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EXTRACTION OF PLATINUM METALS DURING PROCSSING OF CHROMIUM ORES FROM DUNNITE DEPOSITS

Georgii V. PETROV[1], **Yakov M. SHNEERSON**[2], **Yurii V. ANDREEV**[3]
[1] *Saint-Petersburg Mining University, Saint-Petersburg, Russia*
[2] *LLC «Research and Development Center «Gidrometallurgiya», Saint-Petersburg, Russia*
[3] *Peter the Great St.Petersburg Polytechnic University, Saint-Petersburg, Russia*

Currently, the main raw materials sources of platinum group metals in Russia are complex sulfide copper-nickel ores of the Taimyr region and placer deposits. However, in view of the inevitable loss of platinum metals during the metallurgical processing of initial ores and the deterioration of the quality of ore raw materials, along with a decrease in the share of platinum mining from placers, there is a need to look for new non-traditional sources of platinum group metals. Dunnites of the Middle Urals are promising platinum-bearing raw materials. The use of the gravitational-magnetic processing of chromium ores of dunnite deposits makes it possible to identify a magnetic platinum-bearing concentrate with a high content of magnetite and platinum-iron alloys, they can be refined using chemical-metallurgical methods. This article presents the results of research of identifying peculiarities of technological behavior of chromium, iron and noble metals during mechanical processing of ledge chromium ore. The kinetic regularities of the sulfuric acid decomposition of magnetite are determined. Optimum technological parameters of sulfuric acid leaching of iron from magnetic products of chromium ore dressing are established. Based on the conducted studies, the PDF and PID for the complex processing of chromium ores of dunnite deposits is proposed, which ensures the production of a rich platinum-bearing concentrate and a high-quality chromite concentrate that meets the requirements of chemical production.

***Key words*:** platinum group metals, dunnite deposits, chromium ores, magnetite, sulfuric acid leaching

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Introduction. Currently Russia is one of the largest producers of platinum metals in the world. Mineral raw material base of the Russian Federation of platinum group metals consists mainly of platinum deposits of the largest sulfide copper-nickel deposits of the Taimyr region. The production of platinum group metals (PGM) from Norilsk deposits, together with a decrease in platinum production from alluvial deposits, will not ensure the preservation of high volumes of exports and, accordingly, foreign exchange earnings. An essential circumstance complicating the prospects of Russia as a producer of PGMs is the tendency of price changes – at a relatively stable price for platinum, the cost of palladium has sharply decreased (by 3.5-4 times) [2-4, 6, 13].

Analysis of the foreign PGM raw material potential is the evidence to the contrary – there are great opportunities for increasing platinum production in South Africa and increasing palladium production in the USA and Canada (by 20-40 tons annually until 2020) [7, 12, 14, 15]. This, to some extent, means that Russia could be under competitive pressure on the world PGM market, where it is a leading partner [1].

To maintain traditionally strong positions in the world PGM market, it is necessary to increase production of platinum and it is a fundamentally important direction for the development of the Russian platinum-metal complex. The prospecting for ores with other types of platinum-metal mineralization compared to Norilsk and their mining combined with the development of efficient PGM recovery technologies will lead to an increase in the production of platinum metals in Russia and, ultimately, to its independent position in the world market [1, 4].

The most significant in terms of its metallogenic potential is the platinum metallurgical mineralization of the zonal dunnite-pyroxenite-gabbro complexes of the Urals, Aldan and Kamchatka, which are the main sources of now mined out placer deposits.

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The possibility of using chromium-bearing ores as a source of scarce platinum metals is a new issue for the Russian Federation. Up to now, in accordance with the established Russian and world practice, dunnites of zonal assemblages of the Middle Urals have been considered as a mineral raw material for the production of chromium-magnesite refractories without taking into account the PGM. Given the economic importance of platinum-containing dunnites, the question arises not only about assessing their resource potential, but also about the development of technological methods for the associated recovery of platinum group metals from them [9].

Studies of Russian scientists show the promise of MPG recovered from Russian dunnite ores of the zonal assemblages of the Middle Urals (Nizhny Tagil and Svetloborsk), the Aldan shield (Konderskoe and Inaglinskoye deposits) and the Galmoenansky massif of Kamchatka, characterized mainly by platinum specialization [8, 10]. It has been established that platinum is present in dunnites exclusively in its own free mineral forms, which are represented predominantly (65 %) by platinum-ferrous alloys. The ore platinum-chromite mineral association is identified as the main one for ores with a high platinum content.

A comparative analysis of preparation characteristics of alluvium and eluvium from the Nizhnetagilsky deposit and various morphological types of Aldan ore allowed to make a conclusion about the advisability of combining gravitational and magneto-electrostatic methods for the isolation of high grade concentrates in which the content of the PGM can reach 500-1000 g/t. At the same time, beyond the framework of detailed technological studies, the behavior of the ledge ores of the Middle Urals remained, characterized by a lower content of PGMs and represented by significant reserves [4].

Gravitational processing technology of Kamchatka's lodge ores (Galmoenansky massif) with the production of platinum high grade concentrate (up to 5 kg/t), tested in semi-industrial conditions, was proposed for introduction at the construction of a processing plant with a capacity of 5 million tons of ore per year (CJSC «Koryakgeoldobycha») [10].

Being fundamentally different from the products of sulfide copper-nickel ores processing by its chemical and phase composition, platinum-metal concentrates from mechanical processing of dunnites cannot be directly transferred to refining, despite a serious decrease in the input requirements for the quality of refined raw materials (from 5 to 1 % PGM).

Currently, there is a significant number of pyro- and hydrometallurgical methods for processing platinum-metal raw materials, focused primarily on obtaining high grade selective concentrates of platinum-group metals, which are then fed to refining.

Given the siderophilic nature of dunnites from the Middle Ural and available data on the high content of the platinum-iron alloys in the products of their gravitational and magnetic separation as a promising method of recovery of platinum-bearing concentrate may be considered chemical refining magnetite concentrate by dissolving iron in sulfuric acid medium over a reducing agent. An obvious advantage of reductive sulfuric acid leaching is the provision of complete absence of transition of platinum group metals into solution. The usage of iron powder as a reducing agent will provide the production of high grade platinum and saturated sulphate solutions, which can be a source of iron sulphate. Thus, it can be assumed that the combination of gravitationally magnetic concentration methods and reductive sulfuric acid leaching of dunnite makes it possible to produce standard platinum concentrate.

Theoretical and experimental studies. The studies were carried out on the enlarged technological sample of the ledge ore from the Nizhny Tagil massif («Dunitovy» quarry) of the following composition, %: 1.6 Cr; 6.3 Fe; 22.5 Mg; 39.1 SiO_2; 0.21 g/t Pt; 0.08 g/t Rh. The mineral composition of the ore samples was studied on a polarized Zeiss Axiolab microscope. The microanalysis of the minerals was performed using the CamScan S4 electron microscope with Pentafet SuperATW energy dispersive spectrometer and Link ISIS 200 microanalysis system. The results of mineralogical studies using the isolated three fractions (–1.4 + 0.1, –0.1 + 0.071;

0.071 + 0 mm) of ore indicate that the ore minerals are chromite of three varieties (chromium content varies from 37 to 56 % by weight), fine inclusions of sulphides (millerite, pentlandite, chalcocite), as well as magnetite (Fig.1). The magnetic fraction in the ore is no more than 1-2 % by volume. Platinum is predominantly Pt-Fe (up to 65 %) and Pt-Cu alloys with ferromagnetic properties.

Studies of chromium, iron, and PGM behavior were carried out according to the processing flow chart adopted for ores containing valuable specific heavy minerals. The scheme includes screening with distribution into classes and their subsequent jigging (–6+3, –3+1 mm) and classification (–1+0 mm). Concentrates, industrial products and tails of these operations after regrinding and screening by small classes (–1+0.4, –0.4+0.2, –0.2+0 mm) were concentrated on a table to isolate the «head», beneficiated PGM, and chromite concentrates. The refinement of gravity concentrates was carried out by the successive application of magnetic and corona-electrostatic separation (CES).

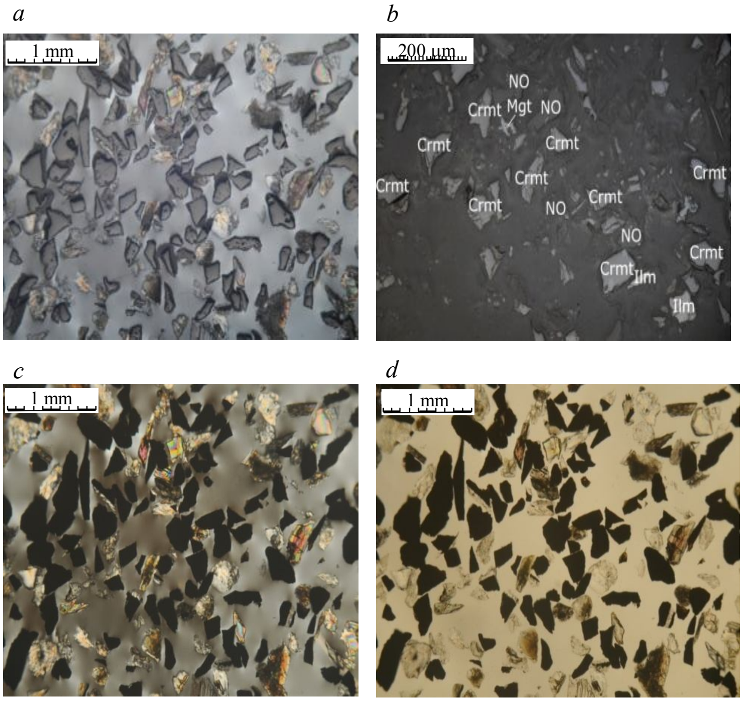

Fig.1. Minerals of chromium ore (fraction –1.4+0.1 mm): *a* – chromite grains (gray color) against non-metallic minerals (serpentite, chlorite and quartz) in the mode of reflected light with an analyzer; *b* – grains of chromite (Crmt), magnetite (Mgt) and ilmenite (Ilm) in the mode of reflected electrons; *c* – chromite grains in the transmitted light mode, parallel Nicols; *d* – chromite grains in transmitted light, crossed Nicols (black grains that do not transmit light – chromite)

The gravity fractionation of chromium ore allows to provide a high degree of concentration of chromium minerals and PGM in the gravity product (up to 80 % chromium and 70 % platinum). With the use of wet magnetic separation, a strong magnetic fraction containing up to 54 % Fe predominantly in the form of magnetite Fe_3O_4 is isolated from the gravity concentrate. The extraction of platinum in a compact magnetic product (yield 0.35 %) is at least 70 % with a hundredfold enrichment relative to the initial ore (platinum content exceeds 20 g/t). Further processing of the platinum-containing magnetic product with processing methods for recovery of PGM without obtaining prolific industrial products is difficult. From the gravity concentrates with the help of electrostatic separation it is possible to separate the conditioned chromite concentrates (yield 3 %) containing 43.5 % Cr_2O_3. Tailings of gravitational concentration meet the requirements for raw materials to produce chromium-magnesite and forsterite refractories [4].

A thermodynamic analysis of the [Fe_3O_4 – (H_2SO_4) – Fe_{met} – H_2O] system was performed within the framework of development of the chemical-metallurgical method for refining platinum-bearing concentrate from iron, with the construction of the Purbe and pFe – *f*(pH) diagrams, their results show that the equilibrium conditions for the existence of ferrous sulfate (II) in the reductive sulfuric acid decomposition of magnetite are determined by the redox potential and the pH of the medium, as well as by the conditions for the formation of an insoluble hydrated bivalent iron [11]

The study of physicochemical regularities of the sulfuric acid reductive decomposition was carried out on a model magnetite concentrate of the following composition, %: 52.1 Fe_3O_4; 1.2 MgO; 15.1 SiO_2; 24.9 Al_2O_3. The test experiments were performed on the platinum-metal strong magnetic fraction (SMF), isolated during the processing of the chromium ore of the Nizhny Tagil dunnite deposit with the following composition, %: 5.8 Cr; 54.6 Fe; 3.32 MgO; 2.6 SiO_2; 2.7 Al_2O_3; 1050.0 g/t Pt.

The influence of the main technological leaching parameters on the behavior of iron (duration 0.5-1.5 hours, sulfuric acid content 50-250 g/l, temperature 20-75 °C) was studied. The consumption of the reducing agent was varied up to 3-fold excess from the theoretically necessary amount for this reaction:

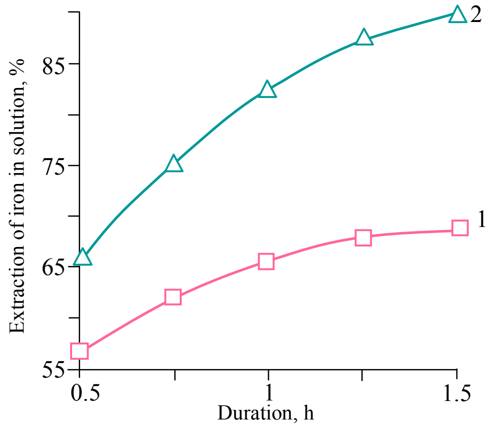

Fig.2. Effect of leaching duration and concentration of sulfuric acid on magnetite concentrate loosening:
1 and 2 – 150 and 250 g/l H_2SO_4 respectively.
Conditions: sample weight 20 g, I:T = 10:1; T = 70 °C, 3-fold consumption of reducing agent

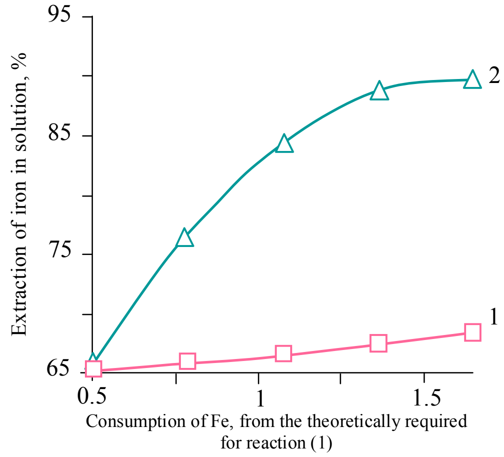

Fig.3. Influence of reducing agent consumption and sulfuric acid concentration on iron behavior
1 and 2 – 150 and 250 g/l H_2SO_4 respectively.
Conditions: ample weight 20 g, I:T = 10:1, T = 70 °C

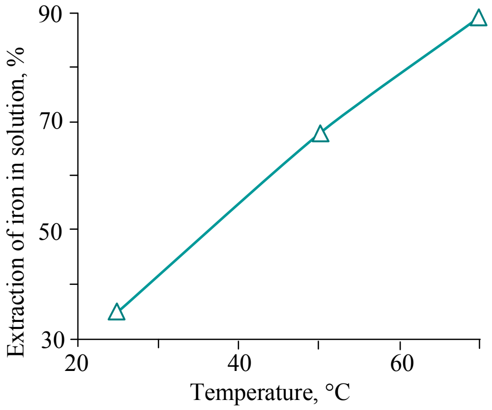

Fig.4. Influence of temperature changes on extraction of iron in solution
Conditions: sample weight 20 g, I:T = 10:1, 250 g/l H_2SO_4, 3-fold consumption of reducing agent

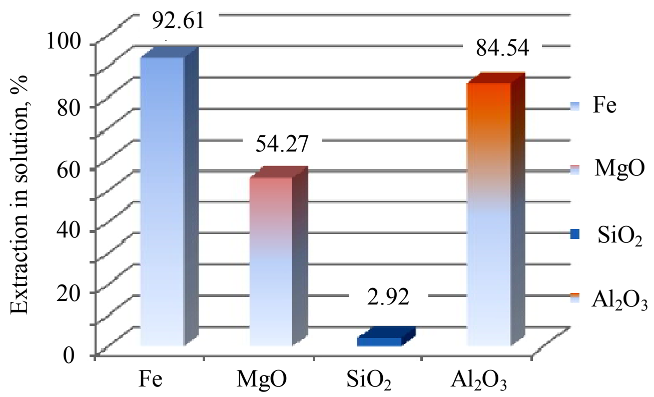

Fig.5. Behavior of iron and rock-forming components in the sulfuric acid reductive leaching of model magnetite concentrate

$$Fe_3O_4 + Fe + 4H_2SO_4 = 4FeSO_4 + 4H_2O.$$

The results of the experiments show that the increase in the leaching time significantly affects the indices of the magnetite concentrate loosening: at an acidity of 250 g/l H_2SO_4, an increase in the process time to 90 min is accompanied by an increase in the transition of iron to the sulphate solution by 20-25 %, which allows to ensure almost complete removal of iron (Fig.2).

The consumption of the reducing agent has a significant effect on the process parameters, which is especially noticeable with a high acidity (250 g/l) of the solution: extraction of iron into the solution reaches 90 % (Fig.3).

With increasing temperature, the process is significantly intensified: with an increase in temperature from 25 to 70 °C, the quantitative parameters of iron dissolution increase almost 3-fold – from 35.3 to 89.5 %. The yield of the insoluble residue is 20.86 % of the initial charge (Fig.4).

The process of reductive leaching with an acidity of 250 g/l, a 3-fold excess of the reducing agent and a temperature of 70 °C is accompanied by a transition to the sulfate solution of the main rock-forming components of the magnetic concentrate, except for silica: in the insoluble residue there is no more than 45 % MgO and 15 % Al_2O_3 (Fig.5).

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In case of chemical conditioning of a rich platinum-containing concentrate (1050.0 g/t) Pt at optimal parameters (80 g sample, sulfuric acid content 200 g/l, 2 times excess of metallic iron of theoretically required amount, temperature 70 °C, duration 1.5 h, I:T = 10:1), the yield of the insoluble residue is 12.9 % with almost complete recovery of iron and chromium in the sulfuric acid solution (according to the analysis of the solution at 95.1 % and 98.9 %, respectively). The content of platinum in the cake was 0.59 %, rhodium – 130 g/t [5, 11].

Based on the results of the research, the PFD and PID for the complex processing of heterogeneous chromium ores of the Nizhny Tagil dunnite massif was developed (Fig.6). Initial ore without additional grinding is subjected to screening with subsequent jigging. Coarse fractions of jigged concentrates after grinding to a grain size of –2 + + 0 mm and screening are mixed with a fine fraction of screens and are submitted for hydraulic classification. The separated fractions of various sizes are processed at concentrating tables. The combined gravity concentrate is subjected to separation by wet magnetic and electrostatic separation methods to obtain a chromite concentrate, a strong magnetic product, processed PGM, and a dielectric fraction representing rock-forming magnesian silicates. The combined tails of gravitational enrichment and electrostatic separation after classification are used in the production of refractories or building materials.

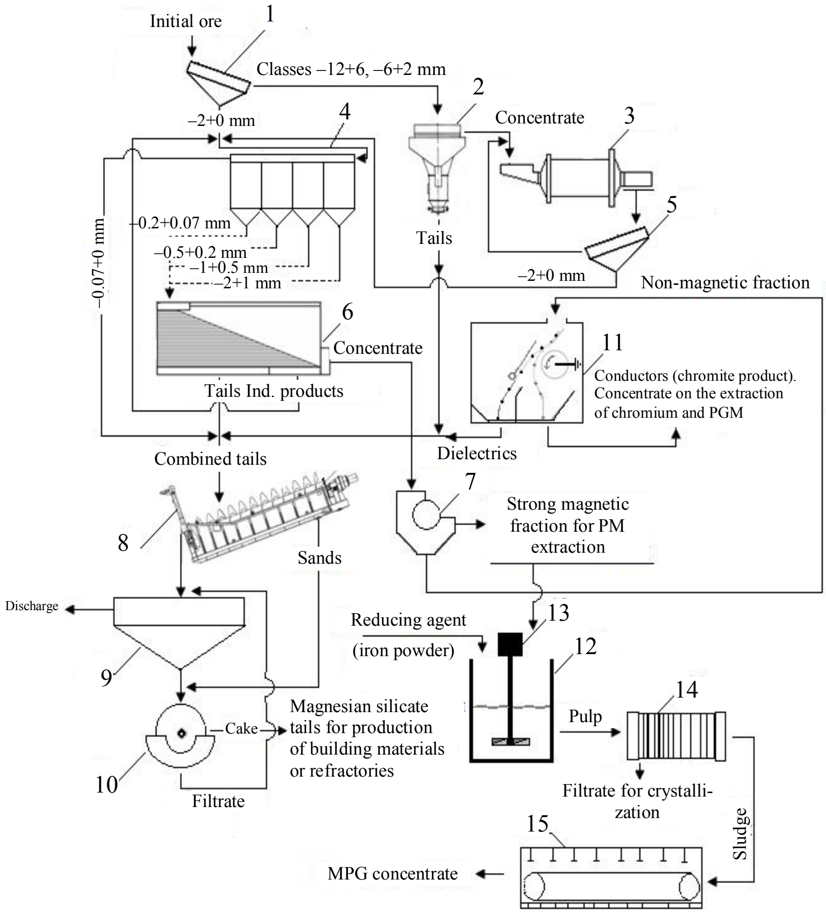

Fig.6. PFD of MPG and chrome extraction from chromium ore from Nizhny Tagil dunnite deposit

1, 5 – screen; 2 – saddling machine; 3 – ball mill; 4 – hydraulic classifier; 6 – concentration table; 7 – magnetic separator; 8 – spiral classifier; 9 – thickener; 10 – vacuum filter; 11 – corona-electrostatic separator; 12 – reactor; 13 – mixer; 14 – filter press; 15 – tunnel drier

The magnetic product produced at the beneficiation stage is subjected to hydrometallurgical processing by the method of reductive sulfuric acid leaching to produce rich platinum metal concentrate.

Conclusions

1. Based on the study of material composition of the chromium ores from the Nizhny Tagil dunnite deposit, it has been established that platinum is predominantly Pt-Fe (up to 65 %) and Pt-Cu alloys with ferromagnetic properties.

2. It has been revealed that the gravitational-magnetic processing of various chromium ores provides high (more than 70 %) concentration of platinum group metals in a compact magnetite product.

3. It has been established that the refining of ferruginous product under optimum conditions of sulfuric acid reductive leaching (sulfuric acid content of 200 g/l, a 2-fold excess of metallic iron, a temperature of 70 °C, a duration of 1.5 hours, I:T = 10:1) provides almost complete transfer of iron into a sulfate solution to obtain a platinum-bearing concentrate.

4. The complex processing technology for chromium ores from dunnite massifs was developed, which ensures the production of a rich platinum-bearing concentrate and high-quality chromite concentrate that meets the requirements of chemical production.

5. The introduction of the developed technology with an annual processing capacity of 200 thousand tons of poor ledge ore (1.64 % Cr and 0.21 g/t Pt) at the enterprises producing chromium-magnesite refractories will additionally provide 15 kg of platinum in the form of commodity concentrate and 6 thousand tons of chromite concentrate. Using a PFD for processing rich ore containing 43.4 % Cr_2O_3 and 1.76 g/t Pt will yield 23.000 tons of chromium concentrate and 160 kg of platinum as a rich platinum concentrate (0.6 % Pt), that is close to the requirements of refining production.

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Authors: **Georgii V. Petrov**, *Doctor of Engineering Sciences, Professor, petroffg@yandex.ru (Saint-Petersburg Mining University, Saint-Petersburg, Russia)*, **Yakov M. Shneerson**, *Doctor of Engineering Sciences, General Director, src@gidrometall.ru, (LLC «Research and Development Center «Gidrometallurgiya», Saint-Petersburg, Russia)*, **Yurii V. Andreev**, *Candidate of Engineering Sciences, Associate Professor, juri19@yandex.ru (Peter the Great St.Petersburg Polytechnic University, Saint-Petersburg, Russia).*

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