further developments of the technology for obtaining platinoids from gravity concentrates [5].

## Results and Discussion

The studied forms of finding precious metals in the tailings present in the oxidized formation led to the verification of all possible options for the concentration of platinoids, methods of screw separation, enrichment on a jigging machine, a concentration table, intensive gravity using centrifugal concentrators. The highest results of enrichment of CPP-1 and CPP-2 tails with a complex scheme of intense gravity were obtained for gold, silver, platinum and palladium, which amounted to over 80% [21].

The tests were carried out on hundreds of samples, for each CPP-1 and CPP-2 tail using FALCON and Knelson concentrators. The main parameters of the sample size class were kept at least 80% -0.074 mm; the water flow rate was 90 l/min; at the same time, the drain rotation speed in the apparatuses was kept at 600-800 rpm./min. The analysis of the obtained concentrates and enrichment tailings was verified by SEM, which concluded that precious metals with a size above 20-40 microns are well concentrated in heavy fractions at 750 rpm in Knelson for an hour for 10 kg each sample with a yield of 1.80% with gold extraction of 76.27%.

High enrichment results were achieved with two-stage tailings enrichment, this is how after the first concentration, the resulting tails were again carried out by the same Knelson apparatus at low water consumption with a high drain rotation. After gravity of the tailings of flotation enrichment, copper polymetallic ores form a gravity concentrate rich in noble metals of the following composition: for gold, an average of 6-28.7 g/t, for silver 32.94-62.24 g/t, for platinum 19-56 g/t, for palladium 27-93 g/t. The best results of experiments on gravitational enrichment of the tailings of a copper concentrator are shown in Table 2.

Table 2. Results of centrifugal enrichment of copper flotation enrichment tailings (CPP-1,2)

Name	Weight, gr	Exit, %	Content, %				Extraction, %							
			Au, g/t	Ag, g/t	Pt, g/t	Pd, g/t	Cu	Ss	Au	Ag	Pt	Pd	Cu	Ss
Results of gravitational enrichment of samples No.1 (CPP-1 tails)														
Concentrate	180,00	1,80	27,23	32,91	31,45	40,35	1,46	1,46	76,27	13,72	83,27	81,62	11,78	2,82
Tails	9820,00	98,20	0,16	0,56	0,22	0,82	0,20	0,92	27,82	86,28	16,73	18,38	88,22	97,18
CPP-1 Tails	10000,00	100,00	0,21	1,31	0,54	0,49	0,22	0,93	100,00	100,00	100,0	100,0	100,00	100,00
Results of gravitational enrichment of samples No.1 (CPP-1 tails)														
Concentrate	192,00	1,92	6,32	57,73	19,22	27,14	17,48	0,58	27,88	21,20	31,98	33,24	25,88	6,27
Tails	9808,00	98,08	0,32	4,20	1,01	1,20	0,98	0,17	72,12	78,80	68,02	66,76	74,12	93,73
CPP-1 Tails	10000,00	100,00	0,35	5,23	1,46	1,80	1,30	0,18	100,00	100,00	100,0	100,0	100,00	100,00
Results of gravitational enrichment of samples No.1 (CPP-2 tails)														
Concentrate	185,00	1,85	28,70	62,24	56,45	93,21	2,20	0,81	32,97	41,18	66,37	70,38	17,17	3,23
Tails	9815,00	98,15	1,10	1,08	0,70	0,80	0,20	0,46	67,03	58,82	33,63	29,62	82,83	96,77
CPP-2 Tails	10000,00	100,00	0,41	1,84	0,92	1,70	0,24	0,47	100,00	100,00	100,0	100,0	100,00	100,00
Results of gravitational enrichment of samples No.1 (CPP-2 tails)														
Concentrate	198,00	1,98	24,32	49,73	31,22	37,14	9,48	0,24	37,88	31,20	41,98	23,24	35,88	16,27
Tails	9802,00	98,02	0,22	0,90	1,01	1,20	0,98	0,11	62,12	68,80	68,02	76,76	64,12	83,73
CPP-1 Tails	10000,00	100,00	0,42	2,35	1,26	1,18	1,49	0,15	100,00	100,00	100,0	100,0	100,00	100,00
Knelson: water l/min, g=90, Shreddability - 60 min, Coarseness -0.074 mm-80%.														

Further experiments are aimed at developing a chemical technology for extracting individual precious metals from platinoid concentrates. For this purpose, the initial sulfuric acid purification of iron and non-ferrous metals from the concentrate was chosen, with further nitric acid leaching for selective dissolution of silver and palladium in the unsolved part of the cake and separation by filtration. A solution of silver and palladium enters the selective deposition of silver using hydrochloric acid solution and the resulting silver chloride precipitate is sent to the extraction of silver. Experimental data allowed us to conclude that an increase in the temperature of nitric acid leaching by 70-80 ° C leads to evaporation of the solvent, resulting in a decrease in the concentration of the solution, and as a result, the degree of dissolution of metals decreases. This is proved by the results of experiments 1510 and 1511, which explain that at elevated temperatures, due to a decrease in the concentration of the solvent and an increase in the process time, the concentrations of silver and palladium in the solution

decreased markedly. This conclusion gave us the opportunity to determine the optimal temperature of nitric acid leaching in the range of 70-80°C. The next thing we investigated was the optimal duration of the process (see the dependencies of Fig. 5.). Experiments to determine the dependence of the degree of dissolution of silver and palladium on the duration of the process and on temperature were carried out as follows.

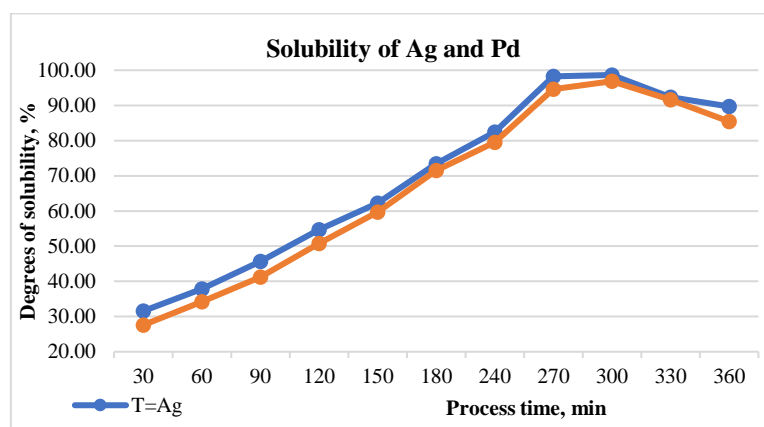


Figure 5. Dependence of the degree of dissolution of silver and palladium on the duration of the process on temperature

The cake after sulfuric acid leaching was poured in small portions into a heated container with a volume of  $V = 0.05\text{m}^3$ , in which nitric acid was prepared in advance in the ratio  $T: W = 1:3$ . The dissolution was carried out with constant heating in the range of 40 °C and gradually rising to 80 °C, while rapid dissolution of noble metals was observed. At a certain process temperature, 11 samples with different leaching durations were studied to determine the optimal process time. Observations have led to conclusions that silver is completely dissolved (fig. 5) for 6 hours. Further continuation of the process does not increase the extraction of silver.

A similar situation was observed with palladium after a 6-hour duration of the process at temperatures of 70-80°C. With this conclusion, the optimal temperature and time of the nitric acid leaching process of samples 1508 and 1509 were established [24]. The palladium containing solution is sent to palladium deposition using a thiourea solution and the resulting precipitate is purified from the impurity and the purest palladium powder is obtained [21]. The remaining cake with a suspended gold and platinum content was subjected to aqua regia leaching, according to the developed scheme in Figure 7. The degree of solubility of metals was found by a chemical method, when analyzing the determination of the metal content in the liquid phase and in the solid cake in an undissolved form. The residual amount of metal is explained by the insolubility of the metal, respectively, the total degree of solubility of the metal in solution comes out [8].

Table 3. Results of chemical analysis of the royal vodka dissolution of gold and platinum cake

№ Sample	C[HNO <sub>3</sub> +3HCl], %	t, °C	τ, min	Detectable elements, mg/l		Degree of solubility, %	
				Au	Pt	Au	Pt
711	30,0	40	30	51,76	20,14	62,12	60,42
712	35,0	45	45	40,55	23,17	68,61	69,52
713	40,0	50	60	78,53	36,23	76,25	72,46
714	45,0	55	75	95,45	45,17	80,82	79,17
715	50,0	60	90	120,27	52,64	86,92	84,56
716	55,0	65	105	150,89	101,78	90,36	91,47
717	60,0	70	120	200,44	180,69	97,18	96,92
718	65,0	75	150	180,55	165,77	94,65	92,33

The obtained results of chemical analysis are given in Table 3, which explains the low leaching temperature, which does not give the expected solubility of metals, in addition, the dissolution time is determined by the basic kinetics of leaching, while without sufficient time the transition of precious metals into the solution is impossible. The main factors affecting solubility are the concentration of the aqua regia solution and its consumption [9,11].

Diagram 6 shows that the degree of dissolution of gold is higher due to its activity than the degree of solubility of platinum, which is more passive than gold. It has been experimentally determined that with an increase in the time of royal-vodka dissolution, the consumption of the solution increases, as a result of which the concentration of gold in the solution increases and amounts to 187 g/dm<sup>3</sup> with a process duration of 120 minutes and a reagent consumption of 2 liters per dissolution for every 100 gr. products obtained [10].

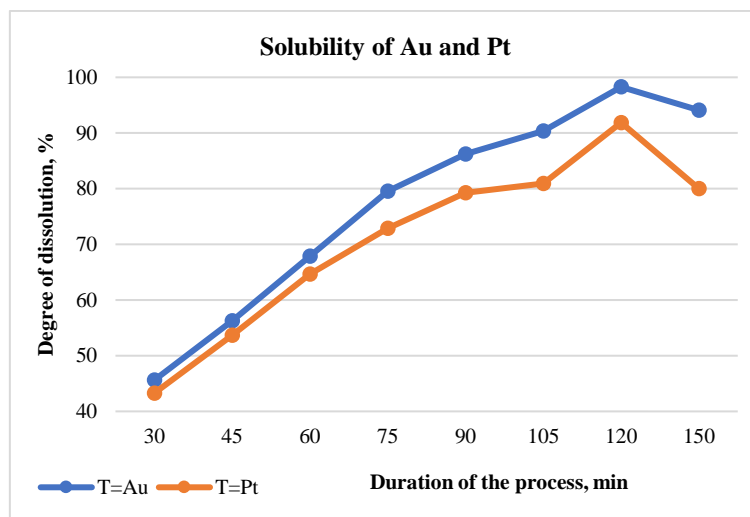


Figure 6. Dependence of the degree of dissolution of gold and platinum on the duration of the process and consumption of aqua regia

Based on the results obtained, the optimal mode of royal-vodka dissolution of the product was determined. In order to remove the undissolved part of the product, a filtration process was carried out, where the cake is removed, and valuable components are in solution. Gold was deposited separately from the platinum-containing solution from the solutions, and the gold precipitate was sent to the refining shop, and the remaining platinum is preserved in the solution [12, 13].

The results of the analysis showed that when adding thiourea with sulfuric acid to a heated platinum-containing solution, PTM is formed with a deposition rate of 98.9% platinum. The obtained platinum of the thiourea complex, the precipitate  $[\text{PtSC}(\text{NH}_2)_2]\text{SO}_4$  was then thoroughly washed with water [14,15].

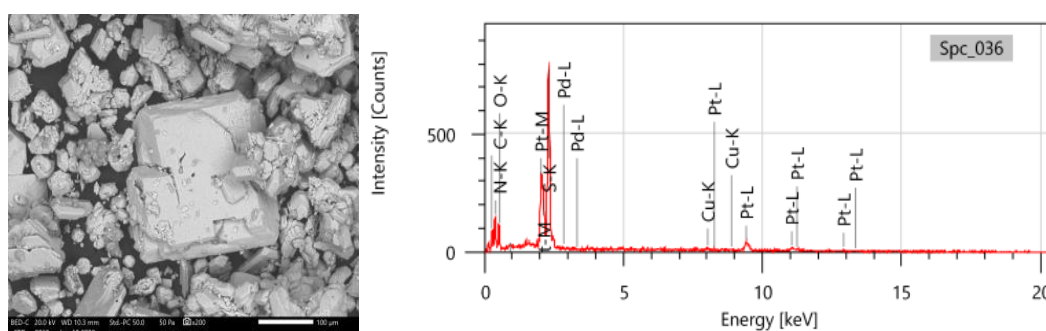


Figure 7. SEM images of the PTM complex (platinum-thiourea complex)

Images of the platinum thiourea complex are shown in Figure 7, which show coarse-grained offsets of a metallic nature. As a result of many experimental experiments and laboratory studies, a technological scheme for processing concentrates containing precious metals (see Fig.8.) with complex extraction of precious metals has been developed and optimal process parameters have been established [16].

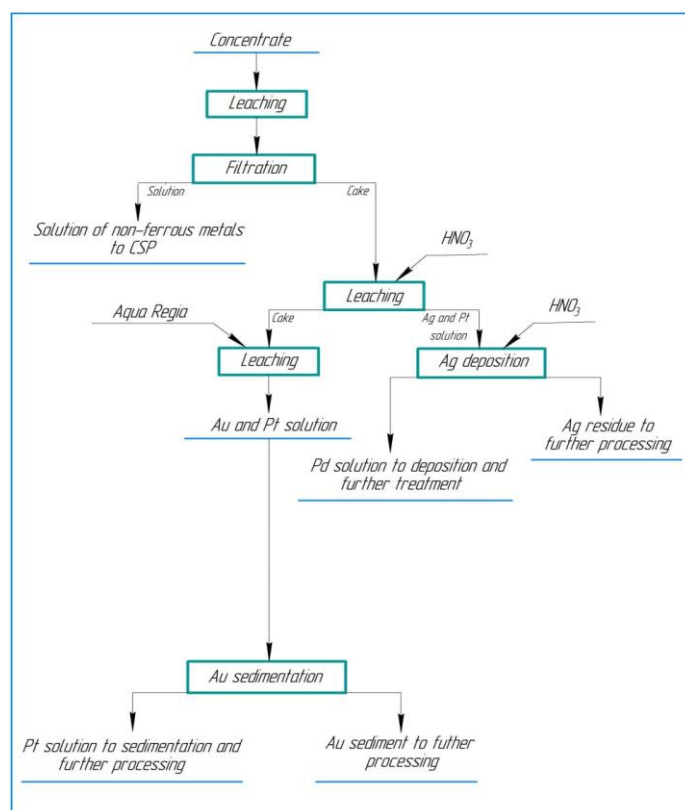


Figure 8. Recommended technological scheme for processing concentrates obtained from the tailings of enrichment with the extraction of precious metals

The result is an affinity platinum powder with a mass fraction of 99.9-99.98% and palladium powder with a mass fraction of palladium of 99.5-99.94% tested in an accredited laboratory of AGMC using atomic emission spectroscopy.

### Conclusion

The introduction of this technology undoubtedly gives a positive economic effect due to the production of precious platinum and palladium, as well as additional extraction of rhodium and improves the environmental situation in places where man-made waste accumulates. According to the stages of the work performed, the following conclusions can be drawn:

For the first time, the technology of gravitational enrichment of the tailings of copper processing plants with the transition of precious metals to the concentrate phase, with further developments of selective extraction of silver and palladium by nitric acid dissolutions, and the optimal parameters of the chemical technology for the extraction of platinum and gold by aqua regia leaching were determined.

The optimal conditions for carrying out the process of royal-vodka dissolution of platinum and gold, produced within 2 hours with a concentration of 60% solution mixture, when heated 60-70°C, where the maximum degree of dissolution of gold is 98.27%, and for platinum 96.92% with a solvent consumption of 20 liters to obtain 1 kilo of the finished product.

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