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ECO-FRIENDLY TECHNOLOGY OF COMMERCIAL COMPONENTS (TITANIUM, GOLD) RECOVERING*

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Abstract

The main features of the mineralogy and geochemistry as well as the mining potential of the titanium placers spatially and genetically connected with the Ariadnensky intrusion of ultrabasites (Primorye) were determined. The composition of the ilmenite, gold and platinum was investigated and assemblage of the associated strategic metals was revealed. The possibilities of the commercial exploitation of ilmenite placers with the use of the environmentally acceptable methods of pyro-hydrometallurgy were assessed. The proposed technical solutions will allow us to expand the prospects of the raw-material base of the southern Far East of Russia in compliance with the principles of the sustainable nature management and environment protection.

Keywords: ecology, gold-titanium-bearing placers, pyro-hydrometallurgy

1. Introduction

The precious metals (PM) have determined since olden times the metallogenic profile of the placer deposits of the southern Far East of Russia (Ahnert, 1928). However, by now, many of these objects have almost completely depleted their resource potential. Under the established conditions, the strengthening of the raw-material base of the region is related to the complex manifestations of exogenous mineralization. The titanium-bearing placers of the Sikhote-Alin orogenic belt belong namely to them. In them, the PM minerals are associated components. Most of them are spatially and genetically connected with the synorogenic intrusions of basite-ultrabasites. The basic lines of their commercial exploitation are detail mineralogic-geochemical assessment and advanced processing of raw materials based on

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principles of the sustainable nature management and environmental security. The example of such approach is the ilmenite placers related to the Ariadnensky massif of ultrabasites in which the authors have first found the virgin gold and platinum (Molchanov and Androsov, 2017).

The main objective of our investigations is a creation, on the basis of the reliable mineralogo-geochemical information, of the foundation of the low-waste technology for the fullest recovery of commercial components (titanium and gold) from ilmenite placers using the pyro-metallurgy methods. The developed technical solutions will create the prerequisites to the commercial exploitation of these objects without causing the serious environmental damage.

The proposed article is composed of three basic parts:

- examination of mineral forms of concentration and features of distribution of commercial components in the magnetic and non-magnetic concentrates of original sands including the basic mass of ilmenite and PM respectively;
- assessment of possibilities to recover titanium from the ilmenite concentrate using the sulfuric technology with the substitution of the liquid sulfating reagent for the solid ammonium sulfate;
- developing the technological schemes of the PM recovery using the environmentally safe thiocyanate- thiocarbamic solutions.

2. Objects and methods

The Ariadnensky massif of basite-ultrabasites (Fig. 1) located in the central part of Primorye (watershed area of the Ussuri River, tributary of Amur River) belongs to the group of the differentiated intrusions of the Sikhote-Alin orogenic belt.

Its southern part is formed by peridotites and pyroxenites while, to the north, the ilmenite gabbro turning into diorites, monzodiorites and syenites predominate. The distinctive features of these rocks are the increased clarkes of gold and metals of platinum group (Khanchuk et al., 2006).

The ilmenite gabbros produce a number of major titaniferrous placers. So, the extensions of placers of Todokhova river and its right creek (Potapov river) are 4.8 km and 1.2 km, respectively, at widths of 520 m and 280 m, average thickness of productive formations of 7.4 m and ilmenite content of up to 375.5 kg/m^3. As of 01.01.2020, the explored reserves of TiO_2 exceed one million tons.

In order to solve the allotted problems, it was required to perform a complex of mineralogical and technological investigations. Within the explored placers, five bulk samples (Pad Todokhova River – 3, Potapov creek -2) with weight of up to 500 kg each which have served as the study objects were taken. The mineralogical studies were performed with the use of the Jeol Superprobe JXA 8100 electron probe micro-analyzer with the system of INCA Energy 350 Oxford Instruments and scanning electron microscope EVO-500XVP with the system of INCA Energy 350 Oxford Instruments.

An analysis of the micro-element composition of samples was carried out using the inductively coupled mass spectrometer (IC MS) Agilent 7500 (Agilent Technologies, Japan) equipped with the Babington injector, Scott cooled spray booth and grounded Fassel burner. The nickel cones of sampler and slimmer were used. The determination of major (petrogenic) elements was performed with the use of the Inductively Coupled Plasma Atomic Emission Spectrometer iCAP 6500 Duo (ICP-AES) produced by Thermo Scientific, USA.

The technological studies were carried out according to traditional for concentration of the ilmenite-containing sands scheme with preliminary gravity concentration and subsequent electromagnetic separation. Herewith, the serial concentration tables and wet electromagnetic separators were used.

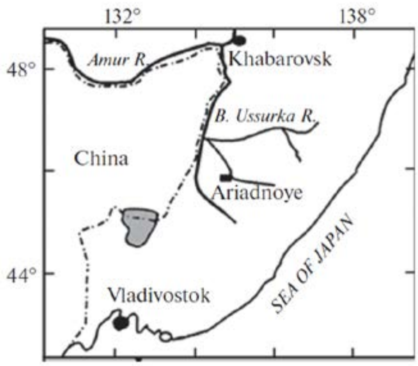

Fig. 1. Location of the Ariadnensky massif of ultrabasites

3. Results and discussion

The preliminary mineralogical studies of original sands have demonstrated that titanium in placers is exclusively presented by ilmenite which is the major mineral for commercial recovery. Among the unavoidable impurities, a quite wide spectrum of high-technology metals is fixed. First of all, the attention should be paid to high level of concentrations of the following elements (g/t): V – 730, Co – 340, Zn – 230, Ta – 100 and Nb – 11. The contents of Au and Pt exceeds seldom 0.1 g/t while Pd is present in the quantity of up to 1.1 g/t.

The placer (schlich) samples underwent the stage of preliminary concentration with subsequent electromagnetic separation. The obtained gravity concentrate is characterized by high output of magnetic fraction (93-95% of total mass) and low one of non-magnetic output (5-7%). The basis of the first fraction is formed by ilmenite while titanomagnetite is fixed in small amounts. The distinctive features of the fraction material (ilmenite concentrate) are high contents (mass.%) of TiO_2 (49.5) as well as insignificant impurities of SiO_2 (1.02) and Cr (0.2) which conforms reasonably to the requirements of the industrial production of titanium with the application of sulfuric technology (Baibekov et al., 1980). The high level of presence in the concentrate of weight parts (up to 300 g/t) of such high-technology metals as Nb, Nd, Co, Cu should be noted.

The non-magnetic fraction represents actually the mixture of anorthite, quartz, hornblende, sphen and zircon. In addition, monazite, rutile and apatite are present in small amounts. As to the ore minerals, the sulfides (few grains of pyrite, arsenopyrite, antimonite and galenite) and virgin metals (gold, platinum, zinc and nickel) predominate. Micro-elements of concentrate can be divided into two groups. The first of them includes the rare and rare earth elements (g/t) (Hf – 830, Ce – 320, Y – 220). The second group contains the precious metals (Au, Ag and Pt) the concentrations of which reach the production scale (0.5-3.0 g/t). The virgin gold is characterized by high values of purity (up to 970-999‰). In some grains, the presence of Cu (0.1-3.2 at. %) and Hg (3.5-4.3 mass %) was noted. The platinum is presented by solid solutions of Fe-Pt where Pt (87.1-90.8 mass %) is the leading mineral-forming element.

As it is known (Korovin et al., 1996; Baibekov et al., 1980), ilmenite is comparatively easy decomposed by acids. For its opening, the sulphuric-acid process is widely used. This is the oldest industrial process for TiO_2 recovery from ilmenite which consists in the transformation of ilmenite into dissoluble sulfates. The process consists of three stages and large number of operations (drying of concentrate to humidity of 0.5%, sulfation by oleum at 80-210°C with the effervescence and spattering of reaction mixture, operation of the porous product maturation, stage of leaching and deoxidation of iron in the solutions using the cast-iron borings and many more). The solution obtained as a result of acid treatment is separated from iron by method of the ferrous iron crystallization on cooling and hydrolyzed afterwards. When tempering the hydrolytic sediment, TiO_2 is produced.

Using the sulfuric technology is related to high consumption of the concentrated sulfuric acid (4000-4500 kg/t of target product) and, in addition, results in the essential environmental contamination because the hundreds of thousands tons of the sulfate-containing waste in the form of $CaSO_4$ and acidic washing waters are discharged year on year. In case of sulfuric opening of ilmenites, many technologies were developed for substitution of liquid sulphatizing reagent for solid one, in part, ammonium sulfate $(NH_4)_2SO_4$. In case with the Ariadnensky ilmenite concentrate, the most environmentally safe but, at the same time, fairly simple and efficient method of processing was used (Lee and Sohn, 1989; Medkov et al., 2020). Herewith, the opening should be carried out in the solid phase by way of concentrate firing in abundance of ammonium sulfate in the role of the sulphatizing reagent at 360-400°C within 4.0-4.5 hours. The obtained product is leached by water with ratio of S:L=1:5.0-5.5. As a result, the solution containing sulfates of iron and titanium is produced. The non-dissolved residual is detached after which, from the obtained solution by way of the thermal hydrolysis at 80-90°C within 1.5-2.0 hours, the anatase titanium dioxide is obtained in the form of deposit which is removed. The thermal hydrolysis is performed in the presence of reducing reagent providing a conversion of the ferric iron to the ferrous one. From the solution remaining after separation of titanium dioxide, the sulfate of iron is obtained. Ammonia in a gaseous state is caught and recycled in the form of ammonium sulfate (Fig. 2).

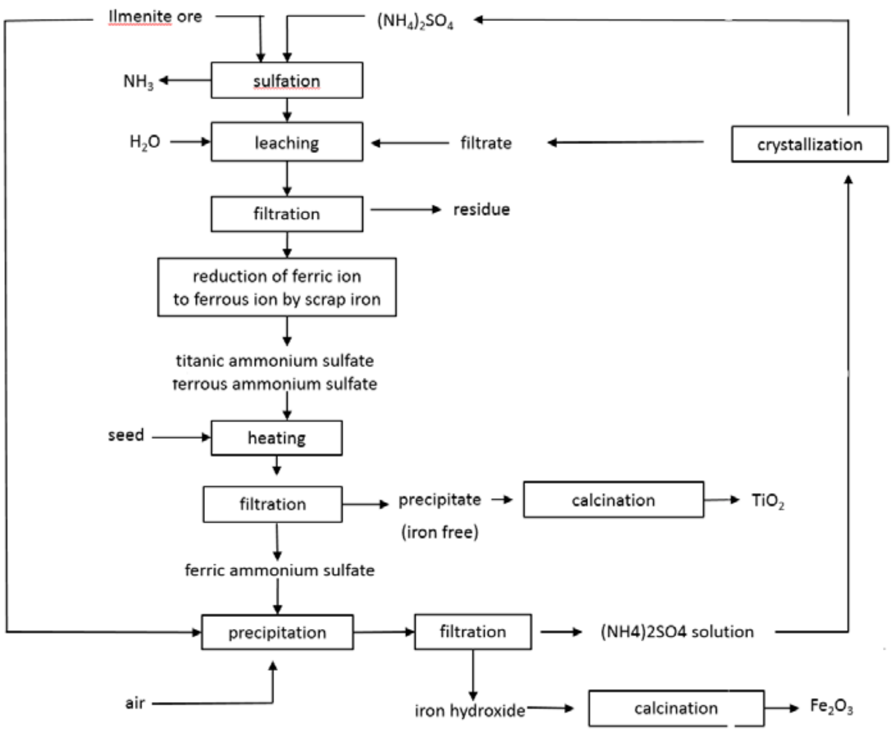

Fig. 2. Technological scheme of producing TiO2 from ilmenite

In the course of performing the experiment for recovery of commercial components from the magnetic concentrate, it was established that the interaction of ilmenite with ammonium sulfate $(NH_4)_2SO_4$ begins upon reaching the temperature of thermal decomposition of $(NH_4)_2SO_4$ (300°C) and proceeds in the temperature interval of 300-400°C with formation of the mixture of double salts: sulfates of iron and ammonium with compositions of $(NH_4)_2Fe_2(SO_4)_3$ and $NH_4Fe(SO_4)_2$ and sulfate of ammonium and titanyl with composition of $(NH_4)_2TiO(SO_4)_2$. The water leaching of the product obtained as a result of interaction between the ilmenite concentrate and $(NH_4)_2SO_4$ allows to transfer to solution practically entire titanium and basic mass of iron and associated commercial components in the form of double salts very soluble in water.

The non-magnetic gravity concentrate including the basic mass of PM was used as the source raw material for the hydrometallurgical studies. When concentrating, the cyanide technology constituting a threat for environment is usually used. Formerly, we have established (Molchanov et al., 2019) that the gold is efficiently extracted from the above kind of raw material in the course of leaching by thiocarbamide-thiocyanate solutions. As the extractive agents, the tributyl phosphate (TBP), diphenyl thiourea (DFTU) and their mixture were used. It has been established that the thiocarbamide gold complexes generated in the course of leaching are practically not extracted by the individual extractive agents and weakly extracted by the mixture of DFTU and TBP. In addition, the gold is extracted by TBP as well as by mixture of DFTU and TBP with high distribution coefficients when entering the thiocyanate-ions into the thiocarbamide solutions. Herewith, it has been established that the release of the sodium thiocyanate to the thiocarbamide solutions does not worsen the degrees of gold extraction at the leaching stage and, most importantly, the extraction is not accompanied by change-over of thiocarbamide to the organic phase because the gold is extracted in the form of thiocyanate complexes. As a result, the use of the liquid extraction at the stage of gold recovery from the leaching solutions allows to avoid the losses of thiocarbamide.

It should be noted that, in the presence in the leaching solutions of the associated components, they change almost completely into the organic phase. In that respect, we have made an attempt to separate out all metals from the organic phase omitting the washing-out stage. The conducted studies have demonstrated that the metals are most effectively deposited from the organic phase by natrium borane. So, on treatment of extract with solution containing 0.5 mole/l of $NaBH_4$, the black sediment emerges at the phase boundary. In this case, the extractive agent is not destroyed and does not lose the capacity for the PM extraction. The filtered interphase sediment, after washing-out by the concentrated nitric acid, was exposed to the oxidizing melting (Fig. 3). The total gold recovery from the raw materials according to the above-noted scheme has reached 89-90%.

4. Conclusion

As a result of the performed studies, the principles of the low-waste technology of recovering the commercial components from the schlich material of the Ariadnensky placers with the use of the complex of gravity, electromagnetic separation and pyro-hydrometallurgy methods were developed. The proposed technical solutions on the extracting the commercial components with observance of the principles of sustainable nature management and environmental safe are only first step in development of ilmenite placers in the southern Far East of Russia. It is evident that the further studies should be carried out on the lines of the comprehensive processing of the gold-titanium-bearing sands which will allow to reduce costs for recovery of some products and to provide the higher effectiveness of production.

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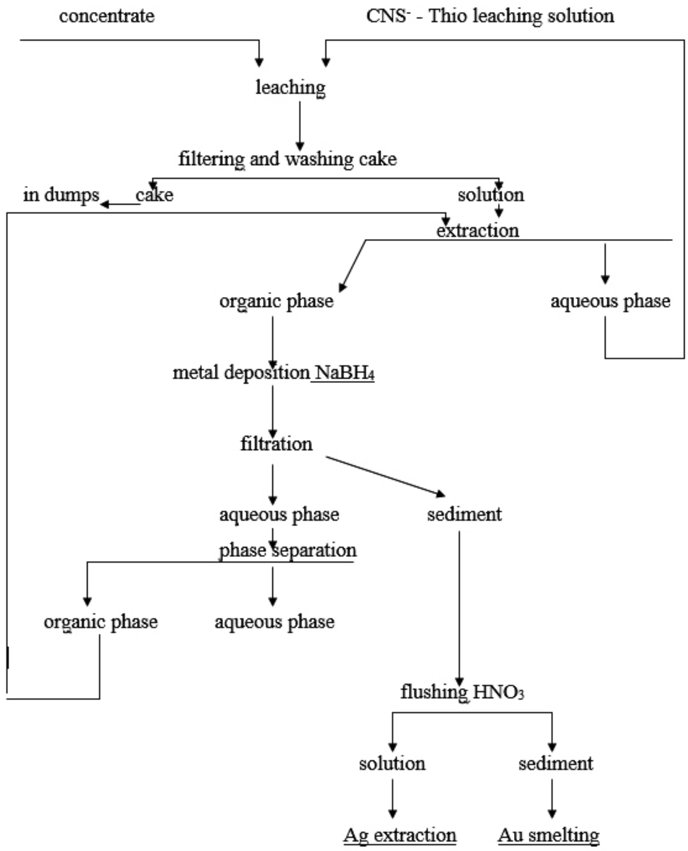

Fig. 3. Hydrometallurgical scheme for the recovery of gold

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