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Research Article

NEW HORIZONS PROCESSING OF TECHNOGENIC WASTE OF THE COPPER INDUSTRY

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ABSTRACT

At the present time, in the mining and metallurgical industry, there are trends in the processing of man-made waste that have accumulated over the course of many years. Since the world's reserves of ore deposits with a high initial content of non-ferrous metals and easily processed ores are currently practically depleted. This is due to a decrease in the volume of processing of conditioned ores and the involvement in the development of industrial waste, refractory ores and off-balance from low-grade dumps. High prices for metals on the world market create a favorable environment for the development of technologies for the extraction of precious metals involving the processing of mineral resources of technogenic origin. The work studies the mineralogical composition of industrial waste from the copper industry in the conditions of JSC "Almalyk MMC", determined the effectiveness of methods for the selective extraction of platinoids and paid attention to the methods of dissolution, reduction of platinum metals and methods of their purification from various impurities. Based on the study of this topic and the analysis of the results of the research, the authors proposed an optimal technology and complex methods for extracting platinum, palladium and rhodium from industrial waste using selective methods suitable for each metal separately using hydrometallurgy and pyrometallurgy. Hydrometallurgical methods have been developed for the purification of palladium, platinum and rhodium with treatment, respectively, with formic, citric and nitric acids. As a result of the developed technologies, the possibility of complex extraction of platinum group metals from industrial waste has been achieved. In this case, the end-to-end extraction of all platinoids is over 80%.

KEYWORDS

Man-made waste, platinum metals, platinum, rhodium, waste electrolyte solution, waste from a copper-processing plant, selective precipitation, aqua-vodka dissolution, washing, oxidation with hydrogen peroxide, calcination.

INTRODUCTION

The Republic of Uzbekistan has a reliable raw material base for the extraction and production of a number of rare and trace metals. Some of them are concentrated in independent deposits, such as honey and molybdenum, others can be extracted as associated components from copper ores, uranium polymetals and other minerals. In Uzbekistan, the main reserves of platinum, palladium, rhodium and radiogenic isotopes of osmium - 187 are in the porphyry copper deposits of the Almalyk ore region. The concentrate also contains palladium telluride with an admixture of platinum-mereskiite - (Pd, Pt)Te_2. In the Chatkal-Kurama region, manifestations of gabbroid magmatism and associated platinum group metals (PGMs) are known, most often palladium, platinum, and rhodium [1].

The total amount of man-made waste generated during the production of copper in the conditions of Almalyk MMC JSC is 1.3 billion tons. These technogenic wastes mainly include waste from the copper processing plant (MOF-1, MOF-2); sludge from copper smelters. Also, solid technogenic wastes include off-balance sulfide and oxide wastes from the Kalmakkyr deposit. Today, in the conditions of JSC "AGMK" there is no integrated technology for the extraction of precious metals through the processing of man-made waste. The presence of precious metals platinum, palladium and rhodium in the composition of industrial waste of JSC "AMMC" indicates that the plant can carry out production activities for their processing without using fresh ore for several years. Processing and neutralization of man-made wastes of the metallurgical industry is one of the urgent problems of many countries of the world, and the extraction of precious metals on the basis of their complex processing is one of the new directions of the future. Currently, in world practice, only 10-15% of man-made waste is involved in production, in fact, their scope of use is very wide. Therefore, there is a need for complex processing of these wastes using innovative technologies [2].

EXPERIMENTAL TECHNIQUE

At the beginning of the research, we studied the chemical, mineralogical and real composition of the objects of study and, on the basis of this, determined the amount of precious metals in industrial waste, developed optimal technological schemes for their extraction. As objects of study, samples were taken from the waste of a copper processing plant (MOF-1, MOF-2), oxidized, sulfide and mixed off-balance ores of the Kalmakkyr deposit, as well as sludge from copper smelters of JSC AGMK [3].

In order to study the material and mineralogical composition of mixed, oxidized and sulfide out-of-balance ores, tailings of processing plants (MOF-1, MOF-2), sludge from copper smelters, samples were obtained for analysis at the Central Analytical Laboratory usingenergy dispersive X-ray fluorescence spectrometer brand NEX CG RIGAKU.

In the tailing dump №1 (MOF-1) there are 546.2 million tons of tailings with a total copper content of 610.5

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thousand tons, 114.0 tons of gold-bearing waste with a gold concentration of 0.21 g/t, silver-bearing waste - 577.8 tons with a silver content of 1.06 g/t. [4]. Tailings №2 (MOF-2) contain 775.3 million tons of tailings containing copper - 801.6 thousand tons, gold - 156.5 tons, silver - 800.9 tons. The concentration of copper, gold and silver is 0.103%, 0.2 g/t and 1.03 g/t, respectively.

As a result of studying the mineralogical composition of industrial wastes, it was found that the main elements of the platinum group are included in sulfide copper-nickel ores in combination with pure minerals of copper, pyrite, chalcopyrite, and their amount is constantly changing.

According to chemical analysis, the average sample of MOF-2 tailings contains, %: SiO_2 – 36,3; Al_2O_3 -6,64; MgO – 1,64; SO_3 – 1,20; K_2O – 2,19; CaO – 3,58; Fe_2O_3 – 42,4; CuO – 0,55; ZnO – 1,32; As_2O_3 – 0,0182; SnO_2 – 0,008; Rb_2O – 0,0138; ZrO – 0,0218; Au – 0,00; Ag – 0,00; PbO -0,286; MnO – 0,232; TiO_2 – 0,301; Ac – 0,0201; Cl – 0,0516; Sb_2O_3 – 0,00678; U_3O_8 - 0.0015; Ir_2O_3 – 0.0072; BaO - 0.191; Co_2O_3 – 0.0891; V_2O_3 – 0.0094. Information on the content of elements in the tailings of MOF-1 and MOF-2 is given in Table 1.

Table 1.

Number of elements contained in the tailings of MOF 1 and MOF-2 (1321.5 tons)

№	Metal	Clark metal	Content in tails	Unit	Quantity in tailings, t
1	Au (gold)	$4{,}3\cdot10^{-7}$%	0,21	g/t	277,51
2	Ag (silver)	$7\cdot10^{-6}$ %	1,06	g/t	1400,79
3	Se (selenium)	500 mg/t	5,0	g/t	6607,5
4	Pt (platinum)	$5\cdot10^{-7}$ %	0,001	g/t	1,32
5	Pd (palladium)	$1\bullet10^{-6}$ %	0,410	g/t	541,81
6	Re (rhenium)	$7\cdot10^{-8}$ %	0,038	g/t	50,21
7	Os (osmium)	$5\bullet10^{-6}$ %	0,0018	g/t	2,37
8	In (indium)	10^{-5} %	0,042	g/t	55,50
9	Ru (ruthenium)	$5\bullet10^{-7}$ %	0,091	g/t	120,25
10	Te (tellurium)	$1\cdot10^{-6}$%	0,007	g/t	9,25

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11	Mo (molybdenum)	$3 \cdot 10^{-4}$ %	49,0	g/t	64753,5
12	W (tungsten)	1,3 g/t	4,50	g/t	5946,75
13	Rh (rhodium)	$1 \cdot 10^{-7}$ %	0,039	g/t	51,53
14	Ir (iridium)	10^{-7} %	0,0084	g/t	11,10
15	Be (beryllium)	3,8 g/t	0,370	g/t	488,95
16	Ga (gallium)	19 g/t	6,80	g/t	8986,2
17	Nb (niobium)	18 g/t	0,200	g/t	264,3

The results obtained indicate that during flotation enrichment, heavy fractions containing precious metals are wetted with water and pass into the tailings. This made it possible to test the possibility of gravitational enrichment of the tails. It is known that carrying out screw separation, intensive gravity during the enrichment of MOF-1 and MOF-2 tailings according to a complex scheme allows the extraction of precious metals gold, silver, platinum and palladium at least 80% [6].

The total amount of off-balance ore from the Kalmakkyr deposit at dumps A-7 and A-8 is 74.5 million tons, which contains 31.6 tons of gold with a concentration of 0.424 g/t and 132.2 tons of silver with a content of 1 .77 g/t [3].

Off-balance oxidized ores of the Kalmakkyr deposit are concentrated in dumps №39, 9, 10, 8a, A-4. The total amount of oxidized off-balance ores in dumps №39, 9, 10, 8a, A-4 is 63.8 million tons, they contain 31.1 tons of gold, 144.5 tons of silver. To study the distribution of precious and rare metals from off-balance ore dumps, monominerals were selected:

pyrite, chalcopyrite, molybdenite, etc. The following distribution of precious metals in g/t was established: Au-3.2; Ag-8.2; Pd - 0.25; Pt - 0.20; Rh-0.02; Ru - 0.93; Os - 0.015. According to chemical analysis, the average sample of sulfide ore contains, %: SiO_2 – 54,3; Al_2O_3 – 16,5; MgO – 2,49; SO_3 – 1,49; K_2O – 5,72; Na_2O - 2.52; CaO – 7,26; Fe_2O_3 – 7,96; CuO – 0,119; ZnO – 0,0214; Ga_2O_3 – 0,0042; As_2O_3 – 0,0057; SnO_2 – 0,0037; Rb_2O – 0,00295; SrO – 0,0566; Au – 0,0019; Ag – 0,0017; PbO - 0,0018; NiO – 0,0022; MnO – 0,312; TiO_2 – 0,571; Ac – 0,0037; Cl – 0,028; Sb_2O_3 – 0,0017; U_3O_8 – 0,0014; MoO_3 – 0,003; Co_2O_3 – 0,0132; BaO – 0,0761; Cr_2O_3 – 0,0042; V_2O_5 – 0,0352 [7].

40 samples were studied, on the basis of which the average amount of precious metals was determined and a separate objective assessment was made for each metal (Table 2).

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Table 2.

Average content of metals in the dumps of the Kalmakir deposit

№	Metal	Amount of metal in oxidized ores, t	The amount of metal in sulfide ores, t	General content, t
1	Au (gold)	31,1	31,6	62,7
2	Ag (silver)	144,5	132,2	276,7
3	Se (selenium)	74	86,42	160,42
4	Pt (platinum)	143,55	167,625	311,175
5	Pd (palladium)	194,59	227,225	421,815
6	Re (rhenium)	16,97	19,817	36,787
7	Os (osmium)	4,568	5,3342	9,9022
8	In (indium)	0,1276	0,149	0,2766
9	Ru (ruthenium)	1,0846	1,2665	2,3511

As a result of studying the chemical composition of waste, the possibility of extracting precious metals from their composition was established using improved methods for processing man-made waste. The process of studying the mineralogical composition and the total mass of technogenic waste and off-balance ores formed as a result of mining operations at Almalyk Mining and Metallurgical Combine JSC shows that the amount of precious metals in waste is of great interest for production, but efficient separation of noble and rare metals is possible using modern hydrometallurgical and pyrometallurgical technologies [8].

Atomic emission spectroscopy methods have also been used to study the composition of copper anode sludge formed during the processing of industrial waste, enrichment of tailings of copper production of rich PGMs. The results of the analysis are shown in table 3.

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Table 3.

Results of chemical analysis of copper anode sludge

Element	Copper sludge, concentration, %	Element	Copper mud, %
Platinum	0,84	Silver	5,0-9,0
Palladium	4,1-5,45	Copper	18-22
Rhodium	0,27-0,35	Nickel	16-24
Iridium	0,175-0,019	Iron	0,5-1,8
Ruthenium	0,095	Selenium	2-5
		Tellurium	0,7-1,1
Osmium	0,102	Sulfur	2-4
Gold	0,729	Silicic acid	2,5-4,5

An objective study of the average content of metals in the dumps of the Kalmakkyr deposit made it possible to use gravity enrichment to obtain precious metal concentrates with their further pyrometallurgical processing. The obtained concentrates after the processing of flotation tailings MOF-1,2, and the enrichment of waste deposits "Kalmakkyr" were combined and sent to the converter smelting with further anode smelting in order to obtain anode copper concentrated on precious metals. The choice of such a complex scheme for the processing of concentrates was justified by researchers based on the practice of obtaining gold, silver, platinum and palladium from the waste of the copper industry by combining pyrometallurgy and hydrometallurgy [9].

RESULTS AND DISCUSSION

The study of spent electrolytes in order to obtain platinoids (platinum, palladium, rhodium) was carried out at the MPZ of AGMK JSC, as a result of which a new technological scheme was developed (Fig. 1).

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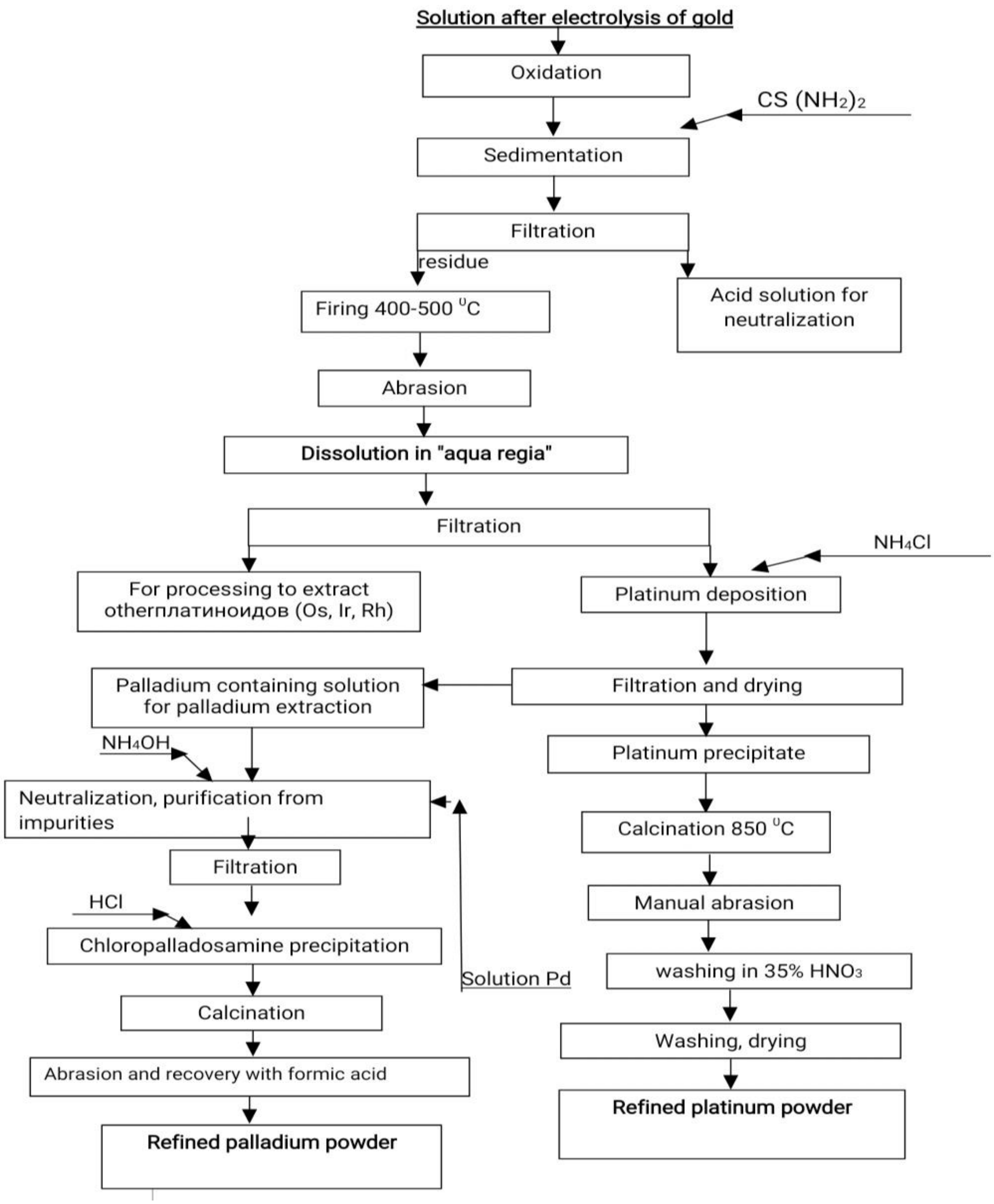

Fig.1. Technological scheme for obtaining refined platinum and palladium powder from spent electrolytes of the gold refining shop

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New operations in this technological scheme are:

- Accumulation of platinum-palladium solutions after gold electrolysis, where the content of platinum and palladium in the solution is more than >100 mg/dm³ and they are in the form of chloride compounds: $PtCl_2$ and $PdCl_2$;
- Oxidation of waste electrolyte solutions with hydrogen peroxide after electrolysis of gold with a concentration of platinum of 100-800 mg/dm³, as a result of which $PtCl_2$ turns into $PtCl_4$;
- Sedimentation of palladio-thiourea complex in thiourea solution, product filtration, cake roasting at 500-600°C. While the firing time was 2-3 hours and the resulting product was subjected to reduction with a solution of hydrazine. The reduced product was sent for washing with distilled water, after which it was dried at a temperature of 100-110°C and dissolved in aqua regia [9].

With increasing duration, the degree of solubility of metals increased, since the aqua leaching of Pd and Pt is associated with the solubility kinetics. Figure 2 shows that the degree of dissolution of Pd is higher than the degree of solubility of Pt. It was experimentally determined that with an increase in the time of aqua regia dissolution, the consumption of the solution increases, as a result of which the concentration of palladium in the solution increases accordingly and amounts to 200 g/dm³ at 120 minutes of the process duration with a reagent consumption of 2 l per 100 gr palladium product [10].

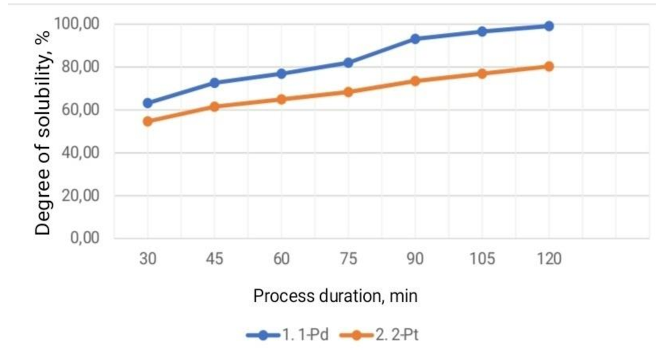

Fig.2. Dependence of the degree of PGM solubility on the duration of the process.

As a result of the research, it was found that palladium is in a solution of tetrachloropalladic acid, and platinum in the form of ammonium hexachloroplatinate precipitates, which makes it possible to accurately separate Pd from Pt without much effort. Based on the results of the research, a technological scheme was proposed (Figure 1), implemented in the production conditions of the MPZ workshop.

CONCLUSION

As a result of extensive research, including a number of experiments and experiments, a new technological scheme was developed, consisting of 20 operations with a cycle duration of 24-26 hours. At the same time, the cost-effective extraction of PGM from solutions containing 50 mg of platinoids per 1 liter reaches more than 84%.

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Table 4.
Results of chemical analysis of the resulting platinum powder

Name material	Element content, %										
	Pt	Pd	Rh	Ir	Ru	Au	Pb	Fe	Si	Sn	Al
Pt powder	99,98	0,01	0,0012	0,0002	0,0018	0,002	0,002	0,0012	<0,002	<0,0001	0,002
	Element content, %										
	Sb	Ag	Mg	Zn	Cu	Ni	Mn	Cr	Co	Ca	
	0,002	0,002	0,0003	<0,0001	0,001	0,001	0,001	0,001	0,001	0,005	

Table 5.
Results of chemical analysis of the resulting palladium powder

Name material	Element content, %										
	Pd	Pt	Rh	Ir	Ru	Au	Pb	Fe	Si	Sn	Al
Pd powder	99,94	0,0022	0,0310	0,0003	0,0039	0,0032	<0,0001	0,0055	<0,0001	<0,0001	0,0003
	Element content, %										
	Sb	Ag	Mg	Zn	Cu	Ni	Mn	Cr	Co	Ca	
	0,0022	<0,0001	0,0001	<0,0001	0,0050	0,0012	0,0001	0,0006	0,0005	0,0004	

The result is refined platinum powder with a mass fraction of Pt 99.9-99.98% (table 4.) and palladium in powder with a mass fraction of palladium 99.5-99.94% (table 5.). The method is also suitable from an ecological point of view, since the resulting acidic filtrates are neutralized with an alkali solution or alkaline filtrates obtained by reducing palladium to metal with formic acid or hydrochloric acid hydrazine. The introduction of this technology undoubtedly gives a positive economic effect due to the production of platinum and palladium, additional extraction of rhodium and improves the environmental situation in places where man-made waste accumulates.

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