Technogenic placers of the Fadeevsky node (Primorye, Russia) as sources of precious metals

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Abstract. Generalization of the obtained materials leads to the conclusion that a significant amount of useful components has been accumulated in the man-made placers of Primorye (south of the Russian Far East), at the same time they pose a considerable threat to the environment. Using the example of the gold mining dumps of the Fadeevsky node, ways to solve this problem are outlined. The essence of the new approach is to implement a scheme of rational environmental management, which allows: 1- to recover precious metals (Au, platinum group elements) and demercurize man-made placers by liquid extraction from thiocarbamide leaching solutions; 2- to obtain raw materials for non-traditional industries in gold mining (powder metallurgy, titanium production, road and civil engineering). The involvement of man-made placers in the production sector will have a beneficial effect on the environmental situation in densely populated areas, and will also contribute to meeting the growing needs of the region for precious metals.

1 Introduction

Long-term intensive extraction of precious metals from the placers of the Primorsky territory led to the depletion of their geological reserves, which could not but affect the decrease in the production of native gold and minerals of the platinum group elements. At the same time, there are good reasons to believe that the resource potential of placer deposits in the region is far from being exhausted, since only large particles of free metal (freed from rock) were extracted from them during operation, and small and thin ones, which account for at least 20% of the initial reserves of precious metal deposits, were lost in the dump tailings of enrichment. It is known that many placers in the region are complex, containing, in addition to native gold and platinoids, other minerals (ilmenite, chromite, sulfides, etc.) containing useful components, including bound noble metals (enclosed inside the grains of these minerals). When working off placers, they were also moved to waste due to imperfections in the technology of enrichment of metal-bearing sands. Modern methods of extraction of precious metals create prerequisites for the reassessment of all man-made placers of Primorye (dumps that arose during the exploitation of deposits) in order to develop them comprehensively, primarily with the extraction of free (small, thin) and bound gold from the tailings of enrichment.

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The use of hydrometallurgical methods based on the dissolution of useful components with active reagents in contact with leaching solutions can help the complex development of man-made placers. Usually, the leaching of precious metals is carried out using cyanide solutions, which is associated with a significant deterioration of the environmental situation. To replace them in the process of utilization of man-made placers, we propose to use thiocarbamide solutions [1,2].

The possibility of using thiocarbamides as substitutes for cyanide solutions for the extraction of precious metals contained in various types of mineral raw materials has been repeatedly discussed in the literature [3-5]. The use of thiocarbamide solutions for dissolving gold, compared with cyanide solutions, has several advantages [6]: reducing the environmental burden, increasing the rate of dissolution of gold by 10 times, reducing corrosion effects on the equipment, reducing the influence of impurity ions. However, there are two limitations that prevent the widespread industrial use of the thiocarbamide gold dissolution process: the price of thiocarbamide is 25% higher than sodium cyanide, and significant losses of thiocarbamide at various stages of the process. The latter are mainly related to gold filtration and extraction operations. At the filtration stage after leaching, part of the mother liquor containing thiocarbamide may be lost with a wet cake; to avoid these losses, repeated washing of the cake is necessary. At the stage of gold extraction from leaching solutions, if extraction and sorption methods are used, gold can pass into the sorbent phase and extract in the form of thiocarbamide complexes [7,8], which affects the loss of thiocarbamide. When using the electrochemical method of separating noble metals from leaching solutions, anodic oxidation of thiocarbamide is possible. During cementation, if it is carried out at elevated temperatures [9], decomposition of thiocarbamide is possible. Various reagent methods of gold deposition, as well as cementation, lead to contamination of leaching solutions. This makes it difficult to use them in circulation without additional regeneration operations of solutions, which also leads to losses of thiocarbamide. The following are the results of studies of the process of extracting gold and platinum group elements from thiocarbamide solutions using liquid extraction as a possible way to efficiently process precious metal concentrates from gold mining dumps of previous years.

2 Materials and methods

The technogenic placers of the Fadeevsky node, located within the densely populated Primorye region, were chosen as the basic object of research. Native gold has been mined here since the end of the XIX century [10]. A French mining company used multi-pile steam excavators in their development, and a processing plant operated. Gold mining was very active in subsequent years up to the present day. The extraction of the precious metal was carried out using technologies based on the use of mercury. As a result, man-made placers with a length of tens of kilometers and volumes of hundreds of thousands of cubic meters were formed. Their material composition is only approximately known. A problem has arisen – whether these wastes can be quite affordable raw materials for the continuation of industrial activity or only one of the significant sources of environmental pollution. Since the end of the 80s of the last century, all finishing operations for the enrichment of metalliferous sands of the node were carried out at dressing and processing plants, where only free gold was extracted. This led to the appearance of large-volume accumulations (thousands of cubic meters) of tails enriched with minerals in the area of location. The material characteristics of the gravitational concentrate of these dumps, according to [11-14], are as follows (wt.%): Fe_2O_3 – 41.2; TiO_2 – 15.5; Al_2O_3 – 1.0; CaO – 0.5; Mg – 0.5; MnO – 1.7; SnO_2 – 20.1; PbO – 4.0; As_2O_3 – 3.8; Cr_2O_3 – 3.6; WO_3 – 0.8; Mo – 0.2; V – 0.1; Cu – 0.2; Zn – 0.04; Ag – 0.006; Hg – 0.2; S – 3.0.

According to its magnetic properties (using magnetic and electromagnetic separation), the gravity concentrate is divided into magnetic, electromagnetic and non-electromagnetic fractions. The ratio of the first two fractions, represented respectively by magnetite and ilmenite, is approximately equal, with a slight predominance of electromagnetic. In both fractions, an increased level of Cr content (0.2-0.4 wt.%) is observed, due to the presence of chromite.

Significant amounts of zircon and sphene are present in the nonelectromagnetic fraction. Of the ore minerals, sulfides predominate (pyrite, arsenopyrite, galena, sphalerite, molybdenum, pyrrhotite). The findings of cassiterite, cinnabar, wolframite, bismuth minerals, platinoids, etc. are noted. Gold is present in the concentrate both in a free and bound state with the predominant role of the latter (170 and 420 g/t, respectively). Many particles of free gold extracted from the concentrate bear traces of amalgamation due to prolonged use in the enrichment process of man-made mercury. The latter is represented by small silvery balls of liquid metal, slightly soluble in water, but easily reacting with oxygen in the air when temperatures rise in the summer. The mobility of mercury and the permeability of its vapors, which are extremely toxic to the human body, are well known.

The sample of unchanged grains of native gold ranges from 840-940‰. The micro-impurities constantly found in it include Cu, Fe (200-400 g/t), As (1-40 g/t), Ni (1-2 g/t) [15-17]. Platinum group minerals are characterized by the predominance of solid solutions of Pt – Fe and a small admixture of osmirides. Microprobe analysis of Pt – Fe alloys [9] showed their chemical proximity to isoferroplatin. The composition of Os – Ir – Ru solid solutions varies from native osmium to native iridium.

A nonelectromagnetic fraction concentrating the bulk of gold, platinum group elements and man-made mercury was used as a starting product in the study of the extraction of precious metals from thiocarbamide leaching solutions.

3 Resutls and discussion

The leaching of raw materials was carried out both with and without pre-demercurization. Solutions of nitric acid were used for demercurization. As can be seen from Table 1. preliminary demercurization can significantly reduce the mercury content in thiocarbamide leaching solutions, as well as reduce the content of arsenic and copper. The transition of mercury from raw materials to solutions of thiocarbamide leaching, which is carried out in the presence of an oxidizer – ferric chloride, is apparently associated with the oxidation of mercury and its transfer to the form of sulema.

Table. 1. Distribution of Hg, As, and Cu during the leaching process.

Content in solutions after demercurization, mol/l			Content in solutions without demercurization, mol/l		
Hg	As	Cu	Hg	As	Cu
$1.69 \cdot 10^{-4}$	$8.80 \cdot 10^{-4}$	$4.40 \cdot 10^{-3}$	$2.14 \cdot 10^{-3}$	$6.01 \cdot 10^{-3}$	$2.91 \cdot 10^{-2}$

At the same time, the demercurization process causes a complication of the technological scheme for extracting gold and silver from raw materials, since it entails additional operations such as agitation with HNO_3 solutions, filtration and subsequent processing of nitric acid solutions. All this leads to the appearance of additional volumes of solutions that are not involved in turnover.

On the other hand, the use of liquid extraction at the stage of extraction of gold and silver from leaching solutions, as shown by our research, allows us to selectively extract precious metals with additional separation from impurities. The only problem that arises in this case is the output of Hg, As and Cu accumulating in revolutions. Nevertheless, this problem is solvable, since the technology provides for the complete neutralization of recycled solutions with lime after five to seven leaching cycles to reduce the overall salt background.

We have conducted studies of the process of extracting gold from thiocarbamide solutions using liquid extraction as a possible way to reduce thiocarbamide losses during the processing of gold-containing concentrates. Tributyl phosphate, diphenylthiourea and their mixture were used as extractants. It was found that the thiocarbamide complexes of gold formed during leaching are practically not extracted by individual extractants and are weakly extracted by a mixture of diphenylthiourea with tributyl phosphate. At the same time, gold is extracted with tributyl phosphate, as well as a mixture of diphenylthiourea with tributyl phosphate with high distribution coefficients when introduced into thiocarbamide solutions of thiocyanate ions. At the same time, it was found that the introduction of sodium thiocyanate into thiocarbamide solutions does not worsen the recovery of gold at the leaching stage and, most importantly, extraction is not accompanied by a transition to the organic phase of thiocarbamide, since gold is extracted in the form of thiocyanate complexes. Thus, the use of liquid extraction at the stage of gold extraction from leaching solutions avoids the loss of thiocarbamide.

The dependences of the distribution coefficients of gold, silver and copper during extraction from leaching solutions depending on the concentration of thiocyanate ions in the initial aqueous solution are investigated. Unlike silver and copper, the distribution coefficients of gold during extraction with a mixture of tributyl phosphate with diphenylthiourea increase with increasing concentration of thiocyanate ions in the initial aqueous solution. In addition, gold is well extracted from thiocarbamide-thiocyanate solutions with tributyl phosphate. The different nature of the extraction of gold and silver tributyl phosphate and a mixture of tributyl phosphate with diphenylthiourea opens up prospects for the selective extraction of these metals from leaching solutions.

The possibility of selective extraction of gold and silver was tested by us on model solutions containing $3.36 \cdot 10^{-3}$ mol/l Au, $4.82 \cdot 10^{-3}$ mol/l Ag, 0.96 mol/l KCNS, 0.1 mol/l H_2SO_4. In the first stage, during extraction with a benzene solution containing 1.82 mol/l T tributyl phosphate (phase ratio 1:1), almost all gold is extracted (D=499.31), and silver mainly remains in the aqueous phase (D=0.12). The separation coefficient for the Au/Ag pair is 4339.47. After gold extraction, silver was extracted from the raffinate with a mixture of tributyl phosphate and diphenylthiourea. At the same time, the extraction of gold in the first extract was 99.82 %, silver in the second extract was 87.85%. Triple reextraction with a thiourea solution (0.92 mol/l) at a phase ratio of 1:1 allows 96.42 % silver to be extracted from the organic phase. Gold re-extraction under these conditions proceeds unsatisfactorily. In this regard, we have conducted research on the re-extraction of gold with various reagents. It was found that gold reextraction with solutions of NH_4OH, KJ, $NaNO_2$, H_2O_2 and $H_2C_2O_4 \cdot 2H_2O$ is also unsatisfactory. The best gold reextraction rates were achieved using Na_2SO_3 and $Na_2S_2O_3$ solutions. In the table.2. Data for three-fold gold reextraction are presented.

As can be seen from the table.2 gold can be extracted from the organic phase by 86.25% with three-fold re-extraction with a solution of $Na_2S_2O_3$.

Table. 2. Threefold re-extraction of Au at a phase ratio of 1:1

Reextragent	R1%	R2%	R3%	ΣR%
Na_2SO_3 1.59 mol/l	80	4.5	1.75	86.25
$Na_2S_2O_3$ 1.27 mol/l	80	3.75	1.25	85

In general, the technological scheme of gold and silver extraction includes the following operations:

- demercurization;
- leaching of raw materials with recycled thiocarbamide-thiocyanate solutions;
- cake filtration and flushing;
- extraction of tributyl phosphate gold from leaching solutions combined with washing solutions;
- extraction of silver with a mixture of diphenylthiourea with tributyl phosphate from leaching solutions combined with washing solutions;
- washing of organic phases;
- gold re-extraction;
- silver reextraction;
- deposition of gold and silver;
- oxidative melting.

The end-to-end extraction of gold from raw materials according to this scheme is 89-90%. The growth of the sample of the obtained ligature gold in the ingot (980‰), compared with free gold, the appearance of Pt (62 g/t) and Pd (18 g/t) in its composition was undoubtedly influenced by the influence of bound gold and platinum group minerals, from which Au and platinum group elements were leached. In addition, Bi – 36 g/t and additional amounts of Cu – 4700 g/t (extracted from the gravity concentrate along the way) were recorded among the impurities.

4 Conclusion

The research carried out makes it possible to outline ways of using technogenic placers as raw materials for various industries. First of all, additional extraction of gold (free, bound) from dumps may have a certain significance in the future. This will significantly affect the level of production of precious metals in the region. The growing demand on the world market for platinum group elements is changing the attitude towards technogenic placers as possible sources of platinum metal raw materials. Simple technological operations (magnetic and electromagnetic separation) make it possible to isolate ilmenite concentrate, which is used by industry for the production of titanium metal, pigment dioxide, electrodes, etc. Waste from processing technogenic placers (pebbles, sand) can be successfully used as building materials.

The above indicates the economic feasibility of using waste-free technology for processing the studied technogenic placers [18-20].

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