

Enhancing optimal performance of the platinum concentrates by reduction sulfuric acid

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Abstract. Extension and restructuring of raw resources of the platinum group metals by low-sulfide ores processing makes an important direction for development of the mining and metallurgical industry of the Russian Federation. The platinum group metals (PGM) concentrates, recovered during low-sulfide ores processing, have too high iron content and do not meet the requirements of the refineries. Objective: create a comprehensive technology for processing of ferrous platinum-bearing products of low-sulfide ores in order to recover PGM-rich concentrates. Methods used: we carried out electrochemical studies of the magnetite cathodic reduction in the sulfuric acid applying the IPC-Pro potentiostat and an electrochemical cell. Experimental studies of the sulfuric acid leaching patterns employed a model magnetite concentrate; and included a study of the influence of technological process variables: consumption of iron powder, duration of the process, concentration of sulfuric acid and temperature. Novelty: the primary novelty of this work is identification of basic kinetic patterns of magnetite sulfuric acid leaching. Results: we calculated the apparent activation energy of the process, which proves that constraining factors of the electrochemical process are mostly kinetic in nature. We also defined optimal variables of the sulfuric acid leaching with a reducing agent, which ensure practically complete leaching of iron from magnetite concentrates. Practical relevance: we proposed a technology of hydrometallurgical refining of the platinum concentrates from iron.

Key words. Low-sulfide ores, PGM concentrates, magnetite, sulfuric acid leaching, refining.

1. Introduction

Various compositions of ores and applied processing technologies greatly affect the content of platinum group metals (PGM), non-ferrous metals, iron and silicates in platinum-bearing products, which dictates principles for their further processing [1, 2].

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The PGM concentrates, recovered during processing of copper and nickel electrorefining anode slime, meet the requirements of the refineries, and their processing does not cause difficulties in general [3–5].

Chemical and phase composition classification of platinum-bearing products of beneficiation of various raw materials allows us to distinguish the following types: rich gravity concentrates, recovered during beneficiation of magnetite tailings of sulfide Cu-Ni ore processing (up to 5 kg/t of PGM) [6]; flotation concentrates from beneficiation of low sulfide ores, containing up to 1 kg/t of PGM [7]; magnetite concentrates, recovered during beneficiation of the Nizhny Tagil alluvial ores (up to 1050 g/t of PGM) and poor dunite raw materials (up to 50 g/t of PGM) [8]; gravity platinum concentrates, recovered during beneficiation of the Aldan chromites (20–300 g/t of PGM).

In low-sulfide concentrates, a highly-dispersed nature of the PGM minerals, which are mostly complex chalcogenides and sulfoarsenides, requires chemical-metallurgical methods of liberation that convert the PGM into a solution, followed by recovery through well-known methods [7]. To process iron-bearing low-sulfide concentrates, it is worthwhile to use hydrometallurgical processes focused on selective dissolution of iron, with precious metals concentrated in a compact insoluble leaching residue. This policy is most often used in technological solutions for the titanium metallurgy, where raw materials are concentrates bearing minerals with high content of iron (ilmenite, titanomagnetite) and silica.

A promising method for purifying a platinum-bearing concentrate from iron is its leaching in a sulfuric acid with a reducing agent. An obvious advantage of the reduction sulphate leaching is that the platinum group metals virtually do not pass into solution.

2. Research methods

Study of the influence of magnetite cathodic reduction on its dissolution rate makes it possible to reveal the nature of the rate-limiting stage and the mechanism of oxide dissolution. We carried out electrochemical studies of the magnetite cathodic reduction in the sulfuric acid applying the IPC-Pro potentiostat and an electrochemical cell consisting of a working magnetite electrode (Fe_3O_4), a chlorine-silver reference electrode, and an auxiliary platinum electrode. The magnetite cathodic polarization was made in the potentiodynamic mode with a sweep rate of 5 mV/s.

Experiments to study the patterns of reductive sulfuric acid leaching employed a model magnetite concentrate containing (%): 52.1 Fe_2O_3 ; 1.2 MgO ; 15.1 SiO_2 ; 24.9 Al_2O_3 . We studied the influence of the main leach technological variables on the behavior of iron: consumption of iron powder (up to triple theoretical value), duration 0.5–1.5 hours, sulfuric acid concentration 50–250 g/l, temperature 323–343 K. Molar ratios $\text{Fepowder}/\text{Feconcentrate}$ and the excess of the reducing reagent was calculated using the reaction:



Iron recovered into the solution was determined as the ratio of the iron passed into the sulfate solution and the sum of iron in the concentrate and iron powder. The

experiments were carried out in a glass jar with mechanical stirring. The agitator rotation speed amounted to 400 rpm. To maintain the temperature, we used the ultra-thermostat UTU-2, with accuracy of $\pm 0.21^\circ$.

3. Research results

Having analyzed the cathodic polarization curves, we came to a conclusion that the dissolution rate increases when the potential shifts to the cathodic zone with the growing solution acidity (50–200 g/l H_2SO_4) and the temperature rise (25–80 °C). The increasing rate of magnetite dissolution during cathodic polarization confirms that the kinetics of the electrochemical process is constrained by transition of protons from the solution to the oxide surface (Figs. 1, 2).

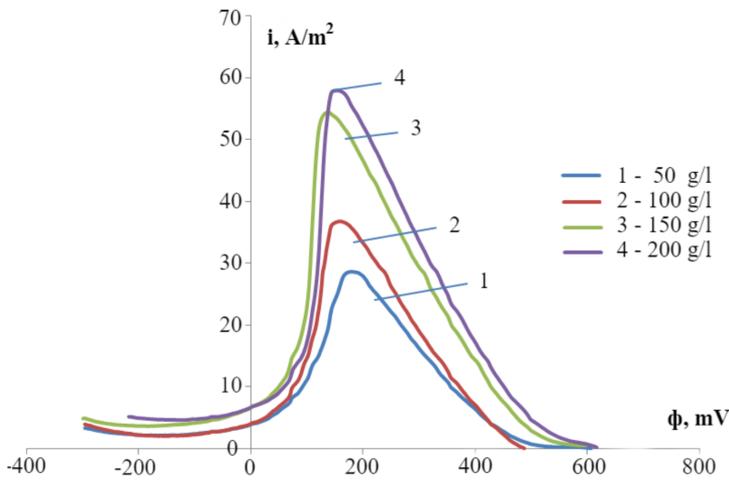


Fig. 1. Influence of acidity on magnetite cathodic polarization

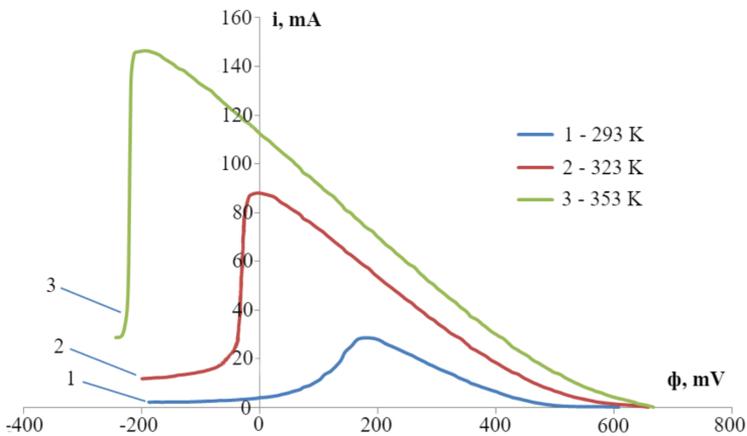


Fig. 2. Influence of the temperature on the magnetite cathodic polarization

The divalent iron ions in the solution minimize the induction period in the low over-voltages zone, thus making the process autocatalytic, and facilitate the accelerated dissolution of magnetite by time (Fig. 3). The calculated apparent activation energy of magnetite electrochemical reduction in the acid amounts to 46 ± 3 kJ/mol, which indicates that the constrains are predominantly kinetic in nature.

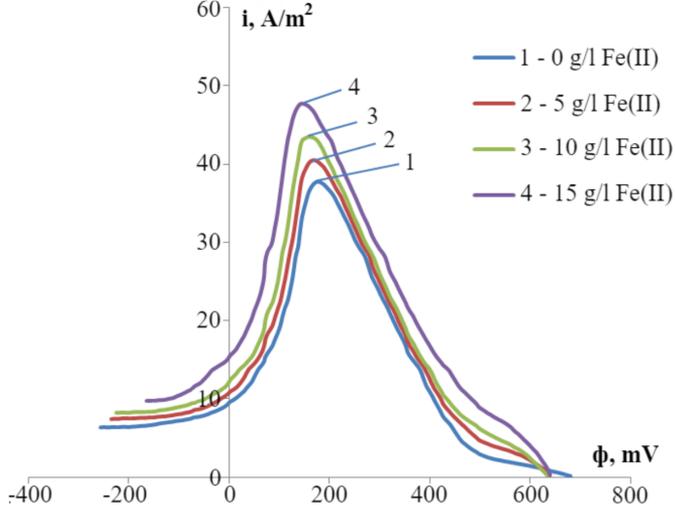


Fig. 3. Influence of the Fe (II) cations on the magnetite cathodic polarization

The experimental results of reductive sulfuric acid leaching are presented as dependency graphs of the iron recovery into the solution (α) and H_2SO_4 concentration on the process duration. The graphs indicate that an increase in the temperature from 323 to 343 K contributes to an increase in the iron leaching by 21 % (from 68 % to 89 %). The boat-shaped kinetic curves, flowing from "parabolic" to linear, indicate a monotonic decay of the process speed after 1 hour of leaching, which is also confirmed by derivation of the experimental dependence of the iron content in the solid phase ($1-\alpha$) on time (Figs. 4, 5).

The general equation of the Fe_3O_4 dissolution rate can be described as follows: (at $T = \text{const}$):

$$\frac{d(1 - \alpha)}{d\tau} = -kS[\text{H}_2\text{SO}_4]^n \cdot [\text{Fe}]^m, \quad (1)$$

where α and $1 - \alpha$, respectively, are the amount of iron (III), which passed into solution and remained in the solid phase, S denotes the surface of magnetite, varying in time (dm^2/g), $[\text{H}_2\text{SO}_4]$ stands for the initial concentration of the sulfuric acid (mol/dm^3), n is the reaction order by acid concentration, $[\text{Fe}]$ denotes the indicator accounting for the consumption of iron for recovery, (stoichiometry ratio), m is the reaction order by reductive agent, and k represents the reaction rate constant, $(\text{g}\cdot\text{dm})/(\text{mol}\cdot\text{min})$.

To account for the change in the surface over time, we assumed that in the leaching process the surface varies proportionally to the amount of iron (III) in the

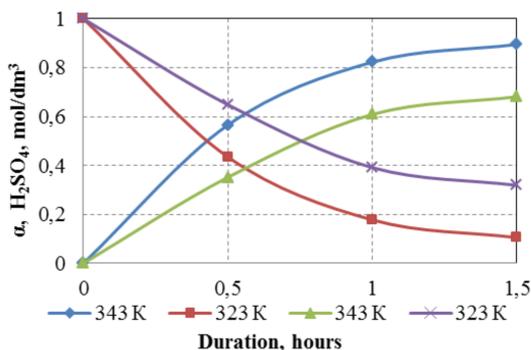


Fig. 4. Influence of the temperature on the liberation rate of the model magnetite concentrate molar ratio $\text{Fe}_{\text{powder}}/\text{Fe}_{\text{concentrate}} = 4.14$, $L/S = 10 : 1$

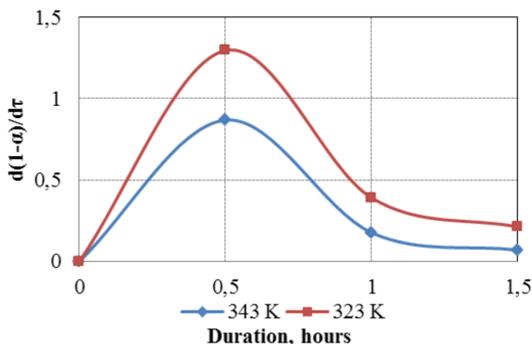


Fig. 5. Dependence of the iron leaching rate on temperature (initial concentration of the sulfuric acid in the solution 1.0 mol/dm^3 , molar ratio $\text{Fe}_{\text{powder}}/\text{Fe}_{\text{concentrate}} = 4.14$, $L/S = 10 : 1$)

concentrate to β power:

$$S = S_0(1 - \alpha)^\beta. \quad (2)$$

Then the rate equation looks as

$$\frac{d(1 - \alpha)}{d\tau} = -kS_0(1 - \alpha)^\beta [\text{H}_2\text{SO}_4]^n \cdot [\text{Fe}]^m, \quad (3)$$

where S_0 is the initial specific surface area of the concentrate sample.

We assume that at different temperatures and concentration of H_2SO_4 are constant during the experiment, Fe content in the concentrate decreases exponentially over time:

$$(1 - \alpha) = e^{CT} \quad (4)$$

where C is a coefficient, depending on the variables of sulfuric acid liberation (temperature, acid concentration and specific surface area of magnetite).

After logarithm and differentiation transformations of the equation (4), we get

$$\frac{d(1-\alpha)}{d\tau} = -C(1-\alpha). \quad (5)$$

Comparing equations (3) and (5) we get $\beta = 1$, $C = kS_0[\text{H}_2\text{SO}_4]^n \cdot [\text{Fe}]^m$ and

$$\frac{d(1-\alpha)}{d\tau} = -kS_0(1-\alpha)[\text{H}_2\text{SO}_4]^n \cdot [\text{Fe}]^m. \quad (6)$$

The calculated process rate constants for temperatures 323 and 343 K amount to 4.21703 and 6.65326, respectively (see Fig. 6).

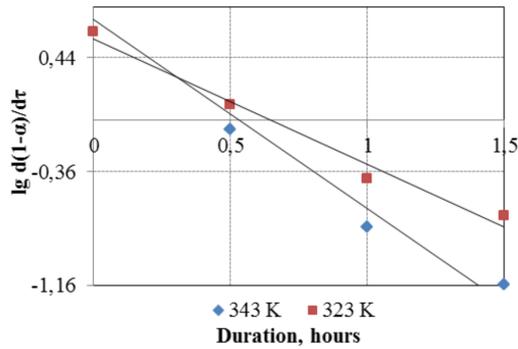


Fig. 6. Temperature-kinetic dependence of the leaching rate of the model concentrate

The dependence of the rate constant on the temperature can be recorded as follows:

$$k = (1.05 \pm 0.02) \cdot 10^4 \exp\left(-\frac{2525}{T}\right). \quad (7)$$

The calculated value of the apparent activation energy of the magnetite concentrate reduction by iron powder (21.1 kJ/mol) is typical for processes occurring in the diffusion zone.

Experimental results indicate that an increase in the reducing agent consumption ($\text{Fe}_{\text{powder}}/\text{Fe}_{\text{concentrate}} = 1.4/4.2$) has a positive effect on the sulfuric acid dissolution of magnetite (see Fig. 7).

The data obtained show that the optimal process variables (sulfuric acid concentration—200 g/l, metallic iron excess - double theoretical value, temperature 70 °C, duration 1.5 hours, $L/S = 10 : 1$) ensure almost complete iron leaching from magnetite concentrates.

4. Conclusion

Application of this process to a platinum-rich concentrate, recovered during beneficiation of the Middle Urals alluvial ore (5.8 Cr %, 54.6 % Fe, 3.32 % MgO, 2.6 %

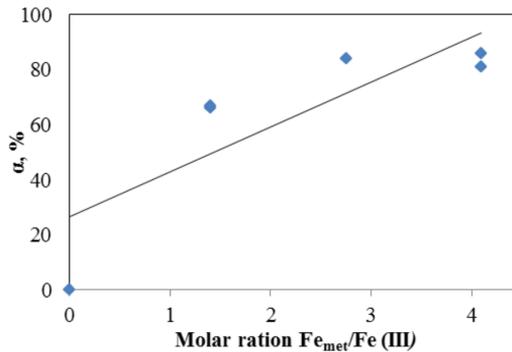


Fig. 7. Influence of the reducing agent consumption on the liberation of magnetite (1.5 hours at the temperature of 70 °C and excess of the solvent)

SiO₂, 2.7%Al₂O₃, 1050.0 g/t Pt), allows to achieve complete purification from iron and a significant reduction in the product (by 5–6 times). Refined platinum-rich concentrate (up to 0.59 % of platinum) can be directly delivered to the refinery facility. In case a poorer product is obtained (100–150 g/t), recovered from dunite raw materials, for example, it can be processed together with platinum-bearing copper-nickel slimes. Summing up, we should note that sulfuric acid reduction leaching is an effective method for refining various types of ferrous concentrates beneficiated with precious metals.

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