

Beneficiation and hydrometallurgical processing of gold-containing sludge

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Abstract. The research results of technogenic objects in the Far East of Russia, in particular, the silt of the settling pond "Chalgany" and the waste of the Chalganov kaolin plant are given. The presence of valuable components in the investigated objects is shown, in particular: gold, noble metals, rare earth elements. It is established that gold in the investigated objects is represented mainly by a difficult-to-extract finely dispersed class of fineness (<5 μm). The methods of preliminary concentration and hydrometallurgical processing, which allow extracting gold from the studied technogenic objects, are proposed. The effectiveness of non-cyanide methods of ammonia-thiosulphate and thiocarbamide leaching was investigated. It is shown, that the efficiency of gold recovery from the silt of the settling pond "Chalgany" by the thiocarbamide method reaches 93.5%. It is established that the waste from the Chalganovskiy kaolin plant, after recovering the concentrate of precious metals from them, can serve as a raw material for the production of chemically pure silicon and silica, as well as aluminum, its compounds, and refractory fibrous materials.

1 Introduction

Currently, the situation in the gold mining industry of the Russian Federation is characterized by a critical imbalance between production and buildup of stocks, which is exacerbated by a decrease in the quality of ores, a decrease in the efficiency of gold mining and the accumulation of significant amounts of technogenic waste. With the depletion of ore reserves containing coarse gold, arises the task of involving into processing of placer mines containing finely dispersed gold.

The prospects for processing of gold-containing ores are largely related to the solution of the problem of refractory ore beneficiation, which is contingent on the cohesion of gold in sulphides (arsenic pyrite, pyrite) and a high proportion of fine-grained gold [1]. In connection with this, various technogenic wastes, including technogenic gold mining wastes, become a competitive source of mineral raw materials for gold mining. These objects are formed due to the imperfection of the applied gold mining technologies, when, depending on the type of the deposit and methods of gold recovery, 10 to 50% of metal can

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remain in the used material [2]. Since gold deposits are recovered by gravitational methods, mainly coarse gold fractions are extracted, it means, that such technogenic objects can contain significant gold reserves, represented by particles ranging in size from tens of microns to micron, densely associated with mineral components of various nature [3, 4], what makes such raw materials close to poor, refractory ores. At the same time, one should pay attention to the fact that technogenic gold-containing objects, as a rule, are located near the infrastructure that has remained since opening of the deposit. Moreover, such objects can be a promising raw material for extraction of other useful components. For example, gravitational methods of gold recovery lead to natural beneficiation of sand. Also, gold placers can contain minerals with stannum, zirconium, tantalum, niobium, tungsten, rare earth elements (REE), etc. Practically for all methods of gold recovery by gravity separation, these minerals can be concentrated together in the place of gold-containing fraction [5].

Since the degree of gold extraction by gravitational technologies is inversely proportional to the size of gold grains[6], the effective use of hydrometallurgy methods turns out to be a promising approach for efficient extraction of fine-grained gold from technogenic waste. At the same time, the most widely spread method of cyanide leaching of gold has its limitations due to the environmental hazard of the reagents and the decrease in efficiency of gold recovery from carbonaceous and organic raw materials as well as from raw materials high in copper, zinc, nickel, antimony, and arsenic. The last fact can be critically important when working with complex technogenic gold-containing raw materials. An alternative to cyanide leaching, capable to work efficiently with cyanide-resistant ores of complex composition, are the methods of thiocarbamide and ammonia-thiosulphate leaching [7, 8].

This article is devoted to the analysis of prospects of gold and other valuable components recovery from technogenic objects in the Far East of Russia, in particular, from the silt of the settling pond "Chalgany" and Chalganovskiy kaolin plant wastes. Hydrometallurgical methods of ammonia-thiosulphate and thiocarbamide leaching are considered as environmentally and economically promising technologies for gold recovery.

2 Materials and methods

The content of noble and rare-earth metals in technogenic gold-containing wastes was determined by atomic absorption spectrophotometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) in the Laboratory of Analytical Chemistry and Micro- and Nano-Studies of the Common Use Center of the Far East Geological Institute of the Far East Division of Russian Academy of Sciences (FED RAS) and the laboratory of Khabarovsk Innovation Analytical Center in Institute of Tectonics and Geophysics of the Far East Division of Russian Academy of Sciences.

To estimate the amount of Au, Pt, and Pd by the AAS method, the samples were successively decomposed with a mixture of concentrated acids HF + HNO₃ at a ratio of 2:1, then with HCl + HNO₃ at a ratio of 3:1 and HCl, followed by coprecipitation with Te according to TSNIGRI-2005. Measurement of Au, Pt and Pd was carried out in the electrothermal atomization regime using the atomic absorption spectrophotometer Shimadzu 6800. For the measurement of Ag by the AAS method, the samples were decomposed by a mixture of concentrated acids HCl + HNO₃ (3:1) and HCl according to HCAM-130-C. The measurement of Ag was carried out in flame using the atomic absorption spectrophotometer Shimadzu 6800.

ICP-MS researches were carried out with the use of spectrometers Agilent 7700 (Agilent Technologies, the USA) and ICP-MS Elan DRC II PerkinElmer (the USA), according to ПНД Ф 16.1:2.3:3.11-98.

To estimate the amount of gold in technogenic objects, the method of instrumental neutron activation analysis (INAA) was used at a compact installation with a radionuclide excitation source based on ^{252}Cf developed at the Institute of Chemistry FED RAS [9]. The detection limit of gold according to isotope ^{198}Au for INAA from the samples of 50-100 g was 0.2 g/t.

The control of gold content in the samples from Chalganovskiy kaolin plant was carried out by an assay test in accordance with МА ИАЦ-43-2004, ФР.1.31.2004.01195 [10].

The chemical composition of samples was determined by X-ray fluorescence analysis (XRF) at the Institute of Chemistry FED RAS (the Common Use Center - the Far Eastern Center of Structural Research) and the Institute of Geology and Nature Management, FED RAS with the use of Shimadzu EDX 800 HS and XRF-1800 Shimadzu spectrometers. The sensitivity for elements from Na to U was up to 1 ppm.

The studies were carried out on two types of samples:

As the first object of study, the silts of the settling pond "Chalgany" were used, which are the technogenic wastes of gold-containing raw materials of various deposits "Solovievsky placer", "Oktyabrsky placer", deposit "Beregovoe", etc. The samples were taken from the experimental site of the laboratory of Amur Complex Scientific Research Institute "Chalgany" after gold recovery from gold-containing sands using gravitational methods of beneficiation.

As the second object of study, the wastes from Chalganovskiy kaolin plant were used. Among them were the tailings dumps of suspended particles of clay minerals transported by process water streams, as well as sand line waste and quartz-feldspar sands concentration tailings. Within the tailings dump, 20 wells with a depth up to 2.5 meters have been traversed with sampling every 0.5 meters. In the second section (in the territory of waste storage and concentration tailings) 16 wells up to 1.5 meters deep have been traversed with sampling every 0.5 meters. Total of 36 wells were drilled, 102 samples were taken. The total amount of waste accumulated at kaolin plant is more than 500,000 tons.

3 Results and discussions

According to the mineralogical analysis, silt samples of the settling pond "Chalgany" represent a complex agglomeration of alluvial-forming minerals, typical for silt-detention basin of gold-processing companies: a large amount of clay, silt, the presence of organic inclusions, the presence of a metal scrub and, as a consequence, a large amount of hydrous ferric oxides, and the entire rock has a brown color due to limonite. The processes of oxidation and decomposition of iron-containing minerals (sulphides, carbonates, silicates) occur due to the access of oxygen and high humidity, which is typical for silt-detention basins of mining enterprises. The sample contains angular crystals of pure white quartz, a small amount of bull quartz, as well as a large amount of K-feldspar brownish and pinkish in color with scales of light and black biotite. Sulfide minerals can be found in the sample in small amounts: pyrite, arsenopyrite, chalcopyrite. Separate grains of galenite, tin stone are noted, there is a hornblende in the sample, a pomegranate of light red color.

Mineralogical analysis of primary raw materials showed the absence of visible gold and other noble metals in the rock under investigation. At the same time, according to AAS and INAA, the sample contains a significant amount of gold (78.6 g/t) and silver (57.5 g/t).

X-ray spectral microscopy studies showed that the maximum particle size of gold is about 50 μm , but most of the particles detected in the study do not exceed 5 μm . With a decrease in size, gold particles become more spongy.

To study the possibility of additional concentration of gold, the material was subjected to magnetic separation. The sample of silt was divided into heavy magnetic fraction (magnetite, ilmenite, metal scrub), heavy non-magnetic fraction (black sand) and light

residue. The results obtained indicate a fairly even distribution of gold between the magnetic and non-magnetic fractions and the ineffectiveness of magnetic separation. The conducted sieving analysis also did not allow us to distinguish the fraction with which gold would have been associated.

The silts of the settling pond "Chalgany" are characterized by a high content of gold, but, gold is represented in the form of finely dispersed particles hardly yielding to mechanical beneficiation. To extract gold from this object, a hydrometallurgical methods was developed. The investigations were carried out at the Institute of Chemistry FED RAS in two regimes: laboratory, weighing 100 grams each with pulp agitation, and large scale on a sample of 40 kg without agitation, simulating heap leaching. The gold content in samples taken for testing was 80-100 g/t. The tests worked out the methods of ammonia-thiosulphate and thiocarbamide leaching.

A preliminary assessment of the efficiency of ammonium-thiosulphate leaching of gold from aluminosilicate rocks was carried out in laboratory conditions on model clays (kaolin) with artificially introduced gold. An optimized composition of the leaching solution was obtained - 0.1 mol/l $\text{Na}_2\text{S}_2\text{O}_3$; 0.2 mol/l NH_3 ; 0.015 mol / l CuSO_4 ; pH 10.4; ratio T: M = 1:2.5. The efficiency of gold recovery from model systems within 2 hours of contact with the ammonia-thiosulfate solution exceeded 90% already at a ratio of T:F 1:1. Application of these leaching conditions to real samples of gold-containing silicate and aluminosilicate samples provided high efficiency of gold recovery (78-97%) [11].

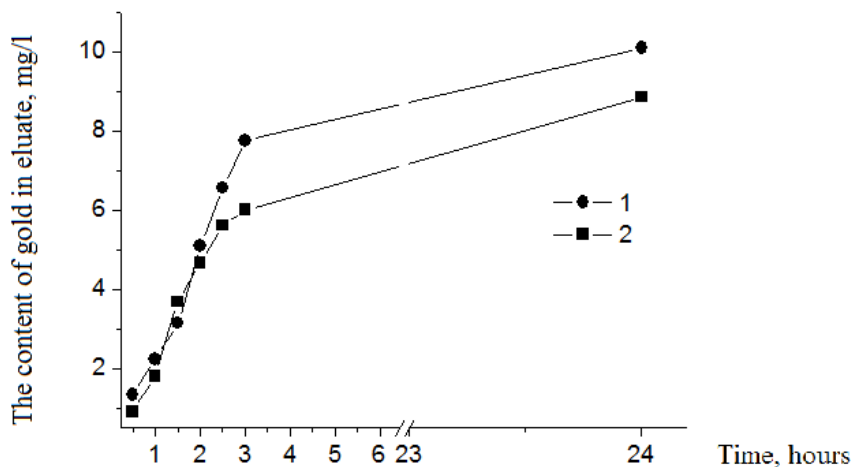


Fig.1. Kinetic of the gold content in the ammonia-thiosulphate leach solution (eluate):
1 - in the laboratory; 2 - in extended tests

When carrying out ammonia-thiosulphate leaching, the reservoirs with a low surface area contacting the atmosphere (0.05m^2) were used, since the arrival of atmospheric oxygen in the presence of iron oxides (the content of which in the sample according to XFA data exceeds 60%) can significantly reduce the rate of ammonia-thiosulphate leaching due to the accelerated oxidation of thiosulfate. For extended tests, a leaching solution was used, optimized at the stage of laboratory tests. The ammonia-thiosulphate leaching tests carried out under these conditions showed an efficiency close to the results obtained in the laboratory (see Figure 1). However, the overall efficiency of gold recovery for the silts of the settling pond "Chalgany", both in laboratory and enlarged conditions, did not exceed 47%. What can be associated with a decrease in the stability of the ammonia-thiosulfate system in the presence of transition metal oxides catalyzing the oxidation decomposition of thiosulfates and the formation of tetrathionates [12, 13]. Additional studies show that in the presence of magnetite, the dissolution rate of gold by the ammonia-thiosulphate solution of

the optimized composition drops sharply [11]. Thus, the significant content of magnetite and titanomagnetite in this technogenic raw material is a factor that reduces the effectiveness of the use of ammonium-thiosulfate solutions for gold leaching.

The concentration of gold from the leaching solution was carried out in a laboratory and extended conditions on the ion exchanger AV-17-8 at the solid/liquid ratio - 1:50, the recovery efficiency in both cases was about 80%.

The testing of thiocarbamide leaching was conducted in same conditions as ammonium-thiosulfate: laboratory, weighing 100 grams and large scale on a sample of 40 kg. In both cases, the thiocarbamide leaching was carried out in the sulfuric acid medium in the presence of an oxidizing agent. In the laboratory, optimal conditions for thiocarbamide leaching were determined: 0.65 mol/L $\text{CS}(\text{NH}_2)_2$; 0.1 mol/L H_2SO_4 ; 0.09 mol/L $(\text{NH}_4)_2\text{S}_2\text{O}_8$, the solid/liquid ratio – 1:2.

Bulk gold leaching tests were carried out for 5 hours until the concentration of gold in the solution according to AAS data did not stabilize at about 14.4 mg/l. The total percentage of gold recovery by cake was 72.5%, which is lower than the percentage of recovery obtained in laboratory conditions for a sample weighing 100 g, where the percentage of gold recovery was 93.5%. The main reason, which resulted in a decrease in the percentage of gold recovery from the sample, was the absence of pulp mixing.

Gold recovery from the solution is the final stage of processing of almost any type of ores using the technology of thiocarbamide gold leaching and electrolysis is the most perfect method of precipitating gold from a solution of thiourea leaching. Previous studies [14] show that for electrolytic gold recovery the flow design turns out to be optimal, as it supposes the separation of the anode and cathode spaces with an ion-exchange membrane using the lead anodes and stainless steel cathodes. Under such conditions, the efficiency of gold recovery from the leach solution exceeds 95%.

Thus, taking into account a small amount of raw materials for gold recovery from the silt of the settling pond "Chalgany", it is perspective to use a low-capacity heap leaching based on the thiocarbamide process.

Studies of the silt of the settling pond "Chalgany" conducted with regard to ISP-MP method showed that these technogenic wastes contain other valuable components, in addition to gold, including the most part of the rare-earth elements (REE) (see Table 1). Such a high content of REE in the samples makes the development of an integrated approach to processing of this type of raw materials potentially productive.

Table 1. The content of rare and rare-earth elements in the samples of the silt from the settling pond "Chalgany" (according to ISP-MS)

Element	C, g/t	Element	C, g/t	Element	C, g/t	Element	C, g/t
Be	0.84	Sr	226.68	Ce	819.60	Tm	1.11
Sc	13.65	Y	105.57	Pr	74.46	Yb	8.91
V	283.52	Zr	3406.04	Nd	315.08	Lu	1.40
Cr	701.40	Nb	120.54	Sm	39.56	Hf	87.60
Co	42.95	Mo	15.71	Eu	1.27	Ta	34.62
Ni	161.49	Cd	2.22	Gd	37.24	W	472.89
Cu	169.92	Sn	906.23	Tb	3.91	Pb	1884.10
Zn	246.04	Cs	3.69	Dy	19.40	Th	206.55
Ga	21.95	Ba	831.33	Ho	3.18	U	29.72
Rb	63.15	La	394.60	Er	9.57		

Thus, the silt waste from the settling pond "Chalgany" is a promising source of various valuable components, including gold and REE, but the reserves of this type of technogenic raw materials are very limited (several hundred tons). As an alternative source of gold and REE, the waste of Chalganovskiy kaolin plant was investigated. According to the research

conducted by the Amur Scientific Center FED RAS in 2014, the volume of waste generated at this facility was more than 500,000 tons.

X-ray fluorescence analysis was used to determine the chemical composition of the formed waste, including not less than 80% of kaolinite, 14% of quartz, feldspar.

The method of assay test proved the presence of gold samples. According to the assay test, the gold content in 46 samples taken from the tailings dump is from 0.0 to 5.5 g/t (see Table 2). The average content is 0.41 g/t. In 31 samples taken from the waste sands, the gold content was from 0.0 to 0.82 g/t. (see table 3). The average content is 0.20 g/t.

Table 2. The gold content in the waste samples from Chalganovskiy kaolin plant, according to the assay test (Object: Tailings dump)

Sample	C, g/t	Sample	C, g/t	Sample	C, g/t	Sample	C, g/t
JI-I-1-0.5	1.02	JI-II-1-0.5	traces	JI-III-3-0.5	traces	JI-IV-2-1.0	0.29
JI-I-1-1.0	0.18	JI-II-1-1.0	0.10	JI-III-3-1.5	0.18	JI-IV-3-0.5	traces
JI-I-1-1.5	0.16	JI-II-2-1.0	traces	JI-III-4-0.5	0.16	JI-IV-3-1.0	0.10
JI-I-1-2.0	traces	JI-II-4-0.5	4.30	JI-III-4-1.0	0.10	JI-IV-3-1.5	0.10
JI-I-1-2.5	0.14	JI-II-4-1.0	traces	JI-III-4-1.5	0.14	JI-V-1-1.0	0.13
JI-I-2-0.5	0.22	JI-III-1-0.5	0.10	JI-III-5-0.5	0.52	JI-V-2-0.5	5.50
JI-I-1-1.5	0.10	JI-III-2-0.5	0.64	JI-III-5-1.5	traces	JI-V-2-1.0	traces
JI-I-3-0.5	0.20	JI-III-2-1.0	0.10	JI-IV-1-0.5	0.10	JI-V-2-1.5	4.40
JI-I-4-0.5	0.12	JI-III-2-1.5	0.08	JI-IV-2-0.5	traces		

Table 3. The gold content in the waste samples from Chalganovskiy kaolin plant, according to the assay test (Object: sand line)

Sample	C, g/t	Sample	C, g/t	Sample	C, g/t	Sample	C, g/t
X-I-1-0.5	0.10	X-II-1-1.0	0.10	X-II-4-1.0	0.22	X-III-1-1.5	traces
X-I-1-1.0	0.42	X-II-2-0.5	0.10	X-II-4-1.5	0.10	X-IV-2-0.5	0.18
X-I-2-0.5	0.16	X-II-2-1.0	0.37	X-III-1-0.5	0.18	X-IV-2-1.0	traces
X-I-1-2.5	0.10	X-II-2-1.5	0.81	X-III-1-1.0	0.10	X-IV-2-1.5	0.56
X-I-3-0.5	0.14	X-II-3-0.5	0.26	X-III-2-0.5	traces	X-IV-2-2.0	0.10
X-I-3-1.0	0.10	X-II-3-1.0	0.82	X-III-3-0.5	0.20	X-III-3-0.5	0.20
X-I-3-2.5	0.10	X-II-3-1.5	0.50	X-III-3-1.0	0.10	X-III-3-1.0	0.10
X-II-1-0.5	0.10	X-II-4-0.5	0.16	X-III-4-0.5	0.28	X-III-4-0.5	0.28

The content of gold in the waste of Chalganovskiy kaolin plant in relation to the total amount of waste is extremely small, what makes it unprofitable to apply hydrometallurgy methods for metal recovery. To efficiently extract valuable components from this raw material, it is necessary to solve the task of reducing the waste rock that is involved in the process of beneficiation and obtaining the concentrate, which will then go to the beneficiation plant and refining. For this purpose, a team of authors developed a model of a centrifugal concentrating-classifying apparatus [14], which allows, in the course of work, to remove an empty rock, silty and clay fractions and obtain a concentrate of useful components, including noble metals, which will be further processed: a concentration table; low-capacity heap leaching; pyrometallurgy; refining. The application of this approach will significantly increase the gold content in the rough concentrate obtained from the waste of Chalganovskiy kaolin plant, especially for waste from the sand line. And then it is possible to use the method of ammonia-thiosulphate leaching for efficient extraction of gold from this technogenic object.

After the recovery of the valuable components, the remaining part of waste from Chalganovskiy kaolin plant will present the secondary kaolin and may be considered as a raw material for the production of chemically pure silicon and silica, as well as aluminum, its compounds, and refractory fibrous materials.

4 Conclusions

It is established that investigated technogenic wastes are a valuable source of mineral raw materials. The silts of the settling pond "Chalgany" contain a significant amount of gold, precious metals, rare earth elements and other valuable components. A promising approach for gold recovery from the silt of the settling pond "Chalgany" is carrying out of a low-capacity heap leaching based on the thiocarbamide process followed by electrolytic precipitation of gold from the leach solution.

Wastes from Chalganovskiy kaolin plant are also of considerable interest as a source of mineral raw materials. The composition of this raw material includes kaolin, quartz, feldspar, and a small amount of REE and PGM. After the recovery of the valuable components, the remaining part of waste can be regarded as the secondary kaolin - a raw material for the production of chemically pure silicon and silica, as well as aluminum, its compounds, and refractory fibrous materials.

Gratitude

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