Coastal-marine and legacy placers of the southern Primorye (Russia): ecology and commercial exploitation

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Abstract. The article is devoted to the development of technology for re-enrichment of waste from the exploitation of old gold-bearing placers that pose a significant threat to the environment. Technogenic and coastal-marine placers of the south of Primorye (Far East, Russia) were chosen as the object of research. At the same time, methods of powder metallurgy, as well as leaching of precious metals and metallic mercury with thiocarbamide-thiocinate solutions with their simultaneous demercurization were used. The application of this scheme for the extraction of useful and toxic components from placer material will allow to involve in industrial circulation numerous man-made and beach placers of the south of the Russian Far East in compliance with resource-saving principles and environmental aspects.

1 Introduction

Primorye is one of the oldest gold mining areas in Russia. Intensive exploitation of placer gold deposits for many centuries led to the depletion of their geological reserves, which could not but affect a sharp decline in the production of precious metals (BM). At the same time, there are good reasons to believe that the golden potential of Primorye is far from being exhausted. One of the alternative sources of BM are technogenic placers (waste from old gold mining), since during operation, mainly only large particles of free metal (freed from rock) were extracted, and small and thin, which account for at least half of the initial reserves of 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 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 the imperfection of enrichment technologies based on the use of mercury. All this has led to the fact that a significant amount of not only useful components, but also mercury has accumulated in the waste of operation. Another potential reserve of BM is the metalliferous placers of the Primorsky Shelf. Modern methods of processing mineral raw materials create prerequisites for revaluation of all these objects in order to develop them comprehensively.

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The main goal of our research is to create, on the basis of reliable mineralogical and geochemical information, the basics of resource-saving technology for the fullest possible extraction of useful components from coastal-marine and man-made placers in the south of the Russian Far East using pyro-hydrometallurgy methods. The developed technical solutions will create prerequisites for the industrial development of these facilities and reduce the level of environmental pollution.

The proposed paper consists of three basic parts:

- examination of mineral forms of concentrating and features of distributing the valuable components in the magnetic and non-magnetic concentrates of initial sands including the ground mass of titano-magnetite and PM respectively;
- assessment of capabilities of titano-magnetite processing with the use of the powder metallurgy methods;
- development of the technological schemes of PM and metallic mercury with the use of ecologically-friendly thiourea–thiocyanate leaching solutions.

2 Object and methods

As the base objects of the studying, the legacy and coastal-marine placers of the Krinichny node (Fig. 1 a, b) accumulating the extensive resources of gold and titano-magnetite [1] were chosen. The attention to the placer occurrence was drawn by their favorable geographical position in the densely-populated coastal area of the southern Primorsky Krai (in the vicinity of Nakhodka town) and well-developed infrastructure creating the efficiency of using the modern technology of extraction of exploitable minerals. The native gold was here mined well before the appearance of the first Russian path breakers [2]. The gold mining was greatly actively carried out in post-revolutionary time. As a result of centuries-old exploitation, the alluvial placer was fully developed. At that, the extraction of the precious metal was for the longest time carried out with the use of technologies based on application of mercury.

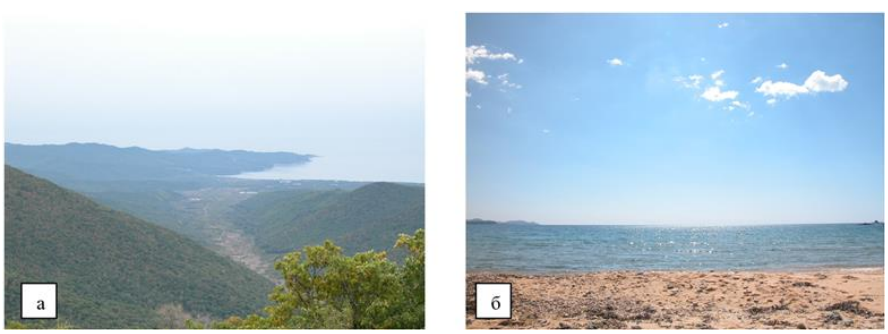

Fig. 1. Below the figure Placers: a - legacy (Bolshaya Rudnevka river); b - coastal-marine (Rudnev bight, Sea of Japan).

In late decade of exploitation (until the mid-1990s), the finishing operations were carried out in the gold-concentrating plants where extraction of native gold was made with the use of concentration tables and, there again, metallic mercury. All of this has resulted in formation of significant accumulations of final tailings of gold mining with volumes of many thousands cub. meters with high concentrations of mercury. The problem has emerged: could be these wastes wholly accessible raw materials for industrial activity or they are only one of essential sources of environment pollution. This question is greatly vital due to the fact that the Rudnevka river is used for water supply of a number of settlements and the sea beach of the Rudnev bight is a zone of mass recreation in summer.

3 Results and Discussion

The taken stream-sediment samples passed previously through gravity concentration with the subsequent division by way of magnetic and electromagnetic separation into the magnetic, electromagnetic and non-magnetic fractions. The obtained gravity concentrate is characterized by high yield of magnetic fraction (up to 80%), low ones of electromagnetic fraction (18-19%) and nonmagnetic fraction (1-2%).

The magnetic fraction, in chemical composition, is in compliance with the highly-titanium variety of magnetite with low level of chromium accumulation. A share of foreign impurities is small. In the electromagnetic fraction, apart from ilmenite forming the basis of material, the singular grains of chromite are registered. The non-electromagnetic fraction represents practically the mixture of zircon and sphen (75-80% of total mass) with leading role of zircon. As concerned the ore minerals, the sulfides (mainly, pyrite, sphalerite, galenite) predominate, and cinnabar, minerals of bismuth, native gold and metallic mercury are present in the lesser amounts. The composite components of fraction can be divided into 2 groups. The first of them includes Zr, Ti, Fe the content of which does not usually exceed 10 mas. %; second group contains Hg, Pb, Cu, Zn, W, Mn, Sc the concentrations of which change within the limits of 0.01-1.0 mas.%. The high level of Hg accumulation (more than 1000 g/g) exceeding the MPC (maximum permissible concentrations) many times should be noted. Its contents in the soil and plants springing up in the dumps of previous gold mining are essentially high.

All gold grains extracted from the non-electromagnetic fraction can be divided into two groups. One of them (predominant) includes the gold particles showing the signs of amalgamation. The phenomena of amalgamation are well developed in all studied placers and caused, as mentioned above, by the long-term application of metallic mercury in the course of exploitation. The amalgamated gold has usually the light-yellow or white color, sometimes, with earthy nuance. In certain cases, the corrosive surface of amalgam is coated with fine crystals.

The other group is composed by the less widespread unaltered alluvial gold which is present in the gravity concentrate, most often, in free form and is observed more rarely in the intergrowths with quartz and sulfides. The values of the metal fineness change in the interval of 770-980‰.

The mercury in the gravity concentrate is presented by fine silvery bulbs of liquid metal slightly soluble in water but easily reacted with the atmospheric oxygen when increasing the temperature in summer season. The mobility of mercury and permeability of its vapors extremely harmful for the human organism are well-known.

A presence of appreciable quantity of one of the most toxic chemical elements – mercury – allows us to ascribe the man-made mineral formations of the Krinichny node to the class of especially toxic matters. Reaching the environment as a result of man-made impact in amounts exceeding the natural background, the mercury exacerbates deeply the environmental situation. A large portion of metallic mercury is usually caught by the organic matter of the upper soil horizons. But, within the limits of large-volume old dumps, the contamination by mercury of the ground and surface waters, soils, potting soils, bottom deposits and vegetation cover takes place. In this case, it should be noted that the soil-plant system is the key link of the food chain in which the flux of mineral constituents absorbed by animals and human forms.

The material characteristics of the black sand from the beach placer are identical to the analogs from old dumps.

The low-waste technology of extracting the valuable components with the use of the pyro-hydrometallurgy methods can help to the integrated development of the legacy and beach placers. As the raw products, the magnetic and non-electromagnetic fractions of the placer material concentrating the basic mass of titano-magnetite and zircon, gold and metallic mercury respectively were used. In the course of processing the titano-magnetite concentrate, the methods of the powder metallurgy were used while the PMs were in turn extracted with application of the hydrometallurgical schemes.

3.1 Pyrometallurgy

Iron, titanium, oxide minerals are widely presented in the sands of the coasts of the Far-Eastern seas including the vast territories from Kamchatka to southern Primorye. Among the natural oxides, the minerals of series of the solid solutions of oxides FeO-Fe_2O_3-TiO_2 are isolated [3,4]. In composition, the Fe-Ti-oxides are divided into three series: titanium-magnetite, hemo-ilmenite and pseudo-brookite [5]. The content of V in the minerals correlates well with the content of Ti.

The basic ore constituent in the placer of the Rudnev bight is titano-magnetite $nFeTiO_4{\cdot}(1\text{-}n)\ Fe_3O_4$ which is observed in the form of roundish grains, disturbed octahedrons and sharp-edged fragments and presents the solid solution with the isomorphous inclusion of titanium into the magnetite grid. Along with titano-magnetite, the oxides and silicates in the form of ilmenite and pyroxenes are present in the placer material in the insignificant amounts, moreover, the ilmenite ($FeTi0_3$) forms the grains with well pronounced crystallographic forms (laminar hexagonal crystals).

Technological process of treating the magnetic fraction of sands by methods of the powder metallurgy [6] includes the concentration of schlich, fine grinding, restoration of concentrate, compaction and agglomeration of the powdered material. For removal of the nonmagnetic constituents, the double magnetic separation was applied. As a result, the rich in iron titano-magnetite concentrate with the following composition: Fe_3O_4 – 85.32, TiO_2 - 8.25, MnO – 0.57, V_2O – 0.47, Cr_20_3 – 0.06, $Zr0_2$ – 0.02 mas. % - was isolated from sand.

For obtaining the metallic phase, the titano-magnetite concentrate is exposed to the recovery annealing in hydrogen. The restoration of titanium component (ulvospinel) using hydrogen can be presented by elementary transformations: $Fe_2TiO_4 \rightarrow FeTiO_3 + Fe_M \rightarrow Fe_M + TiO_2$. These chemical transformations are performed under conditions of the slow formation of the reaction products when the phases with the respective composition are in time to form. In the experimental investigations, the effect of titano-magnetite concentrate processing conditions on the process of its restoration was studied. The samples with masses of 5-10 g were processed in the hydrogen medium at temperatures of 750-1000^{0}C within 1-3 hours. It has been established that, in the course of the recovery annealing, the mass of the titano-magnetite concentrate coagulates forming the agglomerate the strength of which increases with the annealing temperature. For this reason, the treated samples of the powder should be exposed to crushing out in the ball mill. The powder treated at temperature of 750°C does not coagulate and, after three hours of reaction, it is no success to obtain the completely metallized iron. The samples were made of the obtained powder by way of cold pressing at the specific pressure of 7 t/cm^2 and vacuum sintering at temperature of 1150°C. The microprobe investigation of the metallographic specimens of the sintered material shows the firmly differentiable structure of the alloy of two phases: iron containing titanium and phase created by the oxides of titanium, vanadium, aluminium, magnesium and other elements.

As a result of the carried-out experiments, the heavily-alloyed powders of iron with different dispersability having free running and the structure proper for the further alterations were obtained which is particularly true in connection with the increasing deficit of the efficient instrument materials.

One way to get around this problem is the creation of the composition materials on the base of the titano-magnetite concentrate, particularly, such in which iron is the binding phase and the other components are presented by oxides, carbides and carbonitrides of other metals.

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Such material is characterized by high homogeneity of structure, uniformity of properties, balanced shrinkage, perfect reproduction of the intended configuration and is competitive with abrasive materials of carbidosteels type in the durability. As concerned the thermophysical properties, the material is comparable with fireproof alloys of the ferritic composition. Its advantages include the combination of high melting point with small thermal-expansion coefficient and high corrosion resistance.

3.2 Hydrometallurgy

After passing the stage of electromagnetic separation, the nonmagnetic constituents of the gravity concentrate including the basic mass of gold and metallic mercury have served as the original crude for the hydrometallurgical investigations based on dissolution of the useful components by active reagents upon contact with leaching solutions. The leaching of PM is usually performed with the use of cyanides which is associated with the significant environmental deterioration [7]. Earlier on, we have established [8] that the gold and mercury from the mentioned type of raw material are efficiently extracted when leaching by the thiourea–thiocyanate leaching solutions. Because the extensive industrial use of the thio-carbamide dissolution of PM is hampered by the higher price of thio-carbamide and its loss at the stages of filtration and extraction of gold, the process of gold extraction from the thio-carbamide solutions with the use of liquid extraction as possible way of decreasing the losses of thio-carbamide when processing the gold concentrates was proposed. Moreover, the use of liquid extraction at the stage of recovery of gold and silver from the leaching solutions allows us to selectively extract the precious metals with additional separation from impurities. One problem which arises in this case is withdrawal of Fe, As, and Cu accumulated in the turnover. Nevertheless, this problem is resoluble because the technology provides for the full neutralization of reusable solutions with lime after five-seven cycles of leaching for decreasing the total saline background.

As the extragents, the tributyl phosphate (TBP) and diphenyl sulphourea (DSU) and their mixture were used. It has been established that the thio-carbamide complexes of gold forming in the leaching process are practically not extracted by individual extragents and are slightly extracted by the mixture of TBR with DSU. However, the gold is extracted by TBR as well as mixture of DSU and TBR with high distribution coefficients when introducing the thiocyanate to the thio-carbamide solutions. At the same time, it has been established that the release of sodium thiocyanate to the thio-carbamide solutions does not worsen the degree of gold extraction at the stage of leaching and, most importantly, the extraction is not accompanied by the transition of thio-carbamide into the organic phase because the gold is extracted in the form of thiocyanate complexes. Therefore, the use of the liquid extraction at the stage of gold extraction from the leaching solutions allows us to avoid the losses of thio-carbamide.

It should be noted that, in the presence of mercury in the leaching solutions, the last passes almost completely into the organic phase. In this connection, we have made an attempt to release all metals from the organic phase omitting the washing stage. The carried-out investigations have shown that the metals from the organic phase are settled most effectively by natrium borane. So, when processing the extract with the solution containing 0.5 mol/L of $NaBH_4$, the black powder appears at the phase boundary. In this case, the extragent is not destroyed and does not lose the capacity to extract the PM. The filtered interphase sediment was exposed to the oxidizing melting (Fig. 2) after the washing by the concentrated nitric acid. Total gold recovery with the use of the above-mentioned scheme reaches 91%.

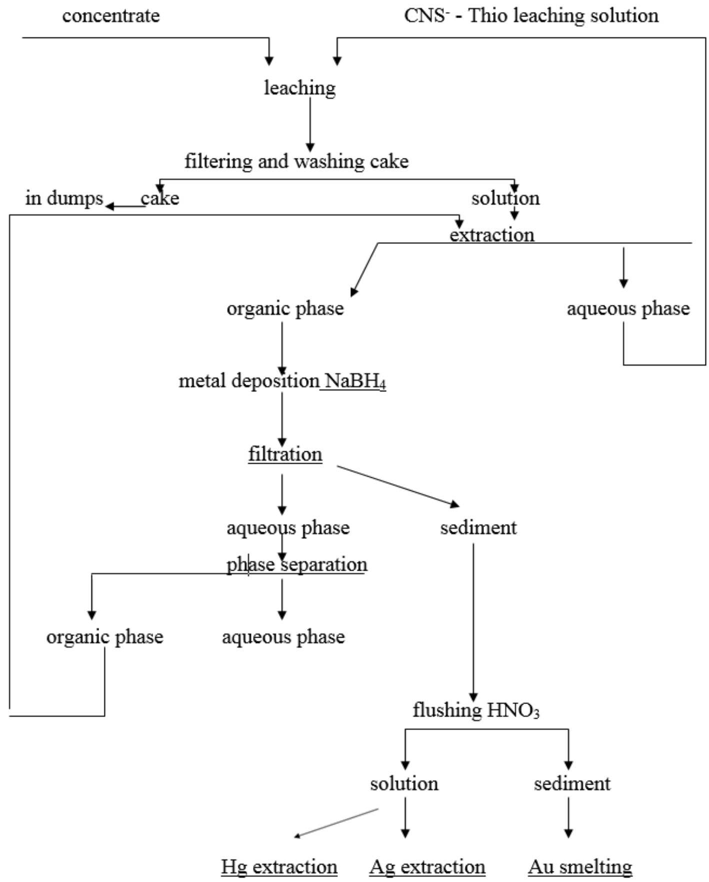

Fig. 2. Hydrometallurgical scheme for the recovery of gold.

4 Conclusion

As a result of the work carried out, the foundations of an original resource-saving technology for extracting useful and toxic components from the slurry material of technogenic and coastal-marine placers using a complex of methods of gravity, electromagnetic separation and pyro-hydrometallurgy have been developed. At the first stage, the initial sands underwent gravitational enrichment, followed by separation by magnetic and electromagnetic separation into magnetic, electromagnetic and non-magnetic fractions. At the second stage, the magnetic material, represented by titanomagnetite, underwent fine grinding, reduction firing in hydrogen and sintering of the powder material. At the third stage, non-magnetic components, which include the bulk of gold and mercury, served as raw materials for exposure to thiocarbamide-thiocinate solutions. The use of this scheme for processing metal-bearing sands allowed not only to obtain native gold and iron powders of various dispersities, but also to demercurize the concentrates. The involvement of waste from the enrichment of gold-bearing placers in the sphere of industrial production will have a beneficial effect on the ecological situation of the densely populated south of the Far East, where they are located.

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