
MINERAL
DRESSING

The Leaching of Sulfide Iron (II) with Sulfuric Acid¹

D. El Bar and D. Barket

*Chemical Industry Department, Faculty of Technology,
University of Biskra 07000, Algeria
e-mail: djenette.elbar@gmail.com*

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Abstract—The leaching of iron (II) sulfate concentrate from Chaabet El Hamra, Algeria bulk sulphide ore with sphalerite concentrate in presence of sulfuric acid and hydrogen peroxide at low stirring rates (100 rpm). The influence of leaching temperature, leaching time, particle size and sulfuric acid concentration were studied. In this paper we focused our attention on the process of direct leaching of iron (II) sulfate concentrate with sulfuric acid. The results of leaching show that the combination of sulphuric acid and hydrogen peroxide enhances the dissolution of the bulk sulphide ore. The Leaching rate was studied as a function of the leaching temperature, the leaching time, the particle size and the sulfuric acid H₂SO₄ concentration. The optimal operational conditions were as follows: leaching temperature 100°C; leaching time 2 hours; sulfuric acid concentration 2 mol/L⁻¹; the smaller particle size 63 μm and the solid-to-liquid ratio 1:10. In these values the maximum extraction of iron (II) sulfates is 0.0416 mol/L⁻¹.

Keywords: Sphalerite, sulphide ore, leaching, sulfuric acid, iron sulfate concentrate.

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INTRODUCTION

Leaching is an interaction process between dissolved reagents and solid phase. Temperature, concentration of reagents, rate of mixing, surface area of solid phase and other parameters affect the rate of leaching [1]. In nature zinc sulphide is present in major form sphalerite which often contain as an impurity significant amount (5–15%) of iron [2]. Pyrite and chalcopyrite, the most common and exploitable sulphide minerals, usually occur together and in contact with each other [3]. Zinc is an important metal required for many applications from metal products to chemical, paint, and agriculture industries. It is mainly recovered from sphalerite (ZnS), which is commonly associated to other sulphide minerals, such as chalcopyrite (CuFeS₂), galena (PbS), Pyrite (FeS₂) and tetrahedrite (Cu, Fe)₁₂(Sb, As)₄S₁₃ [4–8].

Generally speaking, hydrometallurgical processes without pretreatment are more advantageous and less harmful than pyrometallurgical processes from an economic and environmental point of view, especially for complex ores [9]. The hydrometallurgical processes are regarded as more eco-friendly for treating such materials having a low zinc content [10].

The Leaching of zinc concentrates is based on the oxidation of zinc sulphide in an acidic environment. Studies of sphalerite leaching in different mediums have been carried out by several authors [11–16]. However, in industrial scale mostly ammoniacal and sulfuric leaching are used [17]. The kinetics of leaching is very important to fully understand the metals dissolution process. Thus several studies have been done in the leaching kinetics of zinc sulphide [18–19]. The classical model used for description of sulphide minerals leaching mechanism is shrinking core model [20]. The suitability of the shrinking core model in sphalerite leaching has been supported by many authors [21–23].

In the present paper, as a fundamental study, the sulfuric acid and hydrogen peroxide has been applied to the direct leaching iron from sulphide ore of a Chaabet El Hamra, Setif (Algeria),

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considering influencing parameters such as concentration of sulfuric acid, leaching temperature, leaching time and particle diameter.

1. EXPERIMENT

1.1. Material Composition

The feed for this study was copper sulfide concentrate. The bulk concentrate from this ore was produced at cheabet Elhamra mine, Setif, Algeria. The chemical composition of the feed was, %: Zn 41.61; S 39.38; Fe 13.71; Cu 0.14. Figure 1 shows optical micrograph of the bulk concentrate and the mineralogical analysis results of bulk concentrate, respectively. The major minerals present in the concentrate were sphalerite (ZnS), marmatite (ZnFeS), chalcopyrite (CuFeS₂), and other minerals. The feed was determined by electronic microscope.

2.2. Leaching Procedure

The leaching experiments were carried out in flask fitted with a reflux condenser and a mechanical stirrer. The flask was placed on a thermostatically controlled heating mantle. The solution temperature was controlled to specific values with continuously monitored by a thermometer. Samples of clay weighing 10 gm were taken in 100 ml of leaching solution.

The leaching efficiency of Zn metals were calculated according to the following equation:

$$\text{Metal extraction} = \frac{C_1 V_1}{W_1 C_2} \times 100, \quad (1)$$

where C_1 is the metal concentration in the leaching solution, V_1 is the volume of leaching solution, W_1 is the mass of Zn metal content in the hydrometallurgical residue and C_2 is the percent of metal Zn metal content in the hydrometallurgical residue.

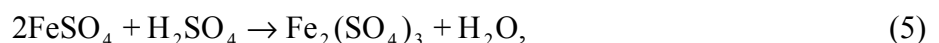
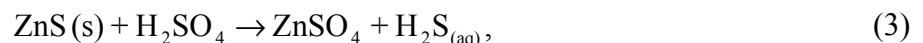
The optimum concentrations of both the acids were determined by leaching in 0.25, 0.5, 1 and 2 M sulfuric acid solutions. The subsequent leaching was performed in the optimized acid concentrations at temperatures of 25, 45, 65 and 100 °C for 30, 60, 90, 120 minutes at each temperature. A variable speed stirrer operated at a speed of 100 rpm was maintained during in all leaching experiments at 1 MPa. At the end of leaching for a specific period of time at a specific temperature of leaching solution was taken out of the round bottom flask by a pipette. The collected sample of leach liquor was cooled, filtered. Metal content was analyzed by atomic absorption spectrometry (AAS Shaker D407).

2.2. Leaching Mechanism

The oxidation reaction of sphalerite in an acid solution ($\text{pH} \leq 2$) is an electrochemical process which entails the dissolution of the mineral; this process releases metal ions and forms elemental sulfur [24]:



The leaching behavior of a zinc sulphide concentrate in moderately acidic solutions, ZnS and sulfate inter-reacted and generated S, ZnSO₄, FeSO₄, H₂O, etc. [5, 25]. To determine the extraction of iron (II) sulfates that can be achieved by the reactions:



Hydrogen sulfide is distributed between aqueous and gas phases according to:



2. RESULTS AND DISCUSSION

2.1. Effect of Leaching Temperature

To study the effect of leaching temperature on solubility of the leaching of iron (II) sulfate concentrate was studied at constant sulfuric acid concentration (2 mol/L^{-1}), solid-to-liquid ratio (1:10), leaching time (2 h), the leaching of iron (II) sulfate concentrate also studied at different particle sizes. These results presented in Fig. 2 show that the effect of extraction of iron (II) sulfates is enhanced with increasing temperature. As it can be seen, also the iron (II) sulfate concentrates increase with increasing the particle size, reaching the maximum extraction of iron (II) sulfates was found of $0.0416 \text{ mol/L}^{-1}$, it is obtained with particle size of $63 \mu\text{m}$ at a leaching temperature of $65 \text{ }^\circ\text{C}$, can be compared with $100 \text{ }^\circ\text{C}$ was found of $0.0412 \text{ mol/L}^{-1}$, it is in qualitative agreement to obtain the maximum enhancement.

2.2. Effect of Leaching Time

Generally study, the leaching time is important parameter in the thermodynamic behavior, because the reaction duration is sensible to the leaching of iron (II) sulfate concentrate, the letter was studied as a function of leaching time with different concentrations of sulfuric acid at a leaching temperature of $65 \text{ }^\circ\text{C}$, the leaching of iron (II) sulfate concentrate also studied at different particle sizes, where the solid-to-liquid ratio is (1:10). Figures 3a–3d show the effect of leaching time with sulfuric acid (H_2SO_4) concentration on the leaching of iron (II) sulfate concentrate at different particle sizes as 63 , 125 , 160 and $200 \mu\text{m}$, respectively. It is seen that with increasing the leaching time and sulfuric acid concentrations, leaching rate increased in all particle sizes; but when the leaching time was over 1.5 h , the curve of leaching rate was changed to be steady; the suitable leaching time is 2 h , reaching the maximum extraction of iron (II) sulfates is $0.0416 \text{ mol/L}^{-1}$ obtained with $63 \mu\text{m}$ at a concentrations of sulfuric acid of 2 mol/L^{-1} . This is in agreement with the findings of Xu et al. [26] that the rate of iron and silica dissolution decreases greatly with an increase in leaching time; it was suggested that particle size less than $-98+74 \mu\text{m}$ is sufficient for the whole experiment. Thus, leaching time for higher productivity was standardized to 120 min on the basis of leaching selectivity of zinc. Akcil [27] and Antonijevic et al. [28, 29] demonstrated that dissolution the rate decreases with increasing particle sizes.

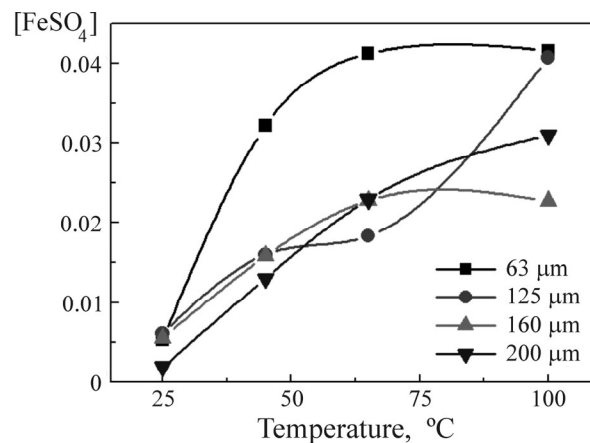


Fig. 2. The variation of iron (II) sulfate concentrate at different particle sizes as a function of temperature of leaching solution.

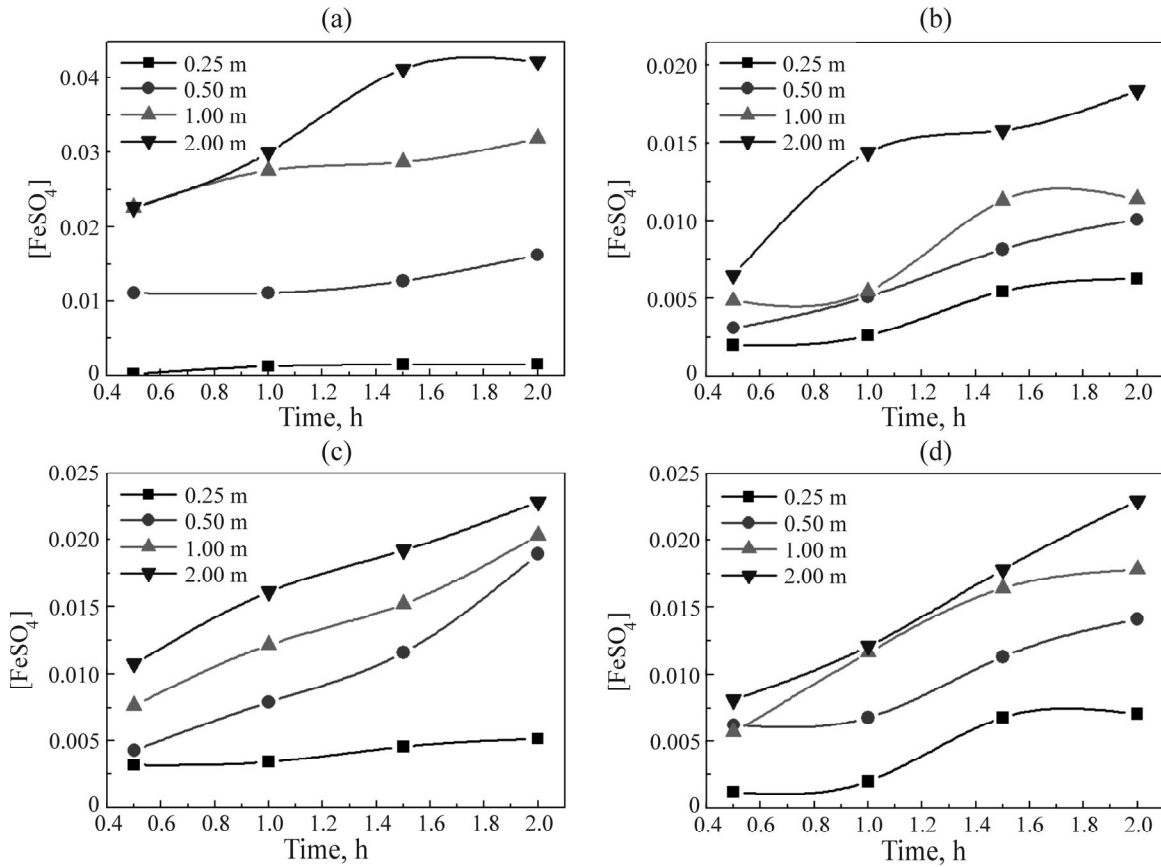


Fig. 3. The variation of iron (II) sulfate concentrate at different sulfuric acid concentrations as a function of leaching time with different particle sizes: (a) 63 μm , (b) 125 μm , (c) 160 μm , (d) 200 μm .

2.3. Effect of Particle Sizes

To obtain more information on the leaching of iron (II) sulfate concentrate, this letter was studied as a function of particle size at various leaching temperatures, which investigate with the constants of sulfuric acid concentration (2 mol/l⁻¹), leaching time (2 h) and solid-to-liquid ratio (1:10). Figure 4 show the effect of the particle size on leaching process at various leaching temperatures. Figure 4 demonstrates that the maximum iron (II) sulfate concentrate was obtained at the particle size of 63 μm , after this point the leaching rate of iron (II) sulfate concentrate was changed to minimum value. The good result was achieved in the particle size of 63 μm at 65 °C. Li et al. [30] observed that the particle size of the sample chosen was as 48–42 μm to obtain a higher extraction percent of zinc and indium.

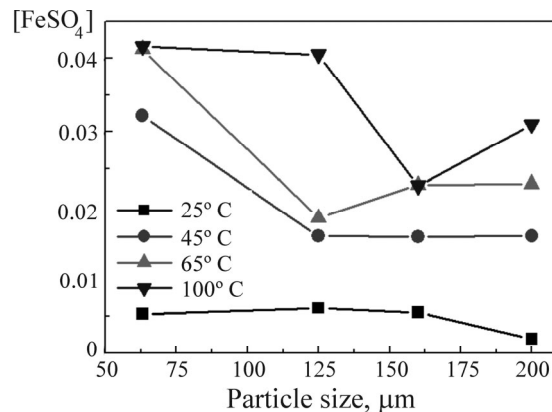


Fig. 4. The variation of iron (II) sulfate concentrate at different temperature of leaching solution as a function of particle size.

2.4. Effect of Acid Concentration

To investigate the effect of sulfuric acid (H_2SO_4) concentration on the leaching of iron (II) sulfate concentrate, the leaching was studied at different experiments on 63–200 μm ore, by varying the initial sulfuric acid concentration over 0.25–2 mol/L^{-1} at 65 °C for leaching time of 2 h and a solid-to-liquid ratio (1:10). The sulfuric acid H_2SO_4 concentration has a significant effect on the recovery of iron (II) sulfate concentrate. Figures 5a–5d shows the effect of sulfuric acid (H_2SO_4) concentration with leaching temperature on the leaching of iron (II) sulfate concentrate at different particle sizes as 63, 125, 160 and 200 μm , respectively. As it can be seen, the leaching rate increased to 0.0416 mol/L^{-1} with an increase in sulfuric acid H_2SO_4 concentration from 0.25 to 2 mol/L in the particle sizes of 63 μm with leaching temperature of 65 °C. Therefore, these values can be chosen as the optimum reaction temperature. Moreover, other researchers who have studied leaching of zinc ferrite with sulfuric acid H_2SO_4 concentration stated that sufficient zinc recoveries could be obtained by using more than 100 g/l of H_2SO_4 at 90–95 °C temperature range in 2–4 hours reaction duration [31–33].

CONCLUSIONS

The leaching of iron (II) sulfate concentrate from Chaabet El Hamra, Algeria bulk sulphide ore was used to leaching of iron (II) sulfate concentrate with varying the leaching temperature, leaching time, particle size and sulfuric acid concentration at low stirring rates (100 rpm). The following conclusions can be drawn from the results presented:

(1) The sulfuric acid dissolution of Chaabet El Hamra, Setif (Algeria) bulk complex sulphide ore in the presence of hydrogen peroxide was studied. The process of direct leaching of iron (II) sulfate concentrate with sulfuric acid operated at low stirring rates (100 rpm).

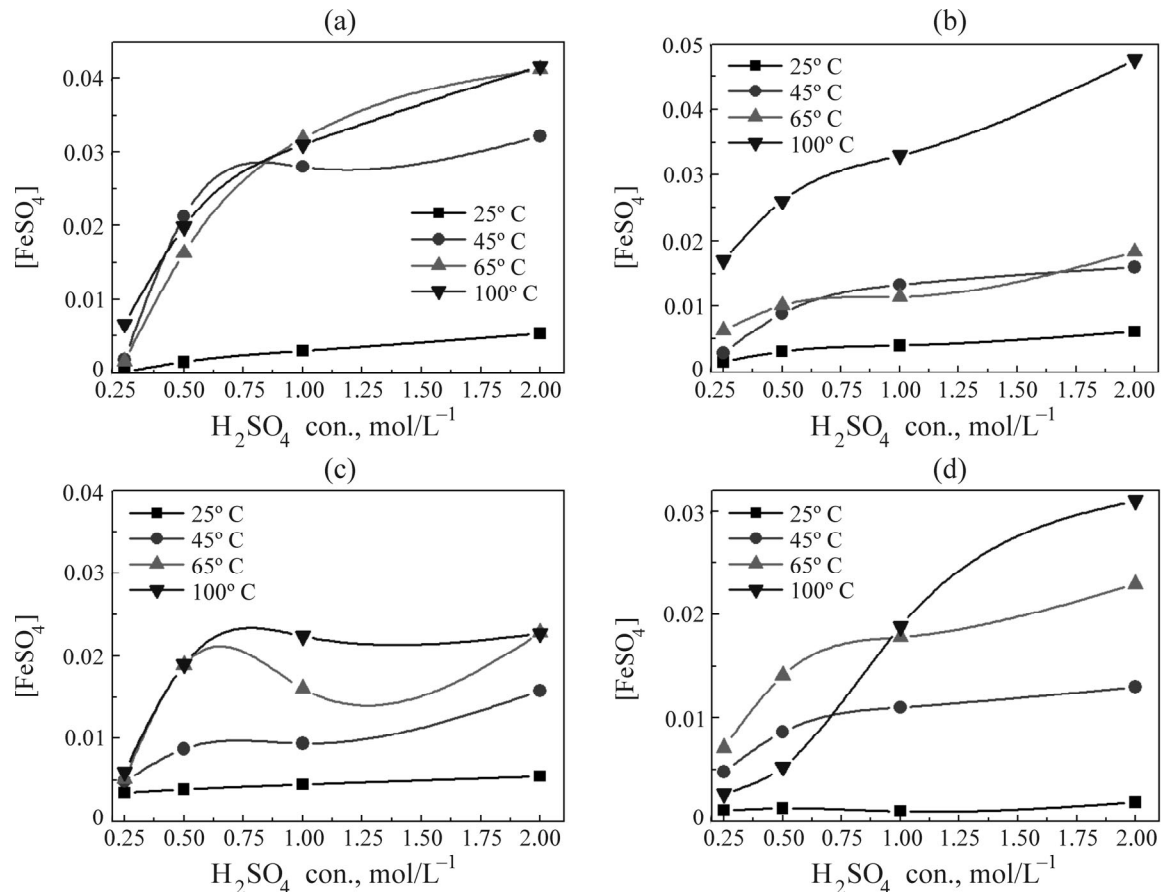


Fig. 5. The variation of iron (II) sulfate concentrate at different temperatures of leaching solution as a function of sulfuric acid concentration with different particle sizes: (a) 63 μm , (b) 125 μm , (c) 160 μm , (d) 200 μm .

(2) The effects of concentration of sulfuric acid H_2SO_4 , leaching temperature, leaching time and particle diameter on leaching rate were investigated. It was found that ore mineralogy plays a major role in the dissolution process. Highest recoveries of iron (II) sulfate concentrate obtained at a particle size of 63 μm .

(3) Based on the results of this study, it was concluded that the combination of sulphuric acid and hydrogen peroxide enhances the dissolution of the bulk sulphide ore.

(4) The optimal operational conditions were as follows: leaching temperature 65 °C; leaching time 2 hours; sulfuric acid concentration 2 mol/L-1; the smaller particle size 63 μm and the solid-to-liquid ratio 1:10. In these values the maximum extraction of iron (II) sulfates is 0.0416 mol/L⁻¹.

REFERENCES

1. Zelikman, A., Voldman, G., and Belyaevskaya, L., Theory of Hydrometallurgical Processes, Moscow: Metallurgy, 1983.
2. Maslenetsky, I., Dolivo-Dobrovolsky, V., Dobrohotov, G., Sobol, S., Chugaev, L., and Belikov, V., Autoclave Processes in Nonferrous Metallurgy, Moscow: Metallurgy, 1969.
3. Dixon, D.G., Mayne, D.D., and Baxter, K.G., Galvanox TM—A Novel Galvanically Assisted Atmospheric Leaching Technology for Copper Concentrate, *Can. Metall. Quart.*, 2008, vol.47, pp. 327–336.
4. Çopur, M., Özmetin, C., Özmetin, E., and Kocakerim, M.M., Optimization Study of the Leaching of Roasted Zinc Sulphide Concentrate with Sulphuric Acid Solutions, *Chemical Engineering and Processing*, 2004, vol. 43, pp. 1007–1014.
5. Gu, Y., Zhang, T.A., Liu, Y., et al., Pressure Acid Leaching of Zinc Sulfide Concentrate, *Trans. Nonferrous Met. Soc. China*, 2010, vol. 20, pp. 136–140.
6. Ruşen, A., Sunkar, A.S., and Topkaya, Y.A., Zinc and Lead Extraction from Çinkur Leach Residues by Using Hydrometallurgical Method, *Hydrometallurgy*, 2008, vol. 93, pp. 45–50.
7. Olubambi, P.A., Borode, J.O., and Ndlovu, S., Sulphuric Acid Leaching of Zinc and Copper from Nigerian Complex Sulphide Ore in the Presence of Hydrogen Peroxide, *The Journal of The Southern African Institute of Mining and Metallurgy*, 2006, vol. 106, pp. 765–770.
8. Santos, S.M.C., Ismael, M.R.C., Correia, M.J.N., Reis, M.T.A., Deep, A., and Carvalho, J.M.R., Hydrometallurgical Treatment of a Zinc Concentrate by Atmospheric Direct Leach Process, *Proc. European Congress of Chemical Engineering (ECCE-6)*, Copenhagen, 2007, pp. 1-11.
9. Xu, H., Wei, C., et al., Leaching of a Complex Sulfidic, Silicate-Containing Zinc Ore in Sulfuric Acid Solution under Oxygen Pressure, *Separation and Purification Technology*, 2012, vol. 85, pp. 206–212.
10. Deniz Turan, M., Soner Altundogan, H., and Fikret Tqmen, Recovery of Zinc and Lead from Zinc Plant Residue, *Hydrometallurgy*, 2004, vol. 75, pp. 169–176.
11. Rath, P.C., Paramguru, R.K., and Jena, P.K., Kinetics of Dissolution of Zinc Sulphide in Aqueous Ferric Chloride Solution, *Hydrometallurgy*, 1981, vol. 6, pp. 219–225.
12. Bobeck, G.E. and Su, H., The Kinetics of Dissolution of Sphalerite in Ferric Chloride Solution, *Metall. Trans.*, 1085, B 16B, pp. 413–424.
13. Suni, J., Henein, H., Warren, G.W., and Reddy, D., Modeling the Leaching Kinetics of a Sphalerite Concentrate Size Distribution in Ferric Chloride Solution, *Hydrometallurgy*, 1989, vol. 22, pp. 25–38.
14. Jin, Z.M. and Warren, G.W., An Investigation of the Electrochemical Nature of the Ferric Chloride Leaching of Sphalerite, *Int. J. Miner. Process.*, 1993, vol. 37, pp. 232–238.

15. Baba, A.A., Adekola, F.A., Mesubi, M.A., and Bale, R.B., The Characterization and Lixiviation of Sphalerite Mineral in Some Acidic Mineral, *J. Chem. Soc. Nigeria*, 2003, vol. 28, pp. 40–44.
16. Al-Harashah, M. and Kingman, S., The Influence of Microwave on the Leaching of Sphalerite in Ferric Chloride, *Chem. Eng. Process.*, 2007, vol. 46, pp. 883–888.
17. Kazanbaev, L., Kozlov, P., and Kubasov, V., *Hydrometallurgy of Zinc, Leaching Processes*, Moscow: Ore and Metals, 2007.
18. Matsumoto, K., Taniguchi, S., and Kikuchi, A., *J. Japan Inst. Metals*, 1991, vol. 55, pp. 853–859.
19. Lochmann, J. and Pedlik, M., Kinetics of Dissolution of Sphalerite in Ferric Sulfate Solution, *Hydrometallurgy*, 1995, vol. 37, pp. 89–96.
20. Hackl, R.P., Dreisinger, D., Peter, E., and King, J.A., Passivation of Chalcopyrite during Oxidative Leaching in Sulfate Media, *Hydrometallurgy*, 1995, vol. 39, pp. 25–48.
21. Markus, H., Fugleberg, S., Valtakari, D., Salmi, T., Murzin, D.Y., and Lahtinen, M., Kinetic Modeling of a Solid–Liquid Reaction: Reduction of Ferric Iron to Ferrous Iron with Zinc Sulphide, *Chemical Engineering Science*, 2004, vol. 59, pp. 919–930.
22. Aydogan, S., Aras, A., Ucar, G., Erdemoglu, M., Dissolution Kinetics of Galena in Acetic Acid Solutions with Hydrogen Peroxide, *Hydrometallurgy*, 2007, vol. 89, pp. 189–195.
23. Safarzdeh, M.S., Moradkhani, D., Ilkhi, M.O., and Golshan, N.H., Determination of the Optimum Conditions for the Leaching of Cd–Ni Residues from Electrolytic Zinc Plant Using Statistical Design of Experiments, *J. Separation and Purification Technology*, 2008, vol. 58, pp. 367–376.
24. Abramov, A.A. and Avdohin, V.M., *Oxidation of Sulfide Minerals in Beneficiation Process*, Gordon and Breach Science Publishers, Netherlands, 1997.
25. Moradi, S. and Monhemius, A.J., Mixed Sulphide–Oxide Lead and Zinc Ores: Problems and Solutions, *Minerals Engineering*, 2011, vol. 24, pp. 1062–1076.
26. Xu, H., Wei, C., Li, C., et al., Sulfuric Acid Leaching of Zinc Silicate Ore under Pressure, *Hydrometallurgy*, 2010, vol. 105, pp. 186–190.
27. Akcil, A.A., Preliminary Research on Acid Pressure Leaching of Pyritic Copper Ore in Kure Copper Mine, Turkey, *Minerals Engineering*, 2002, vol. 15, pp. 695–699.
28. Antonijevic, M.M. and Bogdanovic, G.D., Investigation of the Leaching of Chalcopyritic Ore in Acidic Solutions, *Hydrometallurgy*, 2004, vol. 73, pp. 245–256.
29. Antonijevic, M.M, Jankovic, Z.D., and Dimitrijevic, M.D., Kinetics of Chalcopyrite Dissolution by Hydrogen Peroxide in Sulphuric Acid, *Hydrometallurgy*, 2004, vol. 71, pp. 329–334.
30. Li, C., Wei, C., et al., Oxidative Pressure Leaching of Sphalerite Concentrate with High Indium and Iron Content in Sulfuric Acid Medium, *Hydrometallurgy*, 2010, vol. 102, pp. 91–94.
31. Bhat, K.L. and Natarajan, K.A., *Transactions of the Indian Institute of Metals*, 1987, vol. 40, pp. 361–371.
32. Claassen, J.O., et al., Iron Precipitation from Zinc-Rich Solutions: Defining the Zincor Process, *Hydrometallurgy*, 2002, vol. 67, pp. 87–108.
33. Elgersma, F., et al., Acidic Dissolution of Zinc Ferrite, *Hydrometallurgy*, 1992, vol. 29, pp. 173–192.