

Dissolution Kinetics of Chalcopyrite with Hydrogen Peroxide in Sulphuric acid Medium

A. O. Adebayo*, K. O. Ipinmoroti, and O. O. Ajayi

Department of chemistry, Federal University of Technology, Akure, Nigeria
e-mail:adebayoalbert302@hotmail.com

Original scientific paper

Received: October 19, 2002

Accepted: March 11, 2003

The kinetics of dissolution of chalcopyrite with hydrogen peroxide in sulphuric acid solution, was investigated. The influence of temperature, stirring speed, concentrations of hydrogen peroxide and sulphuric acid as well as particle size, were studied. The dissolution kinetics was found to follow a shrinking-core model, with surface chemical reaction as the rate-determining step. This is in agreement with activation energy of 39 kJ mol⁻¹ and a linear relationship between the rate constant and the reciprocal of particle size. The reaction order with respect to hydrogen peroxide is 1.45. Increase in concentration of sulphuric acid has positive effect on the dissolution of the chalcopyrite; the order of reaction with respect to the acid being 0.77. Stirring speed has a negative effect on the dissolution of chalcopyrite as it enhances the decomposition of the hydrogen peroxide.

Keywords:

Hydrogen peroxide, chalcopyrite, dissolution kinetics.

Introduction

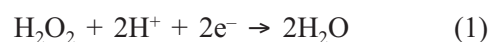
The availability of metals for use is not governed by its abundance alone. Copper is the third metal in tonnage produced after iron and aluminum, its mass fraction in earth's crust is quite low (only about 0.01 %).¹ Tonnage production of a metal depends on the following factors: accessibility of ore deposits, richness of ore deposits, nature of extractant and refining processes for the metal.^{1,2}

The dissolution of mineral ores in aqueous solution may be a physical, chemical or electrochemical process or a combination of these. The crystalline nature of the mineral, its state or subdivisions, its defect structures, and other factors play an important role in the dissolution.³ Chalcopyrite usually occurs together with other sulphide minerals to constitute complex sulphide ores.⁴ There are many studies related to dissolution of chalcopyrite in various media.^{5–7} Direct chlorination of complex sulphide of copper, nickel and iron has been investigated by several authors.^{5,6} Jackson and Strickland⁶ studied the kinetics of dissolution of some common sulphide minerals including chalcopyrite, pyrite, sphalerite and galena, in chlorine saturated water.

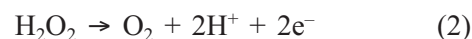
With gradual depletion of rich ore deposits, it is becoming increasingly difficult in many situations to apply the conventional pyrometallurgical methods for metal extraction. Hydrometallurgical processes are suited for lean and complex ores. If there are too much gangues in an ore, then, processing of the ores at high temperature causes waste of energy

as well as disposal of slag and also evolution of gaseous pollutant to the environment.¹ The siliceous gangue in the ore is unaffected by most leaching agents; whereas in pyrometallurgical smelting processes, thermodynamically stable mattes are formed, which reduce the extraction of the metals. In most hydrometallurgical processes, high level of extraction of the base metals is achievable. In these cases high oxidation potential is required.⁸

Hydrogen peroxide is a good oxidizing agent as depicted by the redox potential of 1.77 V in acid medium. The oxidation action of hydrogen peroxide in acidic medium is based on its reduction according to the equation^{9,10}



However, hydrogen peroxide can also act as a reducing agent in accordance with Equation 2:



Hydrogen peroxide has been used as a leaching agent for uranium ores¹¹ and its use has been studied with a zinc-lead bulk sulphide concentrate¹² as well as with concentrate of pyrite¹³ and sphalerite.¹⁴ Oxidative dissolution of chalcopyrite using hydrogen peroxide in sulphuric acid has been studied.

In the present study, kinetics of the dissolution of copper from chalcopyrite was investigated by considering variables such as temperature, concentration of hydrogen peroxide and sulphuric acid as well as stirring speed and particle diameter.

*Correspondence author

Experimental

A sample of chalcopyrite concentrate from a Nigerian deposit was used for these studies. It was crushed and ground into fine powder and sieved with standard ASTM sieve to obtain granulation of $d_p = 100, 200, 250, 300 \mu\text{m}$. The analysis of the sample for some elemental composition was performed using standard method (Table 1).¹⁵

Table 1 – Some Elemental composition of chalcopyrite from a Nigeria deposit.

Element	w/%
Cu	32.49
Fe	17.04
SiO ₂	13.97
S	11.91
Al ₂ O ₃	5.98
MgO	0.78
CaO	0.60

The dissolution experiments were carried out in a 250 ml reactor made up of 3-necked pyrex glass in a thermostatic heating mantle. The reactor was equipped with a condenser and an overhead mechanical stirrer. The reactor was charged with 50 ml hydrogen peroxide and 50 ml sulphuric acid. When the desired temperature was attained, 1.0 g of the chalcopyrite was added to the acidified peroxide solution, stirring continued and the temperature of the reaction mixture was then maintained constant.

2 ml of solution were withdrawn from the reactor at various time intervals and diluted with distilled water to 25 ml in a volumetric flask. The reaction kinetics was investigated by determining the amount of copper in the leaching solution.

For calculation of the fraction of copper leached, an equation developed by Papangelakis and Demopolous¹⁶ was used which includes in itself correction factors to account for the volume and mass losses due to sampling. The fraction was calculated by dividing the amount of leached copper at the moment of sampling by the amount of copper contained in the ore at the beginning of the reaction.

Result and discussion

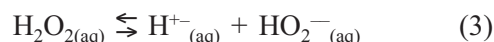
Dissolution process

Direct dissolution of sulphide minerals in strong oxidizing solutions has been investigated by

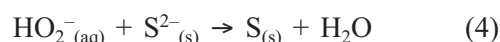
other researchers, and it has been found that sulphide is oxidized in two stages. In the first stage, sulphide is converted to elemental sulphur, and in the second stage the sulphur is converted to sulphate.¹⁷

At low temperature most strong oxidizing agent oxidizes sulphide to sulphur and at temperature above 180 °C sulphate is formed.⁸

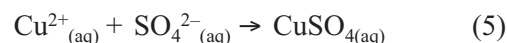
In dilute aqueous solution, hydrogen peroxide dissociates to very reactive radicals.^{9,10}



The peroxide radical reacts with sulphide ion as shown in Equation 4



While the base metal, copper reacts with sulphate as shown in equation



The effects of reaction temperature

The experiments were conducted in the 303–353 K-temperature range with initial H₂O₂ fraction of 20 % and H₂SO₄ concentrations of 0.1 mol L⁻¹. The dissolution curves are shown in Fig. 1, from which it could be seen that dissolution of chalcopyrite increased with increasing temperature. The curves for the temperature at 343 K and 353 K showed a leveling off at 90 min, indicating that dissolution had almost ceased. This might be due to decomposition of H₂O₂ at high temperature, particularly marked at the temperatures above 333 K.

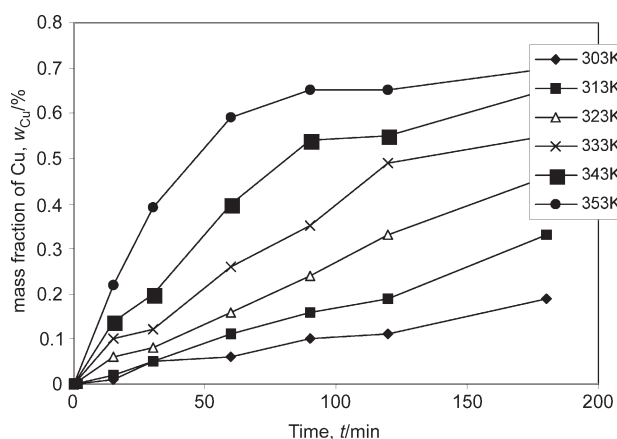
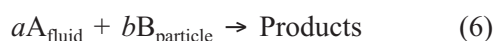


Fig. 1 – Effect of reaction temperature on the leaching of copper from chalcopyrite

The kinetic analysis was tested according to the unreacted – core model. If a reaction such as



is controlled by diffusion through product layer, the integrated rate equation is given as¹

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = \frac{6bDc_A t}{c_B d^2} \quad (7)$$

If reaction given in Equation (6) is chemically controlled, then the integrated rate expression becomes

$$1 - (1 - x)^{1/3} = \frac{bkc_A t}{\bar{c}_B d} \quad (8)$$

where x is the molar fraction; t , the time (min.); \bar{c}_B , the average (apparent) concentration of ore (mol m^{-3}); d , the diameter of the solid particle (m); b , the stoichiometric coefficient of the solid reacting with amount of fluid reactant; k , mass transfer coefficient for surface reaction (ms^{-1}); D , diffusion coefficient ($\text{m}^2 \text{s}^{-1}$); and c_A , the concentration of gas (mol m^{-3}).

On comparing Equations (7) and (8), by plotting the experimental values of the leached copper versus time, the plot of Equation (8) gave a straight line. The rate constants were calculated as slopes of the straight lines. By using these values, the Arrhenius plot in Fig. 2 was obtained, from which apparent activation energy of 39 kJ mol⁻¹ was obtained. The value of activation energy obtained suggested that chemical reaction at the chalcopyrite surface was the rate – determining step⁸ in the dissolution of chalcopyrite by H₂O₂ in H₂SO₄. McKibben¹⁸ determined activation energy of 33.5 kJ mol⁻¹ for pyrite dissolution by millimolar concentrations of H₂O₂ in acidic solutions. A higher value of 68 kJ mol⁻¹ has been reported for the dissolution of pyrite with H₂O₂ in H₂SO₄.¹⁹

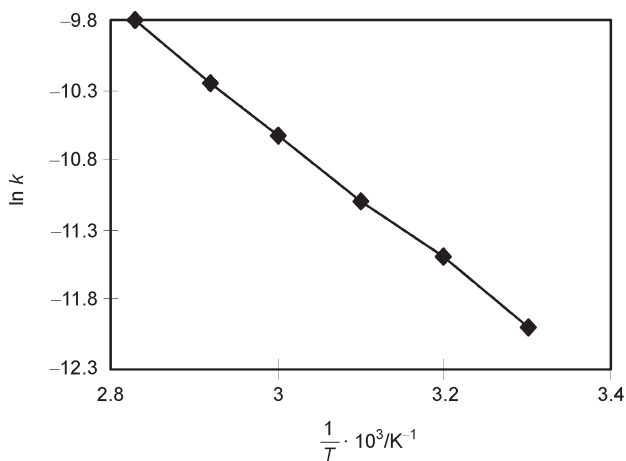


Fig. 2 – Arrhenius plot for the dissolution of chalcopyrite with H₂O₂ in H₂SO₄

Effect of stirring speed

The effect of stirring on the rate dissolution of copper from chalcopyrite was carried out at the speed of 300, 400 and 700 rpm in the concentration of 20 % H₂O₂ and 0.70 mol L⁻¹ H₂SO₄ at the 323 K. The experiment was also examined without stirring, other conditions being constant. The results revealed an irregular pattern (Fig. 3). The fraction of copper leached at 400 rpm were higher than those obtained at 700 rpm, the least values were obtained at 300 rpm. The highest dissolution rate was observed when there was no mechanical stirring. This observation showed that better contacts were made when there was no mechanical stirring. Similar result has been reported for pyrite oxidation.²⁰ As a result of stirring, decomposition of H₂O₂ takes place faster, accompanied by evolution of molecular oxygen that adsorbs onto the particle surface thus hindering particle/peroxide contact. Based on these observations, other experiments were carried out with occasional stirring. It has already been pointed out that during dissolution of ores by hydrogen peroxide, mixing of particles occurs, optionally termed “self mixing”, caused by oxygen bubbles rising in the solutions. These bubbles were produced by hydrogen peroxide decomposition often catalysed by solid particles as well as Fe³⁺ and Cu²⁺, generated.^{11,12} The catalytic decomposition by the particles and the ions were suppressed by addition of H₂SO₄ and acetanilide, which stabilizes the hydrogen peroxide.¹¹

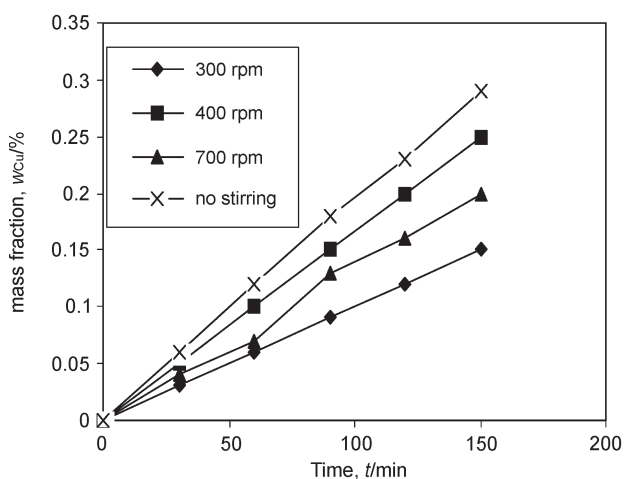


Fig. 3 – Effect of stirring on the dissolution of chalcopyrite

Effect of initial concentration of hydrogen peroxide

The investigation of effect of the initial volume fraction of H₂O₂ on chalcopyrite dissolution was carried out in fraction range of φ 10 – 30 %. Exper-

iments were conducted at 323K and 1.0 mol L⁻¹ H₂SO₄. The results showed that concentration had a positive effect on the dissolution of chalcopyrite. It was observed that there was a linear relationship for 10 and 15 %. As the concentration increased deviation from linearity was noted (Fig. 4). The deviation might be due to decomposition of hydrogen peroxide at higher concentration, which resulted in slight reduction of reaction rate. This observation agreed with earlier report that the rate of H₂O₂ decomposition was proportional to its concentration.^{13,16} This meant that H₂O₂ decomposition was faster at higher concentrations, leading to a significant lowering of its concentration.

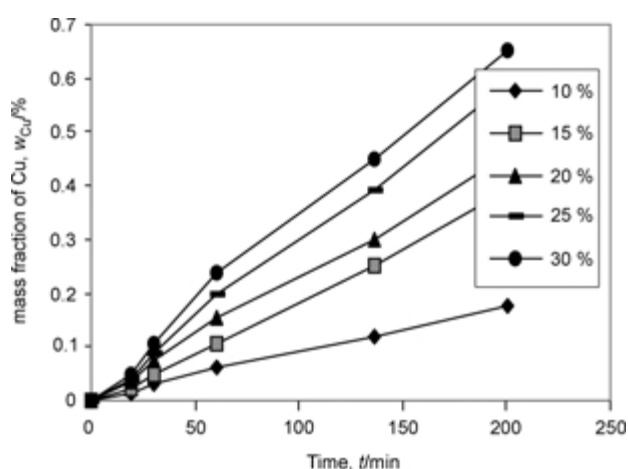


Fig. 4 – Effect of initial fraction of H₂O₂ on the dissolution of chalcopyrite

The kinetic data were linearised by means of Equation (8) as shown in Fig. 5. The mass transfer coefficient was calculated from slopes of the straight lines. A log-log plot of mass transfer coefficient against H₂O₂ concentration was made as shown in Fig. 6. A reaction order of 1.45 with respect to H₂O₂ volume fraction, was determined. A

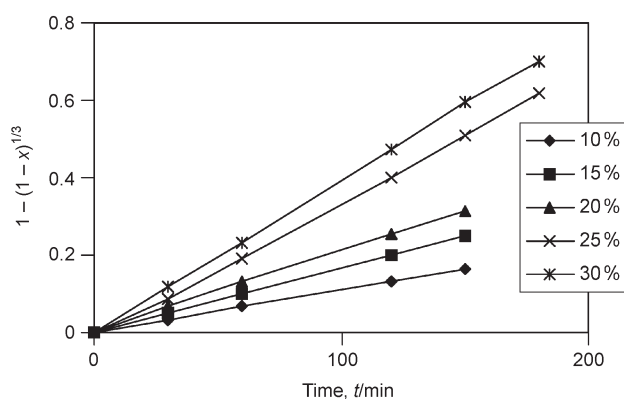


Fig. 5 – Variation of $1 - (1 - x)^{1/3}$ with time at various concentration of H₂O₂

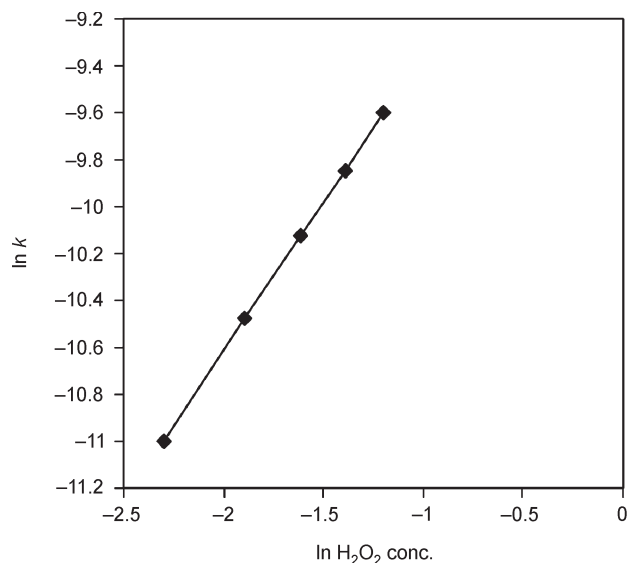


Fig. 6 – Determination of reaction order with respect to H₂O₂ volume fraction

value of 1.09 had earlier been reported for pyrite dissolution using H₂O₂ in H₂SO₄,¹³ while McKibben¹⁸ reported that pyrite dissolution by this oxidizing agent in HCl was of first order.

Effect of sulphuric acid concentration

The effect of initial sulphuric acid concentrations was investigated at concentration range of $c = 0.1 - 6.0$ mol L⁻¹ and 323 K at $\phi = 20\%$ H₂O₂. The dissolution curves are illustrated in Figure 7. It was observed that increase in the concentration of the acid resulted in significant increase in the dissolution of chalcopyrite. At acid concentration of 6.0 mol L⁻¹ dissolution rose to about 80 % in 30 minute of leaching. This suggests that sulphuric acid has significant effect on oxidation of sulphide in order to release the copper ion. The effect of the acid was due to the increase in the redox potential of the oxidant.^{10,21} This means that hydrogen ion concentra-

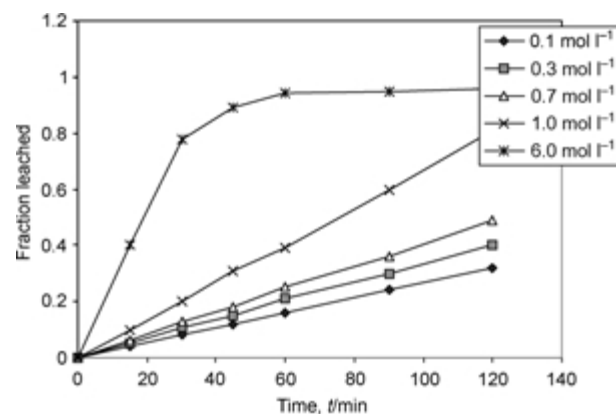


Fig. 7 – Effect of concentration of H₂SO₄ on the leaching of copper from chalcopyrite

tion increases the redox potential of H_2O_2 , which consequently increases the rate of the reaction.

The oxidation curves were linearised by means of Equation (8) and the mass transfer coefficient, k_{ca} was calculated as the slope of the straight lines. A graph was drawn of $\ln k_{ca}$ as a function of natural logarithm of molar concentrations of the acid (Fig. 8). It can be observed that a straight line was obtained with slope of 0.77, which corresponds to the reaction order. Such a positive value of reaction order shows a positive effect of H_2SO_4 as an auxiliary reagent on oxidation behaviour of H_2O_2 .

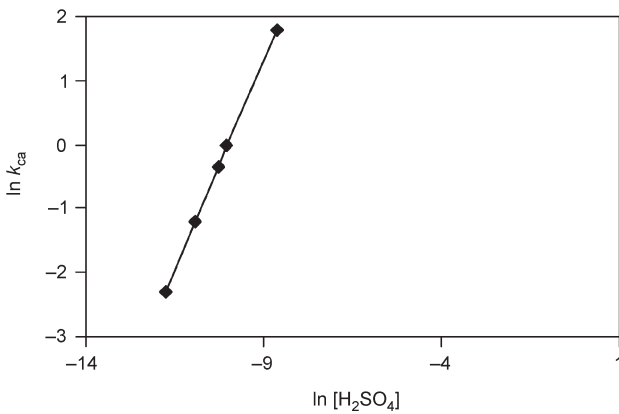


Fig. 8 – Determination of reaction order with respect to $\ln [H_2SO_4]$

Effect of particle diameter

The effect of particle diameter on the rate of chalcopyrite dissolution was studied using four granulated distribution. (100, 150, 200, 300 μm) at 323 K in solutions of 20 % H_2O_2 in 0.1 mol L^{-1} H_2SO_4 . The result (Fig. 9) revealed that, smaller particles have a faster rate of dissolution than larger particles. The kinetic curves were linearised by means of Equation (8) and the apparent rate coefficient

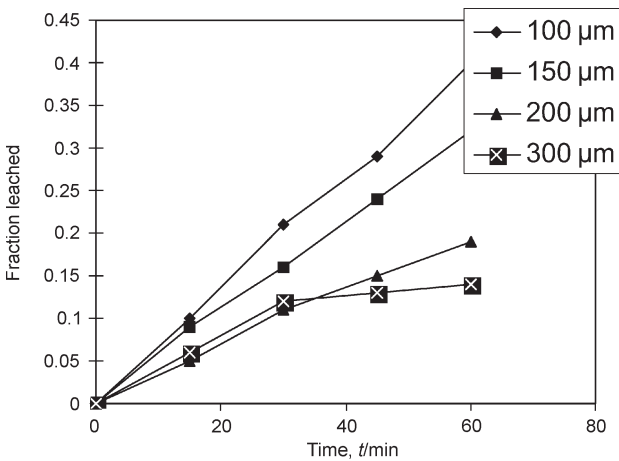


Fig. 9 – Effect of particle diameter on the leaching of copper from chalcopyrite

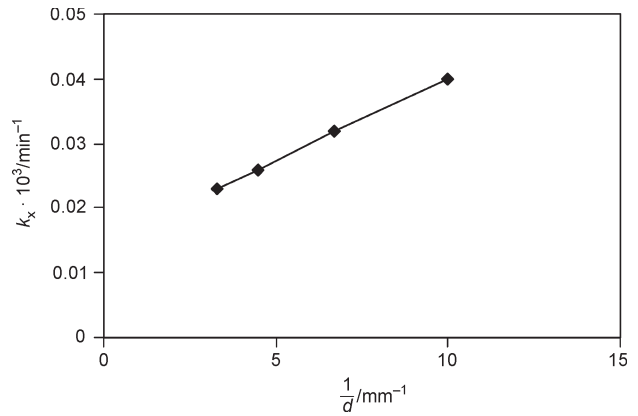


Fig. 10 – Plot of k_x versus $1/d_0$

cient k_x calculated were drawn as a function of the inverse of the particle radius (Fig. 10). A linear relationship between k_x versus $1/d_0$ confirms the chemical reaction on the chalcopyrite surface as the rate-controlling step.^{20,22}

Conclusions

Experiments have been conducted by dissolution of chalcopyrite using hydrogen peroxide acidified with sulphuric acid; it can be concluded that, as the stirring reduced the rate of chalcopyrite oxidation by accelerating the decomposition of hydrogen peroxide the experiment is best conducted without stirring or with occasional stirring. The kinetic analysis followed a shrinking-core model with the surface chemical reaction as the rate-determining step. The value of the activation energy is 39 $kJ\ mol^{-1}$ and the linear relationship between k_x and $1/d_0$ confirmed the surface reaction model. Increasing in the H_2O_2 and H_2SO_4 concentrations has a positive effect on the oxidation of sulphide. The reaction orders were 1.45 and 0.77 with respect to concentration of H_2O_2 and H_2SO_4 respectively.

Nomenclature

ASTM – America Standard and Testing Material

References

1. Ghosh, A., Ray, H. S., Principles of Extractive Metallurgy (2nd edition) Wiley Eastern Ltd. New Delhi (1991) 14.
2. Burkin, A. R., The chemistry of Hydrometallurgical Processes E. & F. N. Spon, London, (1966) 466.
3. Gomez, G., Limpo, J. L., De Luis, A., Blazquez, M. L. J., Gonzalez, F. Ballester, A., Can. Metall. Quart. 36 (1) (1997) 15 .
4. Smith, K. A., Iwasaki, I., Min. Met. Proc. 2 (1985) 42.
5. Pilgrim, R. F., Ingrahm, T. R., Can. Met. Quart. 6 (1967) 39.

6. Jackson, K. J., Strickland, J. D. H., *J. Trans. Met. Soc. AIME.* **212** (1958) 373.
7. Biswa, A. K. (edt), *Frontier in Applied Chemistry*, Narosa Publishing House, New Delhi, pp. 37, 1987.
8. Ekinci, Z., Colak, S., Cakici, A., Sarac, H., *Mineral Engineering.* **11** (3) (1998) 279.
9. Cotton, F. A., Wilkinson, G., *Advanced Inorganic Chemistry A Comprehensive Text.* John Wiley & Sons, NY 1980, 489.
10. Wood, C. W., Holliday, A. K., *Inorganic Chemistry, An Intermediate text*, Butter worth & Co. Ltd. England, 1967, 218.
11. Eary, L. E., Cathles, M., *Metall trans.*, **14** (B) (1983) 325.
12. Vazalis, H. G., *Hydrometallurgy* **20** (1988) 179.
13. Antonijevic, M. M., Dimintrijevic, M., Jankovic, Z., *Hydrometallurgy* **46** (1997) 71.
14. Balaz, P., Ebert, I., *Hydrometallurgy* **27** (1991) 41.
15. Furnna, N. H., *Standard Method of Chemical Analysis*, D. Van Nostrand Comp. Inc., New York, 1963.
16. Papangelakis, V. G., Demopolous, G. P., *Hydrometallurgy* **26** (1991) 309.
17. Copur, M., *Chemical and Biochem. Eng. Q.* **15** (4) (2001) 181.
18. Mckibben, M. A., PhD. Thesis, Pennsylvania state Univ. (1984).
19. Dimitrijevic, N., Autonijevic, M. M. and Dimitrijevic, V., *Mineral Engineering* **12** (2) (1999) 165.
20. Eary, L. E., *Metall. Trans.* **16** (B) (1985) 181.
21. Alimarin, I. P., Fadaeva, V. I., Dorokhova, E. N., *Lecture Experiments in Analytical chemistry*, Mir Publi. Moscow, 1976, pp. 163.
22. Levenspiel, O., *Chemical Reaction Engineering*, John Wiley, N.Y.(2ndEd.), 1972, pp. 375.