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Resource Potential of Stale Flotation Tails of Copper-Oxygen Ores with and Possibe Gold and Silver Extraction

Medyanik N.L.[1], Leontieva E.V.[1], Mishurina O.A.[1], Shadrunova I.V.[2]

[1]Nosov Magnitogorsk State Technical University, Russia.
[2]Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences, Russia.

[1,2,4]Orcid: 0000-0003-0973-8899, 0000-0003-3412-8902, 0000-0003-3520-2705

Abstract

The article analyzes the possibility and efficiency of processing the stale tailings of flotation plants of the copper-pyrite complex. The resource potential, material composition and technological and logical possibilities of processing a number of technogenic objects are considered. The interrelation and influence of mineralogical and technological factors on the choice of tailings processing technology has been analyzed. Based on complex studies, the stale tails refer to the hard-to-disintegrate form of the geothermal resources due to the high pyrite content and low content of gold and silver present in the "persistent" minerals. The paper analyses the influence of the main factors affecting the formation of the elemental composition of tailings: mineralogical, technological and ecological. The heterogeneous morphometric and mineral composition of sulphide aggregates, their difficult opening and high dispersity characterize the stale tails as hard-flocked raw materials. Concluding, it is impossible to extract gold and silver from this resource using traditional technologies and it is necessary to open precious metals thoroughly by chemical processing.

Keywords: Concentration tails, copper-pyrite ore deposits, material composition, gold, silver, technologies, processing.

INTRODUCTION

In the tailings of the mining enterprises of the Southern Urals copper-pyrite complex, the largest of them is the Uchalinsky GOK, to date, tens of millions of tons of stale flotation tailings have been accumulated, which contain a significant amount of expensive heavy metals [5, 8], in particular, about 100 tons of gold and 1200 tons of silver [2, 8]. Consequently, the development of technologies for the integrated development of tailings storage facilities is an urgent scientific and technical task, the solution of which will significantly expand the raw material base of enterprises, and will increase the effectiveness and rationality of subsoil use. In addition, the need to involve tailing dumps in the secondary development is due to a number of environmental problems, the solution of which will improve the situation in the region and reduce the costs of enterprises to pay environmental fines [6-9].

Active development of these technogenic objects is hampered by:

- low efficiency of pre-extraction of gold and silver, other non-ferrous metals by traditional gravity-flotation technologies of enrichment, caused by structural and phase features of their location in waste [1-3];
- Significant costs (autoclave, bacterial oxidation), duration (heap leaching, biooxidation), environmental hazard (cyanidation, heap leaching, calcination) of gold and silver recovery using existing technologies.

Currently, technologies for the extraction of gold and silver from ores and wastes from enrichment are using cyanides [2-4, 7]. However, tails of flotation of pyrite copper-zinc ores are "persistent" for cyanidation, since they contain predominantly fine-dispersed and ionic gold encapsulated in sulphide associations. In addition, cyanides are toxic and environmentally hazardous reagents. Therefore, there is a need to develop innovative chemical methods of opening and recovering gold and silver from the formed volumes of tailing dumps of copper-complexed enterprises using combined methods and cyanide reagents [2, 3, 5].

The solving basis for this issue is a comprehensive approach taking into account the amount of factors: mineralogical, technological and ecological.

In view of the variety of factors determining the efficiency of the processing of stale tails of flotation of copper-pyrite ores, it is advisable to thoroughly study their material composition and technological properties in order to justify the selection of a rational method and reagents for selective extraction of gold and silver and other valuable metals.

METHODOLOGY

General scientific and special research methods were used in the work. During the implementation of the experiments, a set of physico-chemical analysis methods were used: thermodynamic analysis, synchronous thermal analysis (thermogravimetric analysis and differential-scanning calorimetry TG-DTA/DSC using a combined thermal analyzer Netzsch STA 449 F3 Jupiter, NETZCH-Proteus, the analysis was conducted in an argon atmosphere), UV spectroscopy (Cary 60 UV-Vis Agilent Technologies spectrophotometer with an automated data processing system), qualitative chemical and assay assays.

RESULTS AND DISCUSSION

In terms of material composition, copper-zinc pyrite-bearing ores of the Urals region belong to the "persistent" type of

sulphide gold-bearing raw material [5, 9].

In the process of flotation, the ore minerals extracted from the bowels are mechanically and chemically destroyed to various degrees, this process continues after the storage of waste. The presence of oxidizing agents, such as: O_2, Fe^{+3}, Cu^{+2}, MnO_2, leads to the destruction of sulphides, leading to further dissolution and migration of liberated gold ions [4, 5, 9].

The process of gold dissolution depends on the pH of the solution medium: in acid media, on the presence of chloride ions, in neutral and alkaline media, on the presence of thiosulfate ions, humic acids. Minerals, through which gold solutions migrate, precipitate it in the form of colloidal deposits, the main gold concentrators - iron hydroxides, pyrite, a natural sorbent of gold is a carbonaceous substance.

One of the largest tailing dumps in the Urals, the Uchalinsk preparation plant (PP) of Uchalinsky GOK, has a total volume of 25 million m3 and an area of 113 hectares, the capacity of the laid tailings has reached 25 m, the waste volume exceeds 55 million tons. They contain more than 52 tons of gold and 770 tons t of silver. The content of metals in the tails: gold 1,2 - 2,0 g/t, silver 15 - 20 g/t, The main mass of waste (80 - 90%) is composed of particles with a size of -0.074 mm. The share of sulfides is 50-75% of the tail mass, among them pyrite predominates (90-98%) [5, 9].

In the old tailings pond of the Sibayskoye PP of the Uchalinsky GOK with an area of 23.5 hectares, the predicted gold reserves are 4 tons, the content of gold and silver in the old-year tailings is 1.5 to 1.7 times higher than that for newly-stored waste. The sulfides, as a result of weathering in the surface layer, decompose to sulphates, the pyrite content on the surface is 1-7%, at a depth of 2-3 m - about 30-40%, in the internal mass of tailings - 62%. The share of gold, emulsion-impregnated into sulfides, in the thickness of the tailings is 75 - 80% [5, 6].

The old-year waste from the Buribayevskaya factory has a macro-layered character. In the layers of red color are represented iron hydroxides, pyrite, quartz, the content of gold in them is 1.5 g/t, silver is 7.6 g/t, which is 7.5 and 3.1 times higher than in layers of gray color, containing along with pyrite and quartz, silicates and sulfates of copper and iron (II) [3, 5].

For stale tails of PP "Gaisky GOK" with a particle size of 71% - 0.07 mm, the average gold content is 0.83 g/t, silver - 7.0 g/t; up to minerals - 54,8%, total amount of sulfides - 34,2%, pyrite - 33%. The phase analysis of the tailings showed that more than 70% of gold is found in hard-cyanide forms (sulfides, films, in quartz) [5, 9].

According to the data [5, 8], the pyrite-containing tails of JSC "BMCK" are finely divided raw materials with gold content up to 1.27 g/t, the share of "persistent" for cyanidation of gold is 74.4%. In stale tails of the Krasnouralsk Region the content of "persistent" gold is more than 43%, of which 38.6% is contained in sulphides [2].

Thus, tailing dumps of flotation waste of copper-zinc pyrite ores of the Urals, along with individual features, have a number of common characteristics:

- are formed by a finely divided, complex composition with a high content of pyrite (the most stable to oxidation of sulfide) and not high concentrations of precious metals, with their predominance in cyanidation-resistant forms.

- the content of gold and silver in wastes are comparable with those in the initial copper-pyrite ores (0.83-3.48 g/t Au and 16.2-23.9 g/t Ag) [4, 5].

In view of the considerable volumes of man-made raw materials and high preparedness for recycling, the recycling of stale tails with pre-extraction of gold and silver is promising.

The possibility of efficient processing of this technogenic raw material is determined, first of all, by its material composition.

Mineralogical properties of stale tails were studied using waste Uchalinsk preparation plant. According to the results of chemical, granulometric, X-ray phase, optical-microscopic and rational analyzes, waste is a polymineral fine-dispersed raw material with a low content of gold and silver (up to 2 and 20 g/t, respectively), low content of copper and zinc sulfides (1-4 %) and a high content of pyrite (50-56%).

Table 1 shows the chemical analysis of two samples of stale tails, according to which the content of iron and sulfur in the tail varies insignificantly, and the concentrations of copper and zinc vary greatly.

Table 1: Chemical composition of waste.

Chemical element	Au, g/т	Ag, g/т	Fe_{gen}, %	$S_{gen.}$, %	Cgen, %	Cu, %	Zn, %
Content	1,7-2,0	18,0-19,5	23,0-26,8	28,1-28,7	0,22-0,60	0,12-0,73	0,34-1,26

The presence of carbonaceous substance (CS) in waste even in the detected low concentrations (less than 1%) can lead to low gold recovery due to the prebombing effect [6], since in some cases the hydrocarbon has sorption activity to gold. To avoid this, CS must be deactivated during oxidation and oxidation.

Quantitative X-ray phase analysis (Table 2) established: the main ore tail mineral is pyrite (from 50 to 56%); rock minerals, mainly quartz, account for 40 to 50% of the waste.

According to the results of studies of the chemical and mineral composition, samples of stale waste from the existing Uchalinskoy tailings tailings are somewhat different in content of the main elements and minerals. This may be due to the diversity of the qualitative and quantitative composition of the ore processed at the enterprise, as well as the different shelf life of tailings.

Table 2: Mineral composition of stale waste.

Mineral	Mass. %
Quartz	13 - 21
Plagioclase	4 - 5
Chlorite	6 - 9
Mica	до 4
Gypsum	8 - 10
Barite	3 - 4
Pyrite	50 - 56
Sphalerite	до 4
Tennantite	до 1
Hydroniumarositol	до 2

Table 3: Component composition of the stale tailings of the Sibai branch of JSC Uchalinsky MPP.

$Fe_{gen.}$ %	S, %	Cu, %	Zn, %	As, %	Au, g/t	Ag, g/t	Se, g/t	Te, g/t	Sb, g/t
20-35	24-38	0,1-0,4	0,3-1	0,1-0,2	0,5-2,5	8-30	22-50	26-60	24

Data on the material composition of old waste in the preserved tailing dump at the Sibaisky concentrator at Uchalinsky MPP testify to a greater heterogeneity in the composition of the tailings in terms of area and depth (Table 3).

As a result of long-term storage, the ratio of sulphide and non-metallic minerals (mainly quartz) has changed from 3: 1 to 1: 3 due to oxidative destruction of sulphides, especially near the surface. The decomposition promotes the release of gold bound to sulfides, its migration and redeposition in the thickness of stale tailings of enrichment, for which the gold content is up to 1.5-2 times higher than in the current tails. At the same time, oxidation of sulphide waste makes their processing by flotation difficult.

One of the decisive factors determining the choice of the method for processing technogenic raw materials is the analysis of mineral interrelations of gold (phase analysis), the results of which are presented in Table. 4.

Table 4: The results of a rational analysis of gold in the stale tails of the Uchalinsk concentrator.

Forms of gold finding	Content, g/t	Content,%
В сростках (в цианируемой форме)	31,0	
In cyanated form	0,51 - 0,62	30,0 - 31,0
Gold in films	0,08 - 0,10	4,0 - 5,9
In sulfides	0,89 - 1,11	52,3 - 55,5
In quartz	0,19 - 0,20	9,5 - 11,8
General content	1,7 - 2,0	100

According to the phase analysis, only 30 - 31% of gold in the stale tails of Uchalinskaya concentrator is in cyanated form (free gold and gold in the intergrowths). The content of gold coated with acid-soluble films and associated with quartz is 4.0 - 5.9 and 9.5 - 11.8%, respectively.

The main proportion of gold stale wastes (52.3 - 55.5%) is contained in a matrix of sulphide. For comparison, in the stocked tailings of the Sibai concentrator, the share of cyanated gold is less than 25%, covered with films - 2-10%; 75-80% gold is finely impregnated into sulphides.

The results of the conducted rational analysis are consistent with the data of mineralogical studies of the Ural pyrite ores and tailings of their enrichment [3, 5, 9], according to which gold in waste is present not only in native form in gold-silver alloys, but in a significant degree is associated with sulphides in the form of finely dispersed and isomorphic inclusions. For example, in the Uchalinskoye and Uzelginskoye ore deposits, the share of free gold is only 13-16%, about 85% Au is contained as solid solutions and smallest sprouts in sulphides. Gold concentrations reach 16-20 g/t in pyrite, 4.6 g/t in chalco pyrite, 10.6 g/t in sphalerite. When grinding to flotation size, gold sprouts are not disclosed, which does not allow to obtain from the waste large-scale flotation concentrates. Silver is also found in the form of inclusions in sulfides - tennantite, sphalerite. In addition, the waste contains gold-containing and gold-silver-containing minerals - tellurides, selenides, sulfo-salts. Standard reagent flotation regimes for their processing are not effective.

The results of chemical, mineral and phase analysis make it possible to classify the stale tails of flotation of pyrite ores as a kind of difficult-enriching raw material. The resistance to cyanidation is due to the significant quantities of disperse gold conserved in sulfides and quartz, the presence of cover films of natural and technogenic origin. Films, mainly from iron hydroxides, impair the flotational enrichment of tailings. The high content of pyrite tails, which has a low chemical activity, in addition to cyanidation, reduces the efficiency of sulfuric acid leaching of wastes and limits the use of this reagent.

Table 5: Testing for tail enrichment by gravity method.

Products	Yield,%	Au, g/t	Extraction Au,%	Ag, g/t	Extraction Ag,%	Pressure, bar
Sample	100,00	2,00	--	18,0,0	--	0,0
Concentrate	86,77	2,20	95,45	19,00	91,59	0,1
Tails	13,23	0,69	4,55	11,41	8,41	
Concentrate	74,22	2,24	83,12	18,54	76,44	0,2
Tails	25,78	1,31	16,88	16,41	23,56	
Concentrate	59,16	2,25	66,55	18,78	61,72	0,3
Tails	40,84	1,64	33,45	16,87	38,28	

According to the sieve analysis, it was found that 89.42% of the tail material had a particle size of less than 0.04 mm, containing virtually all gold (96.12%) and silver (97.62%). This circumstance indicates the need to use for metallurgical waste metallurgical methods that ensure high efficiency and selectivity of processing.

To test the possibility of recycling waste by gravitational method and obtaining rich in gold, silver concentrate was tested for concentrating on the centrifugal concentrator "ITOMAK-KN-01". The results of the experiment are shown in Table. 5.

From the test results it follows that, despite the high extraction of gold in the heavy fraction (66.55 - 95.45%), its mass fraction in the concentrate in comparison with the initial material does not increase significantly. The increase in pressure did not affect the gravity of the tailings by the gravitational method. A similar dependence was obtained for silver. Consequently, the maintenance of gravitational enrichment of stale tails is impractical, since with a large concentrate yield, there is no increase in the content of precious metals.

CONCLUSION

Elemental composition of tails of flotation of copper-pyrite ores refers to the "persistent" type of sulphide gold-bearing raw material.

Tails of flotation of copper-pyrite ores are a raw material of a complex material-mineral composition, comparable in content to gold and se-ribs with initial ores, which makes their processing promising and efficient;

Solid waste flotation refers to hard-to-digest, "resistant" mineral raw materials. The reasons for "perseverance" are due to the high content of dispersed gold in sulphides and the presence of carbonaceous matter.

Precious metals (gold and silver) in the stale tailings of the flotation of the ores under investigation are found in numerous own minerals, represented by native gold and silver, "persistent" tellurides, selenides and sulphosalts. These minerals form microscopic (5-40 microns), submicroscopic and nano-dimensional discharges, associated with sulfides in intractable splices of a complex structure. In addition, a significant part of precious metals is isomorphously contained in sulphides, which are not only carriers, but also concentrators of gold and silver.

The revealed features of the material composition of the stale tails cause the low efficiency of gold and silver recovery from them by traditional methods and indicate the need for the opening of "persistent" associations by chemical methods using non-cyanide reagents.

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