



ASPECTS OF ELECTROCHEMICAL REACTION MECHANIS OF MAGNETITE REDUCTIVE LEACHING IN SULFURIC ACID MEDIUM

G.V. Petrov, S.B. Fokina, A.Ya. Boduen, B.F. Fidarov and I.E. Zotova

Saint-Petersburg Mining University, Saint Petersburg, Russian Federation (2, 21st Line, Saint Petersburg 199106, Russia)

ABSTRACT

Inevitable depletion of mineral reserves involves search for the new alternative sources of non-ferrous metals, in particular, noble metals. Chromite ores in dunite, conventionally treated as refractory materials, are considered to be a prospecting feedstock of platinum group metals. Studies were performed on platinum group metals production as by-products for low-grade dunite ore processing. Gravity-magnetic flowsheet for dunite concentration allows to extract magnetic platinum-containing concentrate with high content of magnetite and platinum-ferriferous alloys. Reductive leaching in sulfuric acid medium was considered as advanced method of refining of magnetic platinum-containing concentrate from iron. Electrochemical studies of magnetite cathode reduction in sulfuric acid medium showed that magnetite rate of solution is increasing with potential shift to cathode region under increasing solution acidity and higher temperature. Kinetics of cathode process can be determined by electrolyte parameters and catalytic impact of cations of ferrous iron formed.

Key words: concentration, platinum group metals, reductive sulphuric acid leaching.

Cite this Article: G.V. Petrov, S.B. Fokina, A.Ya, Boduen, B.F. Fidarov and I.E. Zotova, Aspects of Electrochemical Reaction Mechanis of Magnetite Reductive Leaching In Sulfuric Acid Medium, International Journal of Mechanical Engineering and Technology, 10(01), 2019, pp.1595–1601

<http://www.iaeme.com/IJMET/issues.asp?JType=IJMET&VType=10&Type=01>

1. INTRODUCTION

Variety of ore material composition and applicable processing technologies have significant impact on content of PGM, non-ferrous metals and silicates in platinum-containing products thus determining the principles of its further processing.

Current industrial practice and present studies in the field of processing of sulphide concentrates that contain precious metals allows to state that to a large extent it is focused on bulk transfer of precious and non-ferrous metals into solution followed by production of selective

concentrates. These methods involve complex equipment, often autoclaves, and aggressive oxidizing medium [1].

In case of almost monomineral character of concentrates, as for its extraction from chromite ores, that are peculiar of high magnetite content - if compared to other components [2-4] – it is more feasible to apply methods of PMG concentration in cake [5].

By considering the fact that iron and its compounds are the essential components of polymetallic ores [6, 7], it has been extensively investigated in terms of behavior in chemical processes, firstly in reduction and autoclave processes, primarily held in sulphuric acid medium aiming at iron concentration in insoluble residue [8].

Application of acid medium for iron oxide dissolution under atmospheric conditions is possible, however, it proceeds at a very low velocity and it is intended primarily for dissolving of surface iron oxide formations, and low solvent concentration is enough here (pH 1-2) [9]. Reducing agents are known for boosting the leaching process of iron oxides. In this case it is rational to use reductive sulphuric acid leaching at higher acidity to refine platinum-containing concentrate from iron compounds [10]. The benefit is evident of reductive sulphuric acid leaching to guarantee the total absence of PGM transfer into solution.

In order to study cathode behavior of magnetite in sulphuric acid medium, the polarization curve method (chronovoltammetric) was selected, dependencies of current density on electrode potential at its continuous linear sweep in time [11, 12].

2. MATERIALS AND METHODS

Studies were conducted using IPC-Pro potentiostat and electrochemical cell consisting of working magnetite electrode (Fe_3O_4), silver-chloride reference electrode, auxiliary platinum electrode. Cathode polarization of magnetite has been held under potentiodynamic mode at sweep velocity of 5 mV/sec. Measurements were taken from magnetite electrode, placed into electrochemical cell filled with sulphuric acid solution, at various temperatures. After fixing the initial steady potential of electrode, cathode, and after that anode, were swept.

Magnetite electrode preparation included the following operations: working electrode grinding using sand paper of different grain sizes, polishing, degreasing by water suspension of Na_2CO_3 , washing by running and distilled water, alcohol and working solution treatment.

Electrochemical cell represents a glass cylindrical vessel with electrodes inside: reference, auxiliary and working electrodes. Polarization of the working magnetite electrode from the external supply source of current was carried out using auxiliary platinum electrode. For measuring potential, chloride-silver reference electrode was applied. Temperature impact (25 to 80 °C), sulphuric acid concentration (50 to 200 g/l) and ferrous iron cation (1 to 15 g/l) were studied during experiments. Prior to each experiment, electrochemical cell was washed by the mixture of concentrated sulphuric acid and hydrogen peroxide, then it was washed by running and distilled water.

For irreversible electrode process, potential E_p in the current peak the following formula was used:

$$E_p = E_0 - RT/(\alpha n \alpha F) (0,78 - \ln k_s + \ln \sqrt{D_{ox} B}), \quad (1)$$

Where E_0 – standard potential value, V;

k_s – standard constant of electrode process velocity;

R – Universal gas constant, 8.31 J/(mol · K);

F – Faraday number, $9.65 \cdot 10^4$ C/mol;

T – Process temperature, K;

B – Coefficient that linearly dependent on $\lg \vartheta_p$, thus allows to determine transfer coefficient by inclination of line value, $B = (\alpha n_\alpha F \vartheta_p) / RT$.

The following equation was used to determine transfer coefficient αn_α :

$$E_p - E_{(p/2)} = 1,857 RT / (\alpha n_\alpha F), \quad (2)$$

Velocity constant of electrode process k_s was calculated using the following equation:

$$E_p = -1,14 RT / (\alpha n_\alpha F) + RT / (\alpha n_\alpha F) \ln k_s / (D_{ox}^{1/2}) - RT / (2\alpha n_\alpha F) \ln \alpha n_\alpha \vartheta \quad (3)$$

Where D_{ox} is a diffusivity coefficient of oxidized form of substance, $1,838 \cdot 10^{-5} \text{ cm}^2/\text{sec}$;

ϑ – Potential sweep velocity, V/sec.

3. RESULTS AND DISCUSSIONS

Study of cathode reduction of magnetite influence on its solution rate provides for revealing the nature of limiting stage and mechanism of oxide solution. Characteristic value in chronovoltammetric method is peak current i_p and peak current potential E_p .

During analysis of cathode polarization curves it is evident that solution rate is increasing with the potential shift into cathode region under increasing solution acidity (50-200 g/l H_2SO_4) and higher temperatures (25-80 °C). Growth of magnetite solution rate during cathode polarization confirms that kinetics of electrochemical process is limited by proton transfer from solution to oxide surface (Figure 1, 2).

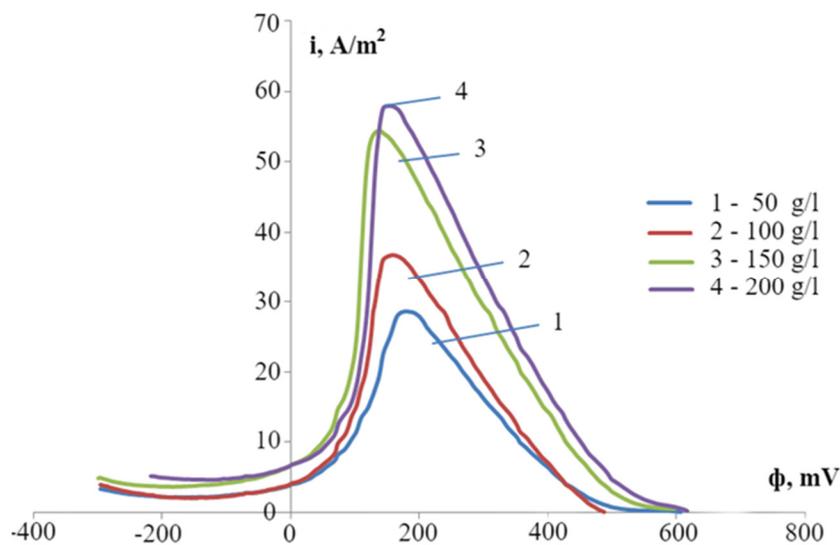


Figure 1 Impact of medium acidity on cathode polarization of magnetite

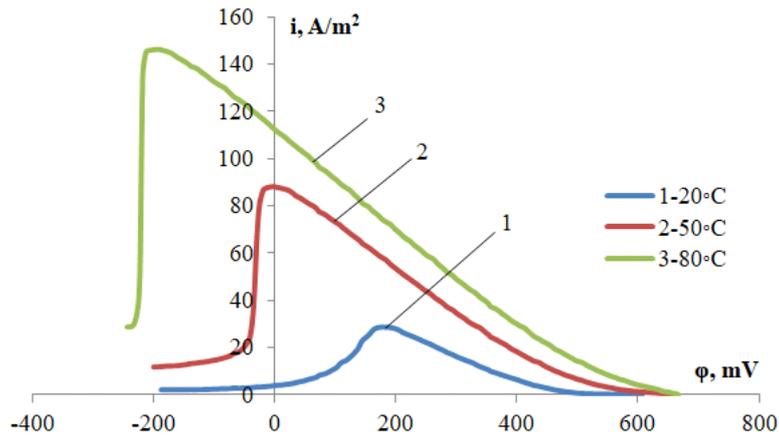


Figure 2 Impact of temperature on cathode polarization of magnetite

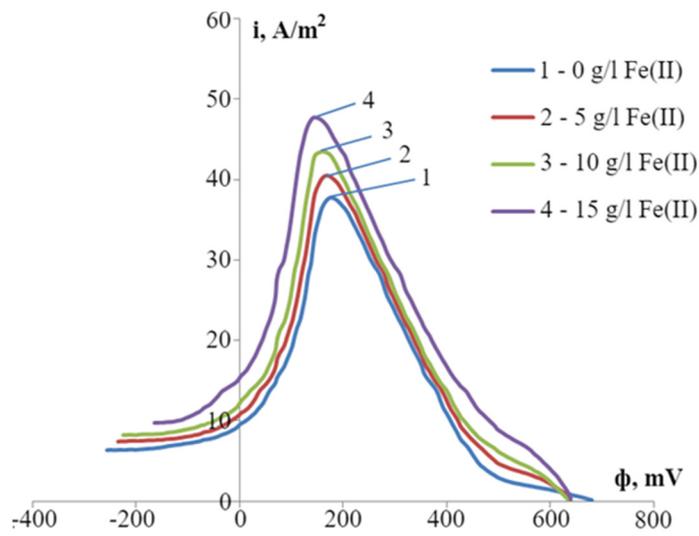


Figure 3 Impact of cation Fe (II) concentration on cathode polarization of magnetite

Chronovoltammometric dependencies at various velocities of potential sweep are presented in Figure 4.

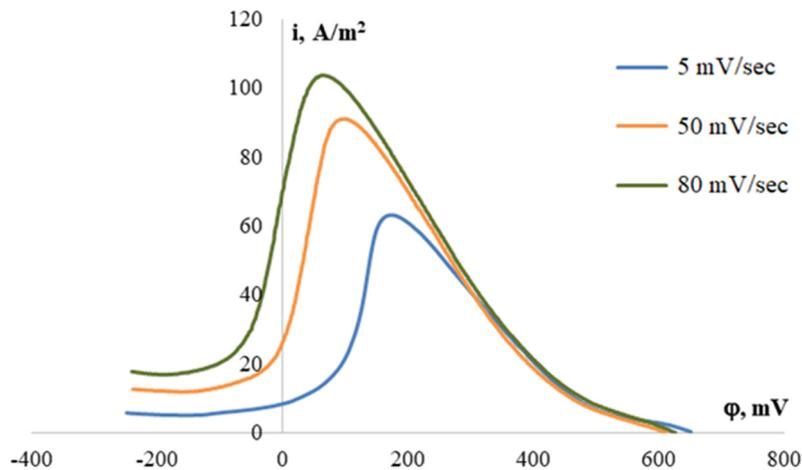


Figure 4 – Chronovoltammometric dependencies of peak current on potential peak current at various velocities of sweep

Based on dependency obtained of current peak on square root of potential sweep velocity (Figure 5) we can draw the conclusion that the process takes place in irreversible region.

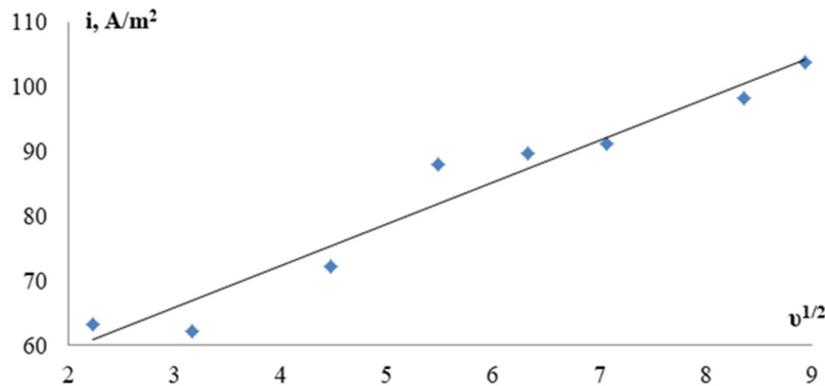


Figure 5 – Dependency of current peak on square root of potential sweep velocity

In order to determine transfer coefficient αn_α , equation (2) was used. Transfer coefficient αn_α at sweep velocity of 5 mV/sec equals:

$$\alpha n_\alpha = 1.857 \frac{RT}{(E_p - E_{p/2}) \cdot F} = 1.857 \frac{8.314 \cdot 298}{(0.180 - 0.09) \cdot 96500} = 0.52$$

For velocity constant k_s equation (3) was used:

$$E_p = -1,14 \frac{RT}{\alpha n_\alpha F} + \frac{RT}{\alpha n_\alpha F} \ln \frac{k_s}{D_{ox}^{1/2}} - \frac{RT}{2\alpha n_\alpha F} \ln \alpha n_\alpha \vartheta$$

By transposing given equation we obtained that velocity constant k_s equals 0.028 at a sweep velocity of 5 mV/sec. Table 1 shows transfer coefficient values αn_α and velocity constants k_s at various sweep velocities.

Table 1 – Velocity constants for various sweep velocities values

ϑ , mV/sec	αn_α	k_s
5	0.52	0.028
50	0.45	0.033

We know the velocity constant k_s of electrode process, so we can estimate energy of activation. Energy of activation amounts 24.6 kJ/mol thus giving evidence to process kinetics of electrochemical reduction of magnetite in sulphuric acid medium run in intermediate region.

Reductive sulphuric acid leaching of magnetite that present in magnetic platinum-containing product of chromite ore concentration is performed based on electrochemical mechanism; kinetic characteristics of the cathode process are determined by electrolyte parameters and catalytic impact of ferrous iron ion formed

4. CONCLUSION

1. The paper shows that application of acid medium for iron oxide dissolution under atmospheric conditions is possible, however, it proceeds at a very low velocity and it is intended primarily for dissolving of surface iron oxide formations, and low solvent concentration is enough here (pH 1-2).
2. Kinetic aspects of electrochemical reduction of magnetite in sulphate medium of higher acidity (up to 200 g/l) were studied using potentiodynamic methods.

3. It has been established that solution rate is increasing with potential shift into cathode region with increasing acidity of the solution (50 to 200 g/l H₂SO₄) and higher temperatures (25-80 °C).
4. Transfer coefficient αn_{α} and velocity constants k_s of cathode process are estimated for various sweep velocities (5-50 mV/sec).
5. Apparent activation energy value was calculated (24.6 kJ/mol) thus giving evidence to process run in intermediate region.
6. It has been revealed that kinetics of electrochemical process of magnetite reduction is limited by proton transfer from solution to oxide surface, as evidenced by magnetite solution rate under cathode polarization.
7. Process of electrochemical reduction of magnetite in sulphuric acid medium in presence of ferrous iron cations (1-15 g/l) in the low overvoltage region proved to be of autocatalytic character thus contributing to higher rate of the process.

REFERENCES

- [1] Shneerson Ya.M., Naboychenko S.S. Tendentsii razvitiya avtoklavnoy gidrometallurgii tsvetnykh metallov [Trends of development of autoclave hydrometallurgy of non-ferrous metals] // Tsvetnyye metally [Non-ferrous metals]. 2011. No. 3. pp. 15-20.
- [2] Gurskaya L.I., Dodin D.A. Mineral'nye resursy platinovykh metallov: perspektivy rasshireniya [Mineral resources of platinum metals: prospects for expansion] // regional'naja geologiya i metallogenija [Regional Geology and Metallogeny]. 2015. No 64. pp. 84-93.
- [3] Chanturia V.A., Kozlov A.P., Tolstykh N.D. Dunitovye rudy novyj vid platinosoderzhashhego syr'ja [Dunite Ore - A New Platinum Source] // Gornyj informacionno-analiticheskij bjulleten' [Gorn. Inform.-Analit. Byull.] / 2011. No. 3. pp. 553-566.
- [4] Chanturia V.A., Kozlov A.P. Platinum-bearing dunitites and their enrichment [Platinosoderzhashhie dunitovye rudy i ih obogatimost']. M.: URAN IPKON RAN, 2009. 148 p.
- [5] Petrov G.V. Concentration of platinum metals in the processing of conventional and unconventional platinum-containing raw materials [Koncentrirovanie platinovykh metallov pri pererabotke tradicionnogo i netradicionnogo platinometal'nogo syr'ja]. SPb: Saint-Petersburg Mining University, 2001. 106 p.
- [6] Sizyakov V.M., Tikhonova E.V., Sizyakova E.V., Cherkasova M.V. Synthesis of hydrocarboaluminates of alkali earth metals from natural magnesium-containing feedstock in conditions of alumina production // Russian Journal of Non-Ferrous Metals. 2017. No 58(1), pp. 36-43.
- [7] Sizyakov V.M., Nazarov Y.P., Brichkin V.N., Sizyakova E.V. Processing of aged dumped tailings of apatite-nepheline ores flotation // Obogashchenie Rud. 2016. No 2. pp. 33-39.
- [8] Diakite Mohamed L.L. Les perspectives d'extraction des métaux de platine et de chrome à partir des dunitites / Mohamed L.L. Diakite, G.V. Petrov // France: Paris: Revue de Métallurgie "EDP sciences". 2011. Vol.108 - N°7-8. P. 447-450.
- [9] Kinetics of leaching of a Chinese laterite containing maghemite and magnetite in sulfuric acid solutions / Liu Kui, Chen Qiyuan, Yin Zhoulun, Hu Huiping // Hydrometallurgy. 2012. V. 125-126. P. 125-136.
- [10] Filippov A.P., Nesterov Yu.V. Redoks protsessy i intensivatsiya vyshchelachivaniya metallov (Redox Processes and Intensification of Metal Leaching), Moscow: Ruda Metally, 2009. 543.
- [11] Guzmán, S. A., Fóster, P. F., Ramírez-Correa, P., Grandón, E. E., & Alfaro-Perez, J. (2018). Information Systems and their Effect on Organizational Performance: An Inquiry into Job

Satisfaction and Commitment in Higher Education Institutions. *Journal of Information Systems Engineering & Management*, 3(4), 26.

- [12] Ngirwa, C. C., & Ally, M. (2018). An ICT Based Solution for Pesticides Authenticity Verification: A Case of Tanzania. *Journal of Information Systems Engineering & Management*, 3(4), 27.