ISSN : 0974 - 7443 Volume 6 Issue 2

CHEMICAL TECHNOLOGY

An Indian Journal

Trade Science Inc.

Full Paper

CTAIJ 6(2) 2011 [78-83]

Dissolution kinetics of refractory gold concentrate by ozone in ferric sulfate solutions

Li Qing Cui*, Li Deng Xin, Chen Quan Yuan
College of Environmental Science and Engineering, Donghua University, Shanghai 201620, (CHINA)
E-mail: liqingcui@mail.dhu.edu.cn

Received: 1st February, 2011 ; Accepted: 11th February, 2011

ABSTRACT

This paper presents a study for leaching kinetics of refractory gold concentrate (RGC) with ozone in ferric sulfate solution. The influence of various parameters such as ozone concentration, temperature, reaction time, solid / liquid ratio and particle size on the iron extraction rate was investigated. The shrinking core model was suggested to describe the leaching process of RGC analyzing the kinetic data. The activation energy for the leaching process was found to be 11.47 kJ/mol in the temperature range of 70-100 ^{0}C. Consequently, the rate of the reaction based on a reaction-controlled process could be expressed as $1- (1-\alpha)^{2/3} = 22303.97e^{-11.47/RT}\, t$. The dissolution of RGC with ozone and ferric sulfate solution was found to be controlled by diffusion-controlled process.

KEYWORDS

Oxidation;
Reaction kinetics;
Refractory gold concentrates;
Shrinking core model.

INTRODUCTION

The gold is frequently finely disseminated in the pyrite matrix and cannot be extracted by conventional cyanidation method[1]. Along with arsenopyrite and pyrrhotite, pyrite is the most prevalent host for gold. The conventional method of recovering gold from RGC involves the roasting-leaching-electrowining process.

The need to utilize small and complex deposits and the environmental restrictions imposed on sulfides (including arsenopyrite) smelters stimulated the development of alternative methods, especially hydrometallurgical routes that avoid the production of SO2 and As2O3 as a pollutant.

The elimination of roasting step is an important advantage and high gold extraction increases the importance of hydrometallurgical treatment processes. For this purpose, various leaching studies have been performed by many researchers, such as pressure oxidation[2-4], chemical oxidation[5-8] and bacterial oxidation[9-12].

Ozone is one of the most important oxidative agents in leaching process and was reported that ozone has more advantage than other oxidative agents. A limited number of investigations[13-15] indicate that gold in RGC can be leached readily after ozone oxidation under certain conditions. Although RGC oxidation by ozone has been investigated by limited researchers, few papers on kinetic modeling of RGC oxidation by ozone and ferric sulfate in acidic media seem to be published.

The dissolution kinetics of a solid compound depends on the processes taking place at the solid–liquid boundary; the processes are complex and involve both chemical reactions and mass transfer. The solid–liquid reaction can occur at the surface of the solid, in the film around the solid or in the liquid bulk phase. Different steps, such as mass transfer, chemical reaction, and charge transfer, can determine the dissolution rate[16-18]. The classical models used for solid-fluid reactions are the shrinking particle and the shrinking core models[19]. The shrinking core model (SCM) is applicable to an initially non-porous particle, which reacts with a reagent leaving a reacted layer around the unreacted core. The shrinking particle model is similar to the SCM except that no product layer is left around the unreacted core. The SCM has been widely used in the area of hydrometallurgy to model leaching systems.

Hence, the objectives of this study were to investigate the main factors involved in the oxidation of RGC by ozone and ferric sulfate, such as ozone concentration, solid/liquid ratio, particle size and temperature, and also to determine what process controls the rate of the dissolution of RGC or what kinetic model can be applied.

MATERIAL AND METHODS

Material

The mineral samples used in this work were gold concentrates obtained from the Zhongyuan Gold Smelting Plant in Henan province. TABLE 1 shows Composition of refractory gold concentrate used in this experiment. Au and Ag were analyzed by fire assay, S was analyzed by gravimetric analysis and Fe was analyzed by titration analysis and other elements were analyzed by XRF. The elemental analysis of the ore was determined by X-ray fluorescence (XRF) analysis and chemical analysis. Furthermore, from the X-ray diffraction pattern of the head sample (Figure 1), the mineral composition of the head sample was calculated to be 24% pyrite, 17% arsenopyrite, 2% anatase, 37% muscovite and approximately 17% quartz.

TABLE 1 : Composition of refractory gold concentrate used in this experiment

Element (%)	Content
Na	0.69
Mg	1.88
Al	7.61
Si	15.8
S	13.91
Ca	3.88
Ti	0.71
Fe	16.8
Cu	0.03
As	7.54
P	0.11
Ni	0.07
Mn	0.08
Au (g/t)	48.03
Ag (g/t)	8.46

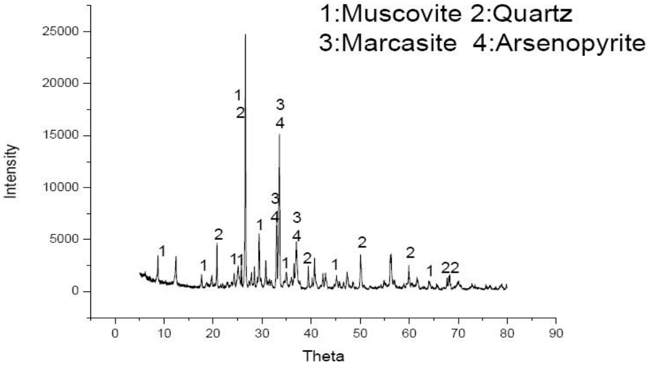

Figure 1 : X-ray diffraction pattern of the head sample

Experimental procedure

The pretreatment process was carried out in a 500-ml three-necked bottle equipped with a water-cooled condenser, thermometer, a magnetic stirrer and a porous nozzle for injection of ozone. The reflux condenser was used to prevent evaporation of the solution and to maintain the pretreatment process under atmospheric pressure. The reactor was heated using a heating mantle, whose temperature was thermostatically controlled by an electrical bar, with a precision of ±1°C. The ozone

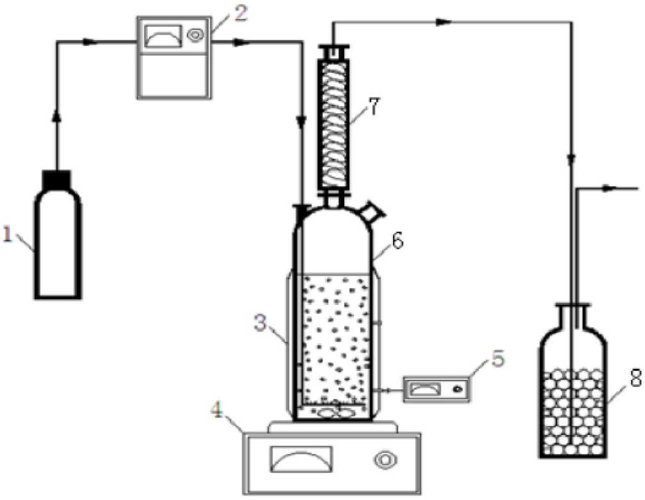

Figure 2 : Experimental apparatus, (1) oxygen steel bottle, (2) ozone generator, (3) heating mantle, (4) magnetic stirrer, (5) thermometer, (6) reactor, (7) condenser, (8) ozone destructor

was produced from extra dry pure oxygen using a Guolin Ozone Technology (L22) generator. Figure 2 shows the experimental apparatus.

In a typical experiment, the glass reactor was filled with 0.25 L 0.7 M ferric sulfate solution and a small amount of sulfuric acid to maintain a pH of 1 and then heated to the desired leaching temperature under specified agitation and ozone flow. Once the set temperature was reached, the mineral samples were charged into the reactor and agitated with a stirrer at 800 rpm. Previous experiments results had shown that further increases of the stirring speed had no effect on the Fe extraction rate. The unreacted ozone was absorbed by the ozone destructor. Experiments were carried out with varied ozone concentration, solid/liquid ratio, reaction times, particle size and process temperatures. The reaction was stopped by placing the reactor in an ice bath at the end of each reaction. The slurry was then filtered and the solid analyzed for Fe content after drying at 100 ^{0}C. The Fe extraction rate was calculated as follows:

$$C_r = (W_1 \times X_1 - W_2 \times X_2)/(W_1 \times X_1) \qquad (1)$$

Where C_r is Fe extraction rate; W_1 is weight of head sample; W_2 is weight of oxidized residues; X_1 is Fe content of head sample; X_2 is Fe content of oxidized residues.

Analysis method

Titration of iron

The iron content of the mineral samples was determined by a titration method according to GB/T7739.7-2007(China Industrial Standard). After the dissolution with hydrochloric acid the mineral sample was decomposed by nitric acid and sulfuric acid, respectively, and then evaporated to dry. Thereafter, the mineral residues was redissolved with dilute hydrochloric acid and titrated with potassium dichromate standard solution.

Gravimetric analysis of sulfur

Determination of sulfur from mineral sample was analyzed by gravimetric analysis of barium sulfate.

Titration of ozone

The ozone content of gas was determined by Iodimetry.

X-ray diffraction (XRD)

X-ray diffraction (XRD) analyses were performed using a Cu Ka (1.5418 A) source (40 KV, 40mA) from Siemens D-501, with a graphite secondary monochromator and a scintillation counter detector. The powdered sample was placed on a flat plastic plate, which was rotated at 30 rpm. The scans were performed at 25 °C in steps of 0.04 °C, with a recording time of 2 s for each step. Where accurate 2θ values were required, Si was added as an internal 2θ standard.

XRF

The chemical composition of the mineral samples was analyzed by energy dispersive X-ray fluorescence (XRF) (Bruker Axs Gmbh S4 Explorer model).

Process chemistry

Previous researchers have also elaborated the oxidation of pyrite[20,21] and the oxidation of arsenopyrite[22]. A few possible reactions may take place in ozonation solutions as follows:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

$$2FeS_2(s) + 6O_3 + 2H^+ \rightarrow Fe_2(SO_4)_3 + H_2SO_4 + 3O_2 \qquad (3)$$

$$FeAsS + 13Fe^{3+} + 8H_2O \rightarrow 14Fe^{2+} + 13H^+ + H_3AsO_4 + SO_4^{2-} \qquad (4)$$

$$FeAsS + 7O_3 + 3H^+ + H_2O \rightarrow Fe^{3+} + H_3AsO_4 + 7O_2 + SO_4^{2-} \qquad (5)$$

$$3Fe^{2+} + 2O_3 \rightarrow Fe^{3+} + 3O_2 \qquad (6)$$

A lot of studies demonstrate that pyrite is normally less reactive than arsenopyrite. So (4) and (5) reactions take place faster than (2) and (3) reactions. There are no means of initially determining which of these reactions are occurring, or if more than one reaction occurs over the lifetime of an experimental run. Therefore, because speciation is unknown and may also shift as the experiments progress, the pre-oxidation effect of ozone may be measured by Fe extraction rate of mineral samples.

RESULTS AND DISCUSSION

Effect of ozone concentration

The effect of ozone concentration on Fe extraction was investigated for an oxidation time of 8 h at 100^{0}C. As observed from Figure 3, the Fe extraction increased with increasing ozone concentration. At the end of 8h oxidation, 50 and 78.3% Fe extraction were achieved with 16ppm ozone and 54ppm ozone, respectively. On the other hand, 40% Fe extraction was achieved without ozone at the end of 8 h oxidation. These results show that ozone has important effects on Fe extraction of RGC. The more ozone involved in reaction is, the more RGC are oxidized. Therefore 54ppm ozone was selected as the optimum ozone concentration.

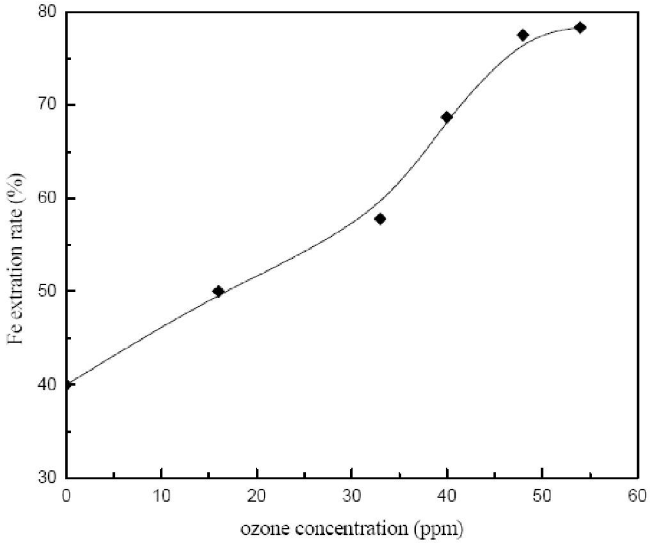

Figure 3 : Effect of ozone concentration on Fe extraction rate from RGC: (temperature: 100^{0}C; particle size: 50-74 um; solid/liquid ratio: 1/20)

Effect of temperature

The effect of temperature on Fe extraction was examined in the range of 70-100^{0}C with ozone concentration of 54ppm. As observed in Figure 4, the Fe extraction increased with oxidation time and temperature in the range. While the Fe extraction after 2h was 27.34 and 33.46%, the extraction after 8 h reached to 64.79 and 80.35% for 70 and 100^{0}C, respectively.

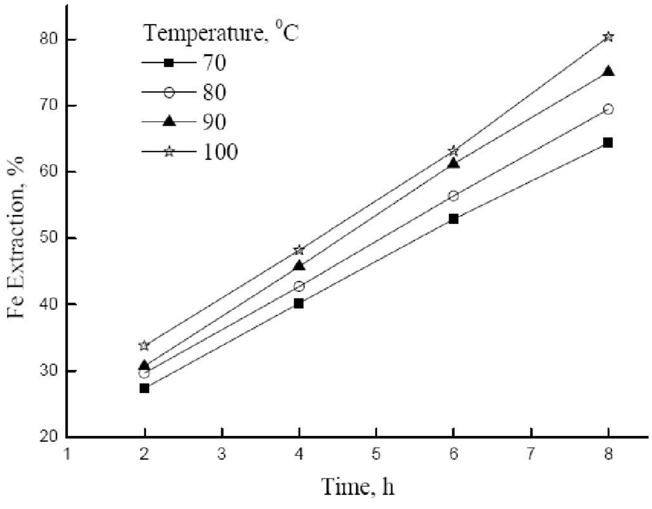

Figure 4 : Effect of temperature on Fe extraction of RGC; (particle size: 50-74 um; solid/liquid ratio: 1/20; ozone concentration: 54ppm)

Effect of solid/liquid ratio

The effect of solid/liquid ratio on the Fe extraction was investigated in the range of 1/10-1/20 (100-50g/L). The results are presented in Figure 5. The Fe extraction increased with decrease in the amount of solid. The Fe extraction after 8 h reached to 54.3 and 80.07% at ratios 1/10 and 1/20, respectively.

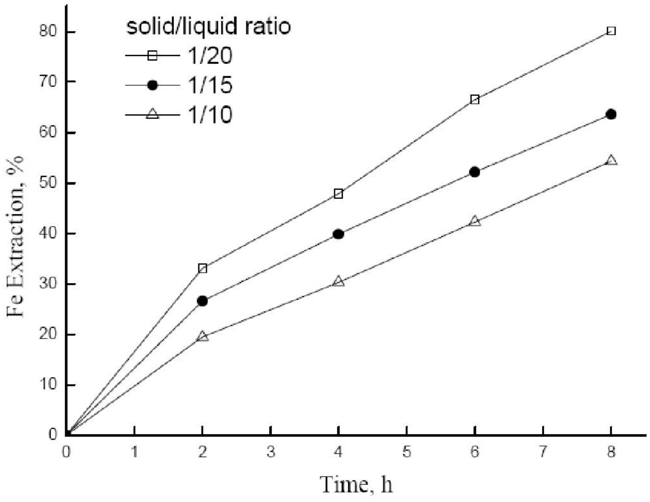

Figure 5 : Effect of solid/liquid ratio on Fe extraction of RGC; (temperature: 1000C; particle size: 50-74 um; ozone concentration: 54ppm)

Effect of particle size

Figure 6 presents the results from oxidation with various particle sizes of gold minerals. The Fe extraction increased with oxidation time, but with the decreasing particle size. The Fe extraction reached 63.44 and 82.23% after 8 h leaching for 50-74 and 74-154 μm

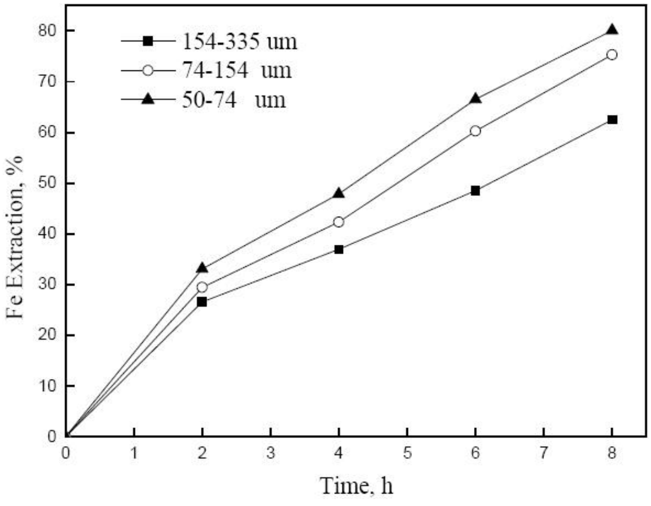

Figure 6 : Effect of particle size on Fe extraction of RGC; (temperature: 100^{0}C; solid/liquid ratio: 1/20; ozone concentration 54ppm)

particles size, respectively.

Kinetic analysis

In an acid leaching process, most sulfides follow a kinetic model known as the shrinking core model (SCM). The shrinking core model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary layer, or through a solid product layer, or by rate of the surface chemical reaction. The simplified equations of the shrinking core model when either diffusion or the surface chemical reactions are the slowest step can be expressed as follows, respectively:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=\frac{2M_B\,DC_A}{\rho_B a r_0^2}\;t=k_d\,t \qquad (7)$$

$$1-(1-\alpha)^{2/3}=\frac{K_C M_B C_A}{\rho_B\,a r_0}\;t=k_r t \qquad (8)$$

where α is the fraction reacted, K_C the kinetic constant, M_B the molecular weight of the solid, C_A the concentration of the dissolved lixiviant A in the bulk of the solution, a the stoichiometric coefficient of the reagent in the leaching reaction, r_0 the initial radius of the solid particle, t the reaction time, D the diffusion coefficient in the porous product layer and k_d and k_r are the rate constants, respectively, which are calculated from Eqs. (7) and (8), respectively.

In order to elucidate the reaction mechanism of RGC dissolution with ozone in ferric sulfate solutions, the experimental data was analyzed on the basis of the shrinking core model (Eq. (7)-(8)).

The application of surface chemical reactions kinetic model is shown in Figure 7. Figure 7 shows the straight line plot of $1-(1-\alpha)^{2/3}$ versus time which allows the rate to be determined from the slope. The rate constants values (k_d and k_r) and their correlation coefficients for each temperature are given in TABLE 2. These results indicate that the extraction rate of Fe is controlled by film diffusion control. Also, it was determined that the integral rate expression obeyed the following equation:

TABLE 2 : The kr, kd and correlation coefficients values for different temperatures

Temperature (°C)	Apparent rate constants (10^{-4} h^{-1})		Correlation coefficient (R^2)	
	*k*d	*k*r	*k*d	*k*r
70	0.880	6. 541	0.968	0.998
80	1.106	7.37	0.952	0.995
90	1.445	8.65	0.951	0.996
100	1.800	9.575	0.912	0.980

$$1-(1-\alpha)^{2/3}=k\,t \qquad (9)$$

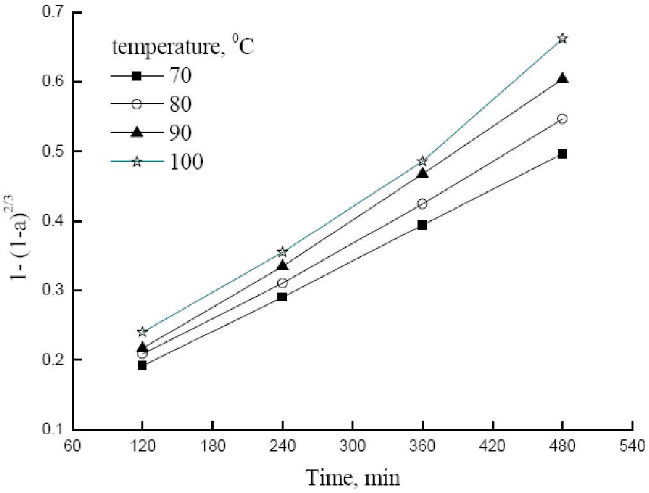

Figure 7 : Relationship between 1- (1-a) $^{2/3}$ and time at different temperatures:

Using the Arrhenius equation, $k=k_0e^{-Ea/RT}$, a plot of lnk vs. (1/T) should be a straight line with a slope of -Ea/RT and an intercept of $\ln k_0$. The equation was plotted as lnk vs. (1/T) for each value of the reaction temperature as shown in Figure 8 and the following values were calculated:

Ea = 13.88 kJ/mol, k_0= 0.08425

The activation energy is found to be 13.88kJ/mol, indicating a film diffusion control mechanism. Thus, Eq. (9) could be given as

$$1-(1-\alpha)^{2/3}=0.084e^{-13.88/RT}\,t \qquad (10)$$

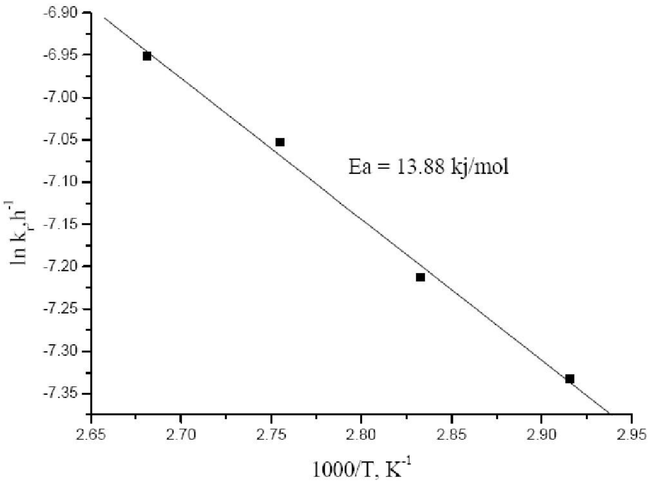

Figure 8 : Arrhenius plot of reaction rate against reciprocal temperature

CONCLUSIONS

The dissolution kinetics of RGC in ozone and acidic ferric sulfate solution was studied in a stirred batch reactor. It was found that the reaction rate increases with increase in ozone concentration, reaction temperature and with decrease in solid to liquid ratio and particle size. Analysis of the kinetic data by different kinetic models indicates that the leaching process follows the shrinking core model with the surface chemical reaction as the rate controlling step. The activation energy was found to be 13.88kJ/mol, which is consistent with film diffusion control mechanism. Dissolution rate can be expressed by Eq. (10).

NOMENCLATURE

a	stoichiometric coefficient of the reagent in the leaching reaction,
C_A	concentration of the dissolved lixiviant A in the bulk of the solution
C_r	Fe extraction rate
D	the diffusion coefficient in the porous product layer
K_C	kinetic constant,
k_d	apparent rate constant defined in Eq. (7)
k_r	apparent rate constant defined in Eq. (8)
M_B	molecular weight of the solid
r_0	initial radius of the solid particle
t	reaction time
T	reaction temperature (K)
X_1	Fe content of head sample
X_2	Fe content of oxidized residues
W_1	weight of head sample
W_2	weight of oxidized residues
α	fraction reacted

ACKNOWLEDGEMENTS

The authors are thankful to the Innovation Foundation of Donghua University for PhD candidates, the Major Project of Educational Ministry (No. 107124), Project of Key Discipline Construction in Shanghai (No. B604) and National High Technology Research and Development Program of China (863 Program, No. 2006AA06Z132) for financial support of this study.

REFERENCES

[1] J.B.Hiskey, M.D.Pritzker; J.Appl.Electrochem., **18(3)**, 484-490 **(1988)**.
[2] Y.Konishi, K.Kogasaki, S.Asai; Chem.Eng.Sci., **52(24)**, 4525-4532 **(1997)**.
[3] M.N.Lehmann, S.O'Leary, J.G.Dunn; Minerals Engineering, **13(1)**, 1-18 **(2000)**.
[4] H.G.Linge, N.J.Welham; Minerals Engineering, **10(6)**, 557-566 **(1997)**.
[5] A.W.Breed, S.T.L.Harrison, G.S.Hansford; Minerals Engineering, **10(9)**, 1023-1030 **(1997)**.
[6] N.Iglesias, F.Carranza; Minerals Engineering, **9(3)**, 317-330 **(1996)**.
[7] R.Ruitenberg, G.S.Hansford, M.A.Reuter, A.W.Breed; Hydrometallurgy, **52(1)**, 37-53 **(1999)**.
[8] L.Tremblay, G.Deschenes, E.Ghali, J.McMullen, M.Lanouette; International Journal of Mineral Processing, **48(3)**, 225-244 **(1996)**.
[9] C.Brombacher, R.Bachofen, H.Brandl; Applied Microbiology and Biotechnology, **48(5)**, 557-587 **(1997)**.
[10] L.Curreli, G.Loi, R.Peretti, G.Rossi, P.Trois, A.Zucca; Minerals Engineering, **10(6)**, 567-576 **(1997)**.
[11] P.I.Harvey, F.K.Crundwell; Minerals Engineering, **9(10)**, 1059-1068 **(1996)**.
[12] D.Langhans, A.Lord, D.Lampshire, A.Burbank, E.Baglin; Minerals Engineering, **8(1)**, 147-158 **(1995)**.
[13] W.P.V.Antwerp, P.A.Lincoln; 'Precious Metal Recovery using UV Ozone', U. S. Patent - 4642134, **(1987)**.
[14] C.F.Patiño, R.E.Salinas, P.Carrillo, F.Raul, A.H.Hernandez, B.Mendez; 'The Use of Ozone to Improve Cyanidation Process for Silver and Gold Extraction from a Refractory Ore', In: Proc. 27th Conference, IPMI, Pensacola, FLA **(2003)**.
[15] E.Elorza-Rodríguez, F.Nava-Alonso, J.Jara, C.Lara-Valenzuela; Minerals Engineering, **19(1)**, 56-61 **(2006)**.
[16] F.K.Crundwell; Hydrometallurgy, **19(2)**, 227-242 **(1987)**.
[17] F.K.Crundwell, B.Verbaan; Hydrometallurgy, **17(3)**, 369-384 **(1987)**.
[18] F.W.Y.Momade, Zs.G.Momade; Hydrometallurgy, **54(1)**, 25-39 **(1999)**.
[19] O.Levenspiel; Chemical Reaction Engineering, John Wiley & Sons, New York **(1972)**.
[20] J.D.Rimstidt, D.J.Vaughan; Geochimica et Cosmochimica Acta, **67(5)**, 873-880 **(2003)**.
[21] J.E.Dutrizac; Canadian Metallurgical Quarterly, **28(4)**, 337-344 **(1989)**.
[22] M.A.McKibben, B.A.Tallant, J.K.del Angel; Applied Geochemistry, **23(2)**, 121-135 **(2008)**.