Strategic Metals Contained in the Ilmenite Placers of the Sikhote-Alin Ultrabasic Rocks: Mineralogical and Geochemical Characteristics and the Peculiarities of the Extraction

V P Molchanov¹

¹Far East Geological Institute FEB RAS, 159 Prospekt 100-letiya Vladivostoka, Vladivostok, 690022, Russia

E-mail: vpmol@mail.ru

Abstract. The main mineralogical and geochemical characteristics, as well as the ore potential of titanium-bearing placers spatially and genetically associated with the Ariadne intrusion of ultrabasites (Primorye), were determined. The composition of ilmenite, gold and platinum was studied, and a complex of associated strategic metals was identified. The possibilities of industrial development of ilmenite placers applying environmentally safe methods of pyro-hydrometallurgy were evaluated. The proposed technical solutions will expand the prospects of the raw material base in the South of the Russian Far East.

1. Introduction

Primorye belongs to one of the oldest areas of gold mining in Russia [1]. Precious metals had been mined here long before the arrival of the first Russian settlers. The intensive exploitation of alluvial gold deposits over many years has led to the depletion of their geological reserves, which could not but affected a sharp decline in volumes of extraction of precious metals. At the same time, there are good reasons to believe that the mineral raw material resource potential of the region is far from being exhausted. We need new approaches to forecasting, searching for and developing of the sources of the strategic mineral resources. One of these alternative sources are the complex manifestations of exogenous mineralization, in which strategic metals are the associated components. The solid types of mineral deposits have belonged to the strategic metals for a long time being essential for national security. Thus, gold provides the financial security of the state. Other metals have become critical for many industrial sectors recently. Moving from the category of exotic metals to strategic resources, they turned out to be extremely popular technologies of the future: rare earth elements are used in the production of mobile phones, computers and and titanium finds application in medicine and aircraft construction, etc. At the end of the last century, the concepts of “critical metals” and “critical mineral raw materials ” appeared in the foreign literature, both of them have established firmly in the economy of the leading industrialized countries [2]. Many of these critical metals (titanium, zirconium, platinum group metals, niobium, tantalum, hafnium, vanadium, cobalt, Surma, etc.) are present in the placers in the South of the Far East, spatially and tend to be related genetically to the intrusions of ultrabasites of the Sikhote-Alin orogenic belt. The main directions of their industrial development are detailed mineral and geochemical assessment and deep processing of raw materials based on the principles of
rational nature management and environmental safety. The ilmenite placers of the Ariadne massif of ultrabasites are an example of this approach, in which the authors discovered gold nuggets and platinum for the first time [3, 4].

The Ariadne array of ultrabasites located in the Central part of Primorye- to be more exact in the mid-channel of the Malinovka river - (the basin of the catchment area of the Ussuri river Ussuri, the tributary of the Amur river) belongs to the group of differentiated intrusions of the Sikhote-Alin orogenic belt, which are associated with the Samarka terrane of the Jurassic accretion prism [5]. The geological structure of Ariadne ore-placer cluster coincides with the contours of the massif of the same name and is comprised of the late Jurassic-early Cretaceous tuff - terrigenous formations, the late Permian siltstone and Sandstone strata, and Middle-Lower Jurassic volcanogenic-silicic-terrigenous rocks with olistostromes. Volcanogenic-sedimentary strata are broken by the Ariadne massif. Its southern part is composed of peridotites and olivine pyroxenites, while the middle part is predominantly formed by ilmenite and hornblende gabbro, passing into diorites, moncediorites and syenites in the North.

The Ariadne massif produces a number of large-size titaniferous mineral deposits, including placers of the Todorova river and its right tributary called Potapova stream. The length of these valley-type alluvial placers is 4.8 km and 1.2 km respectively, with a width of up to 520 m and 280 m, with an average productive reservoir thickness equal to 7.4 m and an ilmenite content of up to 375.5 kg / m3. Balance reserves of TiO2 of category C1+ C2 are equal to 702 thousand tons according to the indications dated by 01.01.2019, with the forecast resources reaching 500 thousand tons.

The main goal of our research is to create the foundations for low-waste technology for the fullest possible extraction of useful components (titanium, gold and platinum) from ilmenite placers using pyro-hydrometallurgy methods with reliable mineralogical and geochemical data being applied. The developed technical solutions will create preconditions for the industrial development of these objects without causing serious damage to the environment.

2. Methodology of experiment
Performing a complex of mineralogical and technological research was necessary for solving the above said tasks. Five bulk samples (the Pad Todokhova river - 3, Potapova key-2) weighing up to 500 kg each were selected from the studied placers, serving as the objects of the research. Mineralogical studies were performed using the Jeol Superprobe JXA 8100 electron probe microanalyzer with INCA Energy 350 Oxford Instruments and the EVO-500XVP electron scanning microscope with INCA Energy 350 Oxford Instruments.

The trace element composition of the samples was analyzed using an inductively coupled plasma mass spectrometer (ICP-MS) Agilent 750°C (Agilent Technologies, Japan) equipped with a Babington disperser, the cooled Scott spray chamber, and the grounded Fassel burner. Nickel cones of the sampler and skimmer were used. The determination of petrogenic elements was carried out on the atomic emission inductively coupled plasma spectrometer iCAP 650°C Duo (ISP-NPP) (Thermo Scientific, USA).

Technological studies were performed according to the traditional scheme for the enrichment of ilmenite-containing sands with preliminary gravitational enrichment and subsequent electromagnetic separation. The series of concentration tables and wet-type electromagnetic separators were used in this case.

To study the possibilities of interaction of ilmenite concentrate with ammonium sulfate, the studied ilmenite concentrate and (NH4)2SO4 were mixed with the purpose of forming of (double) sulfates containing either two components of the concentrate or ammonium. The obtained mixture contained in the glass-carbon crucibles covered with a lid was placed in a muffle furnace controller produced by the company Nabbertherm GmbH (Germany) and heated at a speed of 2.5 degrees/min to a predetermined temperature and was kept at this temperature for 4-6 hours. The quantities weights were equal to 10-40 grams.
Changes occurring with the substance during heating were controlled according to the decrease of the mass of the initial mixture with a subsequent usage of both the x-ray phase analysis method and x-ray fluorescence one.

The X-ray images of the samples were taken by means of using an automatic D-8 ADVANCE diffractometer with sample rotation in Cu Kα radiation. The X-ray phase analysis was performed using the EVA search program with the PDF-2 powder data bank.

The content of the main components of the solid phase was determined by means of the x-ray fluorescence analysis using a Shimadzu EDX 800 HS spectrometer (tube with a rhodium anode, vacuum) at room temperature in the form of a polytetrafluoroethylene (PTFE) tablet. The sample quantities weighing 1 gram were ground in an agate mortar with 0.5 g of PTFE with the further placing in a mold with a diameter of 20 mm and pressing for 2 minutes under a pressure of 20 Mpag.

The process of leaching the ilmenite concentrate treated with ammonium sulfate was carried out at room temperature by dissolving the resulting product in water for 15-30 minutes and further filtering through a "blue ribbon" filter. The content of elements in the obtained filtrates was determined by the atomic absorption analysis on the Solar 6 M spectrometer using the analytical lines of the elements-components of the concentrate.

Thermogravimetric studies were performed on the q-1000 derivatograph in platinum crucibles in air at a heating rate of 2.5 deg / min using quantities weighing of 100-200 mg.

3. Results of experiment and their discussion

The preliminary mineralogical studies of the initial sands have shown that titanium is exclusively represented by ilmenite in placers, the last one being the essential mineral for industrial extraction. The material composition of the initial productive sands is characterized by a predominance of the following elements (wt %), namely: TiO₂ – 19.55, SiO₂ -19.72, Fe₂O – 19.9, MgO – 4.48. The rare, rare earth and noble metals are recorded among the permanent impurities. The rare element composition is characterized by the presence of Ta (up to 100 g/t) and Nb (up to 11 g/t). The concentrations of the rare earth elements are relatively low. The content of Au and Pt rarely exceeds 0.1 g/t, while the quantities contain up to 1.1 g/t of Pd. It is impossible not to pay attention to the high level of concentration of the following elements (g/t), namely: V up to 730, Co- up to 340, Zn- up to 230 [3].

The placer samples passed the stage of preliminary concentrational enrichment followed by the further electromagnetic separation. The obtained gravitational concentrate is characterized by the high yield of the magnetic fraction (93-95% of the total mass) and a low yield of the non-magnetic fraction (5-7%). The basis of the first of them is ilmenite and titanomagnetite is fixed in small quantities. The distinctive features of the fraction material (ilmenite concentrate) are high content (wt %) TiO₂ (49.5), as well as the minor impurities of SiO₂ (1.02) and Cr (0.2), which fully meets the requirements of the industrial production of titanium with the usage of the sulfuric acid technology [6]. It is necessary to note the high level of content of such high-tech metals as Nb, Nd, Co, Cu in the concentrate of the mass fraction (up to 300 g/t).

The non-magnetic fraction is in fact a mixture (wt %) of anorthite (36.9), quartz (24.3), hornblende (17.6), sphene (15.4) and zircon (3.8). In addition, monazite, rutile, and apatite are contained in small quantities. The sulfides (single grains of pyrite, arsenopyrite, antimonite and Galena) and native metals (gold, platinum, zinc and Nickel) predominate among the ore minerals. The non-magnetic concentrate is characterized by the following chemical composition (wt %): SiO₂ – 49.6; CaO -13.2; Al₂O₃ – 11.0; TiO₂ – 9.4; ZrO₂ - 4.23; P₂O₅ – 4.15; Fe₂O₃ – 3.23; MgO – 1.84; Na₂O – 1.67; K₂O – 1.18; V₂O₅ – 0.096. The trace elements of the concentrate can be divided into two groups. The first of them includes rare and rare earth elements (g/t): Hf - 830, Ce - 320, Y - 220, the second group includes noble metals-Au, Ag and Pt, the concentrations of the last ones varying within the limits of 0.5-3.0 g/t.

Ilmenite is known to be decomposed relatively easily by acids [7, 8, 9, 10], so the sulfuric acid method is widely used for the opening of the first one. This is the oldest industrial method of extracting TiO₂ from ilmenite, which consists in converting ilmenite into soluble sulfates. The process
includes three stages and a large number of operations, for example, drying the concentrate to a humidity of 0.5%, oleum sulfation at 80-210°C accompanied by the effervescence and dispersing of the reaction mixture, aging of the porous product, leaching and revivification of iron in solutions with cast iron chippings, and many others. The solution obtained from acid treatment is purified from iron by the method of crystallization of the ferrous nitrate by means of cooling with the further sending to hydrolysis. TiO₂ is obtained due to calcining the hydrolytic sediment.

The use of sulfuric acid technology leads to a large consumption of concentrated sulfuric acid (400⁰-450⁰ kg/t of the target product) and, in addition, leads to significant environmental pollution, since hundreds of thousands of tons of sulfate-containing waste in the form of CaSO₄ and acidic wash water are dumped annually. The solid sulfatizing reagent is proposed to be used [11, 12, 13] instead of the liquid one during opening of ilmenites with the usage of sulfuric acid. The most environmentally safe, but rather simple and effective method of solid-phase interaction of Ariadne ilmenite concentrate with ammonium sulfate (NH₄)₂SO₄ was used in our case [14, 15]. That is the opening was performed in the solid phase by firing the concentrate containing an excessive quantity of ammonium sulfate as a sulfatizing reagent at a temperature of 300-400⁰ for 4.0-4.5 hours. The reaction resulted in the formation of a mixture of the sulphates highly-soluble in the water-ammonium sulphate (NH₄)₂Fe₂(SO₄)₃ and iron sulphate NH₄Fe(SO₄)₂ compositions and ammonium titanyl sulphate (NH₄)₂TiO(SO₄)₂. The resulting product is leached with water at a ratio of S:W=1.5:0.5 to 5.5 to obtain a solution containing iron and titanium sulfates. The insoluble residue is separated from the resulting solution by thermal hydrolysis at a temperature of 80-90°C within 1.5-2.0 hours, then the titanium dioxide of anatase modification is obtained in the form of a precipitate, which is removed. Thermal hydrolysis is performed in the presence of a reducing agent that provides the transition of trivalent (ferric) iron into (ferrous) divalent one. Iron vitriol is obtained from the solution remaining after separation of titanium dioxide. The ammonia released in the gas form is captured and returned to circulation in the form of ammonium sulfate.

Non-magnetic gravity concentrate, which includes the bulk of precious metals (BM), served as the raw material for hydrometallurgical research. The cyanide technology is usually used for enrichment, which poses a significant threat to the environment. Previously, the gold was found to be effectively extracted from the above said type of raw materials by means of leaching it with thiocarbamide-thiocionate solutions. Tributyl phosphate (TBP), diphenylthiourea (DPTU) and their mixture were used as extractants. The thiocarbamide complexes of gold formed during leaching were found not to be hardly extracted by individual extractants and to be able to be poorly extracted by a mixture of DPTU and TBP. At the same time, gold is extracted by TBP, as well as by a mixture of DPTU and TBP with high distribution coefficients when thiocarbamide solutions are introduced with thiocinatan ions. The release of thiocyanate sodium into the thiourea (thiocarbamide) solutions was found not to worsen efficiency of gold extraction at the stage of leaching and, most importantly, extraction is not accompanied by the transition into the organic phase of thiourea (thiocarbamide), because the gold is extracted in the form of thiocyanate complexes. Thus, the use of liquid extraction at the stage of extracting gold from leaching solutions allows to avoid the loss of thiocarbamide.

It should be noted that if the associated components are contained in the leaching solutions, the latter almost completely pass into the organic phase. In this regard, we have attempted to separate all metals from the organic phase, bypassing the washing stage. Due to the studies conducted the metals were found to be most effectively precipitated by sodium borohydride. Thus, a black precipitate appears at the phase interface due to the processing the extract with a solution containing 0.5 mol/l NaBH₄. In this case, the extractant is not destroyed and does not lose the ability to extract the BM. The filtered interphase precipitate was subjected to oxidizing melting after washing with concentrated nitric acid. Total gold recovery from raw materials reached 89-90% due to applying the above described scheme.
4. Conclusion

Thus, the above described scientific studies have led to working out of the fundamentals of the original low-waste technology of extraction of useful components from placer material of Ariadne alluvial deposits using the complex of methods of gravity, electromagnetic separation and pyrometallurgical principles of environmental management and to improving the ecological status of the environment. The basis of the magnetic concentrate of the initial sands is the ilmenite concentrate (over 50% TiO₂), which meets the regulations of technological schemes for industrial production of titanium products. The presence of high concentrations of V, Nb, Nd, Co is its distinctive feature. The non-magnetic concentrate is remarkable for not only containing the industrial concentrations of Au, Ag, Pt, but for the presence of such metals as Hf, Ce and Y that are scarce for industry.

During conducting of the experiment of extracting useful components from a magnetic concentrate the interaction of ilmenite with ammonium sulfate NH₄Fe(SO₄)₂ was found to begin when the temperature of thermal decomposition (NH₄)₂SO₄ equal to 300°C is reached and to proceed in the temperature range of 300-400°C to form a mixture of double salts (sulphates)-ammonium sulfate(NH₄)₂Fe₂(SO₄)₃ and iron sulphate compositions NH₄Fe(SO₄)₂ and ammonium and titanyl sulphate of the composition (NH₄)₂TiO(SO₄)₂. Water leaching of the product of interaction of ilmenite concentrate with (NH₄)₂SO₄ allows converting almost all titanium and the bulk of iron and associated useful components into a solution in the form of water-soluble double salts (sulphates).

The precious metals were extracted from the non-magnetic concentrate by leaching with thiocyanate-thiocarbamide solutions. The degree of gold recovery is 89-90%.

The proposed technical solutions for extracting useful components in compliance with the principles of rational nature management and environmental safety are only the first step in the development of ilmenite placers in the South of the Russian Far East. It is obvious that further research should be carried out in the direction of complex processing of gold-titanium-bearing sands, which will reduce the cost of obtaining individual products and ensure higher production efficiency.

5. References

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