

Valorization of waste from old gold mining in the south of the Russian Far East using pyro-hydrometallurgy methods

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Abstract. The basics of the original technology for the development of man-made placers in the south of the Russian Far East have been developed. The necessity of using methods of hydrodifluoride conversion, hydrometallurgy, fluoride autopsy is substantiated. To create an environmentally safe resource-saving technology for the enrichment of man-made formations, methods of powder metallurgy, leaching of raw materials by liquid extraction with simultaneous demercurization, as well as fluoride autopsy are used. The application of this scheme for extracting useful components from placer material will allow the industrial turnover of numerous man-made placers in compliance with resource-saving principles and without causing significant damage to the environment.

1 Introduction

Gold has long been one of the strategic metals that ensure the financial security of the country. Currently, it is an extremely popular element in the field of electronics, nanotechnology, medicine, cosmetics, as well as space technology, jewelry production, etc. [1-4]. The development of the mineral resource base of precious metals in the Russian Far East, due to high demand and lack of natural resources, is becoming increasingly dependent on the search and development of non-traditional sources. The fundamental principles of their recycling strategy should be common to all developed facilities and meet the requirements of rational environmental management. The parameters of development are determined not only by the degree of use of scientific and technical achievements in the field of enrichment technologies, but also by identifying the specifics of the material composition of man-made material.

One of the alternative sources of precious metals is man-made placers (waste from old gold mining), widespread in the south of the Russian Far East. It is known that the development of placer deposits of precious metals is usually aimed at extracting gold. At the same time, during operation, mainly only large particles of free metal (freed from rock) were extracted, and small and thin ones, which account for at least half of the initial reserves of precious metals (BM) objects, were lost in the dump tailings of enrichment. It is known that many placers in the region are complex, containing, in addition to gold, other minerals

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containing useful components (titanomagnetite), including bound gold enclosed inside the grains of these minerals. When working off placers, such useful components were also moved to the tailings due to imperfections in the technologies for enriching metal-bearing sands.

Regardless of which associated useful components accompany the gold in the placer, their separation from the collective concentrate is a difficult technological task. It should be borne in mind that in addition to the obviously useful minerals of the heavy fraction, other impurities are present in the concentrate, further complicating the process. This includes, first of all, man-made mercury, previously used in the extraction of gold. However, gold mining waste and by-products are valuable secondary resources because they contain significant amounts of precious and strategic metals that can be extracted. In addition to their economic importance, the valorization of waste through recycling can improve the state of the environment. All previously proposed technological approaches for separating gold from associated minerals and impurities include processes that are either harmful to human health and the environment, or difficult to implement in a mining enterprise. The purpose of our research was to create the foundations of non-traditional environmentally friendly ways to involve old gold mining dumps in the industrial turnover of the south of the Far Eastern region for their integrated development, including the extraction of critically important metals.

2 Materials and methods

To solve the tasks set, it was necessary to perform a complex of mineralogical and technological studies. Several large-volume samples (up to 3 tons each) were taken from each of the studied placers, which were enriched at a gravity installation. The obtained concentrates were separated into magnetic, electromagnetic and nonelectromagnetic fractions by magnetic and electromagnetic separation.

The analysis of the trace element composition of the samples was performed on an inductively coupled plasma mass spectrometer (ICP-MS) Agilent 7500c (Agilent Technologies, Japan) equipped with a Babington sprayer, a cooled Scott spray chamber and a grounded Fassel burner. Nickel cones of the sampler and skimmer were used. Petrogenic elements were determined using an atomic emission inductively coupled plasma spectrometer iCAP 6500 Duo (ISP-NPP) (Thermo Scientific, USA).

For mineralogical studies, the Jeol Superprobe JXA 8100 electron probe microanalyzer with the INCA Energy 350 Oxford Instruments system and the EVO-500XVP electronic scanning microscope with the INCA Energy 350 Oxford Instruments system (Great Britain) were used.

The gold content was determined by instrumental neutron activation analysis on a compact installation with a radionuclide excitation source based on Cf-252 developed at the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences [5].

The technogenic placers of the Krinichny node, located within a densely populated area of the south of the Primorsky Territory (near Nakhodka) and a developed infrastructure ensuring the efficient use of modern technologies for extracting minerals, were chosen as a reference object.

Native gold has been mined here since ancient times. Back in the early 20th century, E.E. Ahnert [6] wrote that the ancient workings in this area were "so grandiose that all attempts by modern industrialists to extract gold from them were unsuccessful." Mining was also very active in the post-revolutionary period. As a result of more than two centuries of operation, the alluvial placer was completely worked out. At the same time, the extraction of precious metal has been carried out for a long time using technologies based on the use of mercury. In the last decade of operation (until the mid-90s), the final finishing operations were carried out at dressing plants, where native metal was extracted using concentration tables and, again,

metallic mercury. All this led to the formation of significant accumulations of dump tailings of gold mining in volumes of many thousands of cubic meters, enriched not only with valuable minerals, but also with mercury. The material composition of gravity concentrates extracted from them is characterized by a high yield of magnetic fraction (up to 74%) and low – electromagnetic (24-25%) and nonelectromagnetic (1-2%).

The magnetic fraction corresponds in chemical composition to a high-titanium type of magnetite with a low level of chromium accumulation. The proportion of foreign impurities is small: Au concentrations do not exceed 4-6 g/t. In addition to ilmenite, which forms the basis of the material, chromite and gold (1-2 g/t) are present in the electromagnetic fraction. The nonelectromagnetic fraction is essentially a mixture of zircon and sphene (75-80 % of the total mass) with the leading role of the first. Of the ore minerals, sulfides predominate (mainly pyrite, sphalerite, galena), cinnabar, bismuth minerals, native gold and metallic mercury are present in smaller quantities. The constituent components of the fraction can be divided into 2 groups. The first of them includes Zr, Ti, Fe, the content of which usually does not exceed 10 wt. %; the second group includes Hg, Pb, Cu, Zn, W, Mn, Sc, whose concentrations vary between 0.01–1.0 wt. %. It should be noted that the high level of accumulation of Hg (over 1000 g/t) is many times higher than the maximum permissible concentrations.

3 Results and discussion

Low-waste technology for extracting useful components using methods of hydrodifluoride treatment, hydrometallurgy and fluoride dissection can help the industrial development of man-made placers. The raw materials used were the dressing material of magnetic (titanomagnetite), electromagnetic (ilmenite) and nonelectromagnetic (zircon, gold, metallic mercury) fractions of gravity concentrates. In the process of processing the slurry material of magnetic and electromagnetic fractions, solid-phase opening techniques were used with a mixture of hydrodifluoride and ammonium sulfate [7], and BM and zirconium concentrate, in turn, were extracted with thiocarbamide-thiocyanate solutions [8] using fluoride conversion methods.

Hydrodifluoride autopsy. In recent years, worldwide, and especially in Russia, there has been a sharp increase in interest in titanomagnetite and ilmenite as important industrial sources of titanium [9]. Titanomagnetite ($n\text{FeTiO}_4 \cdot (1-n)\text{Fe}_3\text{O}_4$) is the main ore component of the magnetic fraction, where it is noted in the form of rounded grains of disturbed octahedra and sharp-angled fragments and is a solid solution with isomorphic entry of titanium into the magnetite lattice. Ilmenite (FeTiO_3), which forms the basis of the electromagnetic fraction, forms grains with well-defined crystallographic shapes in the form of lamellar hexagonal crystals.

For the decomposition of mineral raw materials in industry, acidic methods of opening samples in open vessels or in autoclaves are usually used, as well as fusion with alkaline agents and subsequent leaching. Relatively recently, reagents such as fluoride or ammonium hydrodifluoride have been used in the sample preparation process [10]. Unlike acidic opening with hydrofluoric acid, when the process temperature is limited by the boiling point of the solution, fluoridation of samples with dry salts can be carried out at temperatures of 230-250°C in open vessels [10,11], which significantly increases the speed and completeness of fluorination. The opening process is carried out by solid-phase interaction of ammonium fluoride/hydrodifluoride with mineral components. The fluorinated products are dissolved in nitric acid with subsequent analysis of the obtained solutions by instrumental methods, for example, using inductively coupled plasma mass spectrometry [12]. As a result of the interaction of fluorides and minerals that make up rocks, a number of water-soluble complex fluoroammonium compounds of metals (such as iron, aluminum, titanium, zirconium, etc.)

and silicon are formed, as well as practically insoluble fluorides of calcium, magnesium and rare earth elements. At the same time, as shown in [13, 14], these insoluble fluorides can be converted to soluble sulfates by solid-phase interaction with ammonium sulfate.

When interacting with ammonium hydrodifluoride, oxygen-containing compounds of transitional and many non-transitional elements form ammonium fluoro- or oxofluorometallates, which, due to their physico-chemical properties, ensure the solubility of products and allow the main part of complex salts to pass into solution during subsequent leaching of the product with water, which makes the use of NH_4HF_2 very attractive for opening mineral raw materials [15].

When using a mixture of hydrodifluoride with ammonium sulfate, a more complete opening of the mineral raw materials occurs if only ammonium hydrodifluoride were used. At the first stage of heat treatment (up to 200°C), the interaction of titanium-containing mineral raw materials with NH_4HF_2 destroys the crystal structure of minerals with the formation of metal fluorides or their complex fluoroammonium compounds, and at the second (350°C) sulfatization occurs with the formation of acid-soluble metal sulfates. The effect of using a mixture of NH_4HF_2 with $(\text{NH}_4)_2\text{SO}_4$ is achieved due to the fact that NH_4HF_2 is able to effectively destroy the crystal lattice of minerals, including silicate ones, breaking Si–O bonds, but at the same time slightly soluble fluorides of some elements may occur, and $(\text{NH}_4)_2\text{SO}_4$ turns them into sulfates.

The aqueous leaching of the product of the interaction of titanium-containing mineral raw materials with a mixture of NH_4HF_2 and $(\text{NH}_4)_2\text{SO}_4$ makes it possible to transfer almost all titanium into solution in the form of water-soluble double salts.

Hydrometallurgy. Special attention in technological research was paid to hydrometallurgy methods based on the dissolution of useful components by active reagents in contact with leaching solutions. BM leaching is usually carried out using cyanides, which is associated with a significant deterioration of the environmental situation [16]. Cyanide is a cheap but highly toxic reagent that is very effective in leaching gold from low-grade minerals and mining waste. It is the most widely used method of extracting gold from mining waste. Despite its advantages, it is considered an unacceptable and extremely dangerous approach.

Health and safety concerns related to the use of cyanide as a leaching agent were raised after several technological accidents that severely damaged the environment [17-19]. Such incidents led to the development of a voluntary program in the gold mining industry called the International Cyanide Management Code for the safe management of cyanides and the protection of human health and the environment [20, 21]. To replace them in the process of utilization of man-made placers, we propose to use thiocarbamide solutions [22, 23].

The possibility of using thiocarbamides as substitutes for cyanide solutions for the extraction of BM contained in various types of mineral raw materials has been repeatedly discussed in the literature [24]. The use of thiocarbamide solutions for dissolving gold, compared with cyanide solutions, has several advantages [25]: reducing the environmental burden, increasing the rate of dissolution of gold by 10 times, reducing the corrosive effect on equipment, reducing the influence of impurity ions. However, there are two limitations that prevent the widespread industrial use of the thiocarbamide gold dissolution process: a significantly higher price of thiocarbamide 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 enter the sorbent and extract phase in the form of thiocarbamide complexes [26], which also leads to losses. When using the electrochemical method of separating BM from leaching solutions, anodic oxidation of

thiocarbamide is possible. During cementation, if it is carried out at elevated temperatures, decomposition occurs. 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 causes this valuable reagent to be lost.

We have developed a method for extracting gold from thiocarbamide solutions using liquid extraction as one of the effective ways to reduce thiocarbamide losses during the processing of gold-containing concentrates. In addition, the use of liquid extraction at the stage of extraction of gold and silver from leaching solutions makes it possible to selectively extract noble metals with additional separation from impurities. The only problem that arises in this case is the withdrawal of Fe, As, and Cu accumulating in circulation. 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.

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 weakly by a mixture of diphenylthiourea with tributyl phosphate. At the same time, gold is extracted by tributyl phosphate, as well as by a mixture of diphenylthiourea with tributyl phosphate with high distribution coefficients when introduced into thiocarbamide solutions of thiocinate ions. At the same time, it was found that the appearance of the last thiocinate in 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.

It should be noted that in the presence of mercury in leaching solutions, the latter almost completely passes into the organic phase. In this regard, we have attempted to isolate all the metals of the phase from it, bypassing the washing stage. The conducted studies have shown that metals from the organic phase are most effectively precipitated by sodium borohydride. Thus, when the extract is treated with a solution containing 0.5 mol/l NaBH_4 , a black precipitate appears at the interface. At the same time, the extractant does not break down and does not lose the ability to extract BM. The filtered interphase sediment was subjected to oxidative melting after washing with concentrated nitric acid.

Fluoride autopsy. The cake, undissolved as a result of hydrometallurgical processing, concentrating significant amounts of zircon, is used to produce commercial zirconium products. Among the known methods of processing zirconium concentrates, preference should be given to the method of fluoride opening of zircon, which provides for dry fluorination of the concentrate with ammonium bifluoride with transfer to the gas phase of ammonium fluorosilicate. After removal of silicon, the resulting ammonia and excess fluorinating agent from the fluorination products, zirconium tetrafluoride is sublimated, from which commercial zirconium dioxide of monoclinic modification with a purity of about 99.9% is obtained by pyrohydrolysis. This technological scheme differs from the traditional chloride one in lower energy consumption and lower environmental costs. In addition, the formation of an intermediate product of zirconium tetrafluoride makes it possible to obtain high-purity zirconium fluoride compounds used in fiber optics as the final product. In particular, a method for separating zirconium from impurities was previously developed, the content of which in zirconium fluorides used for the manufacture of fibrous LEDs based on them should not exceed 10^{-6} - 10^{-7} wt.%. Such a degree of purification of zirconium tetrafluoride is not achieved using distillation and sublimation methods [27, 28].

The developed method for separating zirconium from impurities, in particular from iron, is based on the extraction of zirconium from fluoride solutions with a solution of

trialkylbenzylammonium fluoride, followed by washing the organic phase and re-extraction with a solution of hydrofluoric acid and its mixture with ammonium fluoride. The method combines well with the fluoride method of opening zirconium concentrate and reduces the content of impurities in the resulting zirconium tetrafluoride to the required level.

4 Conclusion

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. As a result of the conducted research, the basics of resource-saving technology for their disposal have been developed using a complex of methods of gravity, magnetic and electromagnetic separation, hydrometallurgy and fluoride autopsy. The application of this re-enrichment scheme opens up new opportunities for extracting strategic metals from man-made formations of Primorye, and also allows expanding the prospects of the region to strengthen the mineral resource base for further increasing their production volumes in compliance with the principles of rational nature management and improving the ecological state of the environment.

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