S.Ü. Müh.-Mim. Fak. Derg., c.20, s.2, 2005
J. Fac.Eng.Arch. Selcuk Univ., v.20, n.2, 2005

OXIDATIVE AMMONIA LEACHING OF SPHALERITE CONCENTRATE

Salih AYDOĞAN[1], Ali ARAS[1] and Mehmet CANBAZOĞLU[2]

[1]Selçuk University, Eng. and Arc. Faculty, Dep. of Mining Eng., Campus, KONYA
[2]Cumhuriyet University, Eng. Faculty, Dep. of Mining Eng., Campus, SİVAS

Makalenin Geliş Tarihi: 07.03.2005

ABSTRACT: This paper presents a study of kinetics of leaching of sphalerite concentrate in ammonia solutions. The effects of ammonia concentration, oxygen partial pressure, reaction temperature and particle size on the leaching rate were investigated. The shrinking core model was applied to the results obtained from these experiments. Reaction order with respect to P_{O_2} (1-10 atm.) and NH_3 concentration (1.05-5.20 M) were 0.22 and 0.63 and the activation energy was determined to be 43.59 kj/mol in the temperature range of 90-130 °C. In addition, the apparent rate constant is in inverse relationship with the mean initial particle radius. The results of this study showed that the leaching of sphalerite was a reaction controlled process.

Key Words: Sphalerite, ammonia, kinetic model, reaction controlled process.

Sfalerit Konsantresinin Oksitleyici Amonyak Liçi

ÖZET: Bu makalede, sfalerit konsantresinin amonyak çözeltisinde liç kinetiğine ait bir çalışma sunulmuştur. Amonyak konsantrasyonunun, oksijen kısmi basıncının, reaksiyon sıcaklığının ve tane boyutunun liç hızına etkisi araştırılmıştır. Deneylerden elde edilen sonuçlara küçülen partikül modeli uygulanmıştır. Oksijen kısmi basıncına P_{O_2} (1-10 atm) ve NH_3 konsantrasyonuna (1.05-5.20 M) göre reaksiyon dereceleri sırasıyla 0.22 ve 0.63 olarak bulunmuştur. 90-130 °C aralığında aktivasyon enerjisinin 43.59 kj/mol olduğu belirlenmiştir. Görünür hız sabitinin ortalama başlangıç tane yarıçapı ile ters ilişkili olduğu görülmüştür. Bu çalışmadan elde edilen sonuçlar sfalerit liçinin reaksiyon kontrollü bir proses olduğunu göstermiştir.

Anahtar Kelimeler : Sfalerit, amonyak, kinetik model, reaksiyon kontrollü proses.

INTRODUCTION

Sphalerite is (ZnS) mainly associated with other metal sulphide minerals such as chalcopyrite ($CuFeS_2$), galena (PbS) and pyrite (FeS_2). They are collected in separate concentrates through selective flotation applied to separate each other. The conventional method of recovering the zinc from the sphalerite concentrates involves roasting the concentrate to zinc oxide or sulphate, leaching the resultant calsine with dilute sulphuric acid and electrodepositing of zinc from purified leach solution (Roasting – Leaching - Electrowining, RLE). SO_2 is produced from sphalerite during the roasting step. These problems have necessitated the development of new metal extraction technologies, such as hydrometallurgical processes.

Many investigations have been reported on direct leaching of sphalerite using various reagents such as aqueous sulphuric acid (H_2SO_4) (Demopoulos and Baldwin, 1999; Parker, 1961), nitric acid (HNO_3) (Çopur, 2001), hydrochloride acid (HCl) solution (Mizoguchi and Habashi, 1981; Majima et al.,1981; Canbazoğlu and Özkol,

1980) aqueous solutions of ferric ion (Fe^{3+}) (Dutrizac and MacDonald, 1974, 1978; Bobeck and Su, 1985; Warren et al., 1987; Crundwell, 1987; Perez and Dutrizac, 1991; Akçıl and Çiftçi, 2002; Aras et al., 2003; Ablanov et al., 1960) and by ammonia (NH_3) (Nelen and Sobol, 1959; Majima and Peters, 1966; Umetsu et al., 1967; Rao and Ray, 1998; Ghosh et al., 2002; Babu et al., 2002).

Ammonia leaching of copper concentrates has been widely investigated (Evans and Mackiw, 1964; Stanzyk and Rampacek, 1966). The important advantages of ammonia leaching are as follows: low toxicity, low corrosivity and easy regeneration due to its low vapour pressure and good complexing ability. The well known dissolution reaction of ZnS in ammoniacal medium is given by the following equation (Tozawa et al., 1976):

$$ZnS + 4NH_3 + 2O_2 = Zn(NH_3)_4SO_4 \qquad (1)$$

In ammonia leaching, the oxidation of sulphur in sulphide minerals is rather complex. For various reasons, the order of extraction as estimated from the reaction potential does not agree with those determined experimentally. The ZnS concentrates are usually containing small amounts of $CuFeS_2$, Cu_2S, CuS, CoS, NiS, Sb_2S_3, FeS, FeS_2 and Ag_2S. Majima and Peters (1966) have studied oxidation rates and compared the oxidation order of single sulphide minerals in terms of decreasing order of oxidability in ammonia at elevated temperatures as: $Cu_2S > CuS > CuFeS_2 > Sb_2S_3 > PbS > FeS = FeS_2 = ZnS$. Rao et al. (1992) have examined the role of galvanic interaction during the dissolution of $CuFeS_2$, ZnS, and PbS minerals.

Ghosh et al., (1989) and Nelen and Sobol, (1959) reported the effect of various minerals and metal ions during ammonia leaching of pure ZnS. Addition of Cu^{2+}, Ag^{+} and Pb^{2+} showed catalytic activity in the increasing order of $Cu^{2+} > Ag^{+} > Pb^{2+}$. Various chemical reactions take place during the exchange and oxidation of ZnS in the presence of metal ions have been suggested.

The objectives of this study were to investigate the main factors involving the leaching of sphalerite with oxygen in ammonia solutions. The effects of variables such as ammonia concentration, oxygen partial pressure, temperature, and particle size on the reaction rate were analyzed.

Reaction Models

Dissolution rate during the leaching decreases with time and it is directly depended on the activation energy. Habashi, (1980) stated that if the rate of reaction in the bulk of the solution is fast, the process will be governed by the rate of diffusion of the ions from the surface of the solid through the boundary layer. On the other hand, if the rate of reaction is slow, the process will be chemically controlled, thus diffusion through the boundary layer will not play any critical role.

Leaching reactions are heterogeneous processes. Most of the models, that are used to describe these processes, are similar to those used for non-catalytic heterogeneous processes, such as the shrinking core model (Levenspiel, 1972). 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 reaction is the slowest step, can be expressed as follows, respectively.

$$\left[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}\right]=\frac{2M_B D C_A}{\rho_B a r_0{}^2}t=k_d t \qquad (2)$$

$$\left[1-(1-\alpha)^{1/3}\right]=\frac{k_c M_B C_A}{\rho_B a r_0}t=k_r t \qquad (3)$$

Where α is the fraction reacted, k_c is the kinetic constant, M_B is the molecular weight of the solid, C_A is the concentration of the dissolved lixiviant A in the bulk of the solution, ρ_B is the density of the solid, a is the stoichiometric coefficient of the reagent in the leaching reaction, r_0 is the initial radius of the solid particle, t is the reaction time, D is the diffusion coefficient in the porous product layer, k_d and k_r are the rate constants, which are calculated from Eqs. (2) and (3), respectively.

Eq. (2) reveals that if the diffusion through the product layer controls the leaching rate, there must be a linear relation between the left side of equation and time. The slop of the line is the rate constant k_d, it must be directly proportional to $1/r_0^2$. If the surface reaction controls the rate, the relation between the left side of Eq. (3) and time must be linear. The slop of this line called the apparent rate constant k_r and must be directly proportional to $1/r_0$.

It has been stated that a diffusion-controlled heterogeneous process is characterised by being slightly dependent on temperature, while the chemically controlled process is strongly dependent on temperature (Habashi, 1999). The reason for this phenomenon can be attributed to linearly dependency of diffusion coefficients and exponentially dependency of chemical velocity constants on temperature. Thus, the activation energy of the diffusion-controlled process is characterised as being 4-12 kJ mol^{-1}, while it is usually over 40 kJ mol^{-1} for a chemically controlled process.

MATERIAL AND METHODS

Material

The sphalerite concentrate, obtained from Menka Mining Corporation-Turkey, was used in the present study. The obtained concentrate was concentrated again by flotation method in order to remove $CuFeS_2$ and PbS, which exist in small amounts in concentrate. Cu^{2+} and Pb^{2+} ions have catalytic effect in ZnS in oxidative ammonia leaching conditions (Nelen and Sobol, 1959; Majima and Peters, 1966; Umetsu et al., 1967; Rao and Ray, 1998; Ghosh et al., 2002; Babu et al., 2002; Evans and Mackiw, 1964; Stanzyk and Rampacek, 1966; Tozawa et al., 1976; Rao et al.,1992; Ghosh et al., 1989). The enhanced concentrate used in the experiments was wet-sieved to -106 +75, -75 +63, -63 +45 and -45 +38 µm particle size fractions. The composition of the concentrate for the each size fraction is given in Table 1.

Experimental Procedure

Leaching experiments were carried out in 1-2 litre capacity stainless steel autoclave, manufactured by the Paar Instrument. Temperature was controlled within ±2 °C by a temperature control system, manipulating both an electrical heating mantle and a water-cooling stream. For each run, 1000 ml of aqueous ammonia solution of predetermined molarity along with ammonium sulfate was charged into reactor and 10 g sphalerite concentrate was added into it, and the reactor closed properly. First, the reactor was heated to the desired temperature under nitrogen pressure with mild agitation and the set temperature was reached. Oxygen was introduced and full agitation was applied and the reached time counts from this point. The required volume of leach liqueur sample was acidified, diluted, and analysed for Zn by Vista AX CCD model ICP-AES.

Standard experimental conditions were: stirrer speed 700 rpm, slurry density 1%, particle size -45 +38 µm, 120 °C, 2 atm P_{O_2} , pH 10.80, $[NH_3]$ 3.0 M, and 4 h leaching time. In order to keep the pH of the solution constant, ammonium sulphate was also added during leaching because of its buffering action.

Table 1. Chemical analysis of Zinc concentrate, % wt.

Tablo 1. *Çinko konsantresinin kimyasal analizi, ağırlıkça %.*

Particle Size (µm)	Zn (%)	Cu (%)	S (%)	Fe (%)
-106 +75	65.17	0.01	32.11	0.02
-75 +63	65.04	0.03	32.05	0.06
-63 +45	65.73	-	32.38	-
-45 +38	66.08	-	32.55	-

Results and Discussion

Effect of NH_3 Concentration

Total ammonia concentration was varied from 1.05 to 5.20 M by keeping the solution at a pH of 10.80 through the ratio of $[NH_3]/[(NH_4)_2SO_4$. The results of Zn extraction versus time plots are given in Figure 1. As seen from Figure 1, Zn extraction increased with increasing NH_3 concentration in the range of 1.05 to 5.20 M.

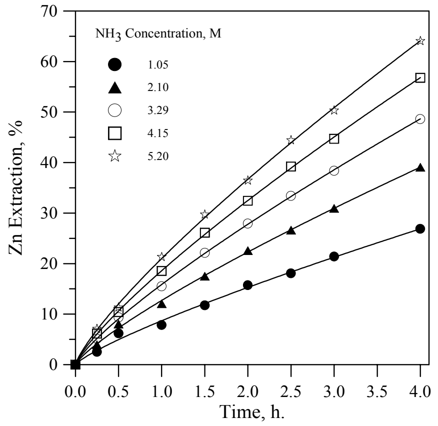

Figure 1. Effect of NH$_3$ concentration on Zn extraction (Conditions: Temperature 120 °C, P_{O_2} 2 atm., particle size –45 +38 µm, pH 10.80).

Şekil 1. *Çinko ekstraksiyonuna NH$_3$ konsantrasyonunun etkisi (Şartlar: Sıcaklık 120 °C, P_{O_2} 2 atm., tane iriliği –45 +38 µm, pH 10.80).*

Application of Eq. (3) to the experimental data obtained at different NH$_3$ concentrations resulted in linear plots as shown in Fig. 2.

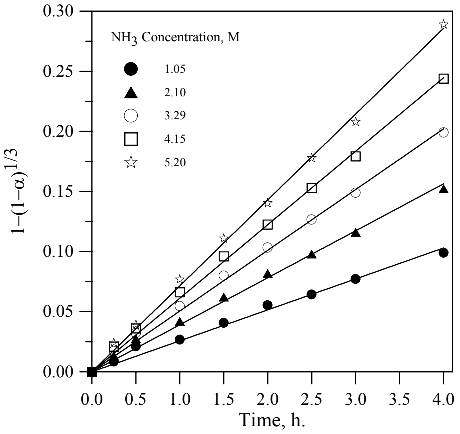

Figure 2. Plot of 1-(1-α)$^{1/3}$ against time for various NH$_3$ concentration (Conditions as Fig. 1).

Şekil 2. *Farklı NH$_3$ konsantrasyonları için zamana karşı 1-(1-α)$^{1/3}$ grafiği (Şartlar: Şekil 1'deki gibi).*

Fig. 2 shows the linear kinetics plot of 1-(1-α)$^{1/3}$ versus time at various NH$_3$ concentrations. From the slopes of the plots, apparent rate constant (k_r) values were determined. The apparent rate constant and the correlation coefficients are given in Table 2.

The natural logarithm (ln) of k_r vs [NH$_3$] plot (see Fig. 3) is constructed to determine the order of dependency with respect to NH$_3$ concentration. Reaction order with respect to ammonia concentration is 0.63.

Table 2. The k_r values and correlation coefficients for each NH$_3$ concentration.

Tablo 2. *Her NH$_3$ konsantrasyonu için k_r değerleri ve korelasyon katsayıları.*

NH$_3$ Concentration, M	Apparent rate constant, k_r (10^{-3} h^{-1})	Correlation Coefficient, (R^2)
1.0	25.749	0.996
2.0	39.094	0.998
3.0	50.529	0.999
4.0	61.158	0.999
5.0	71.460	0.999

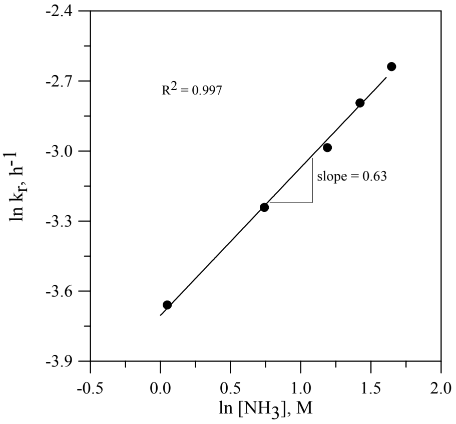

Figure 3. Plot of lnk_r versus ln[NH$_3$] for the estimation of reaction order.

Şekil 3. *Reaksiyon derecesinin tahmini için ln[NH$_3$]'e karşı lnk_r grafiği.*

Effect of Oxygen Partial Pressure

Oxygen partial pressure was varied from 1.0 to 10 atm. The results obtained Zn extraction versus time plots are given in Fig. 4. As seen from Fig. 4, increasing the oxygen partial pressure increases the Zn extraction in the range of 1 to 10 atm. Figure 5 shows the linear kinetics plots for apparent rate constant (k_r) values. From slopes in Fig. 5 k_r values were determined, and lnk_r versus ln(P_{O_2}) plot (Fig. 6) is constructed to determine the order of dependency with respect to oxygen partial pressure.

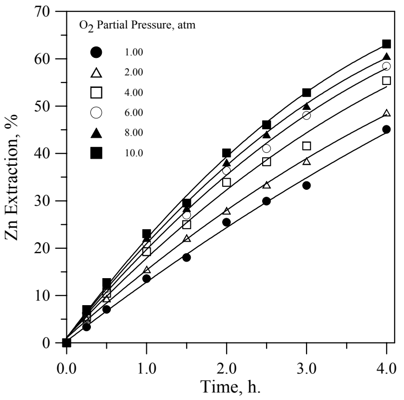

Figure 4. Effect of oxygen partial pressure on Zn extraction (Conditions: Temperature 120 °C, $[NH_3]$ 3.0 M, particle size –45 +38 µm, and pH 10.80).

Şekil 4. *Zn ekstraksiyonuna oksijen kısmi basıncının etkisi (Şartlar: Sıcaklık 120 °C, $[NH_3]$ 3.0 M, tane iriliği –45 +38 µm, pH 10.80).*

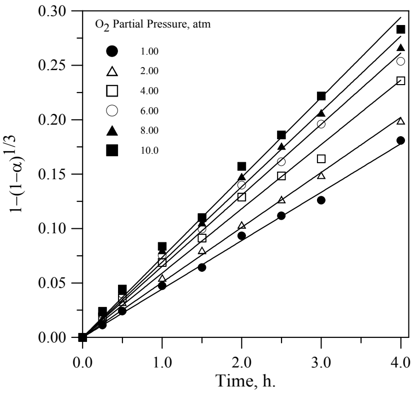

Figure 5. Plot of $1-(1-\alpha)^{1/3}$ against time oxygen partial pressure (Conditions as Fig. 4).

Şekil 5. *Farklı oksijen kısmi basınçları için zamana karşı $1-(1-\alpha)^{1/3}$ grafiği (Şartlar: Şekil 4'deki gibi).*

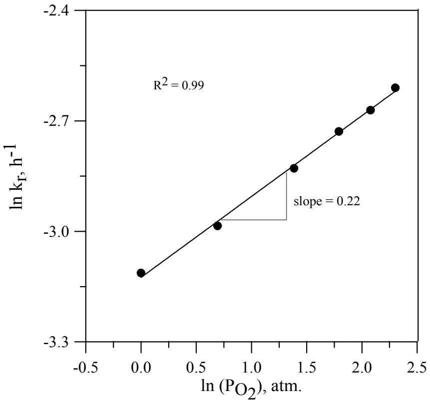

Figure 6. Plot of lnk_r versus ln(P_{O_2}) for the estimation of reaction order.

Şekil 6. *Reaksiyon derecesinin tahmini için ln(P_{O_2})'e karşı lnk_r grafiği.*

The k_r values and the regression coefficient for various oxygen partial pressures were given in Table 3. Reaction order with respect to oxygen pressure is 0.22.

Table 3. The k_r values and correlation coefficients for each oxygen partial pressure.

Tablo 3. *Her P_{O_2} için k_r değerleri ve korelasyon katsayıları.*

O_2 partial pressure, Atm	Apparent rate constant, k_r (10^{-3} h^{-1})	Correlation Coefficient, (R^2)
1.0	44.457	0.999
2.0	50.529	0.999
4.0	59.072	0.997
6.0	65.296	0.998
8.0	69.185	0.998
10.0	73.516	0.998

Effect of Temperature

The effect of temperature on the Zn extractions is shown in Fig. 7. As seen from Fig. 7, the leaching rate was very sensitive to temperature. By increasing the temperature from 90 to 130 °C the Zn extraction increased from 15.68% to 54.88% after 4 hour.

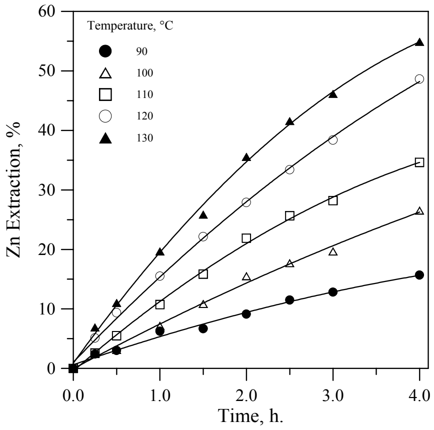

Figure 7. Effect of temperature on Zn extraction (Conditions: $[NH_3]$ 3.0 M, P_{O_2} 2 atm, particle size –45 +38 µm, and pH 10.80).

Şekil 7. *Zn ekstraksiyonuna sıcaklığın etkisi (Şartlar: $[NH_3]$3.0 M, P_{O_2} 2 atm, tane iriliği –45 +38 µm, pH 10.80).*

Application of Eq. (3) to the experimental data obtained at different temperatures resulted in linear plots as shown in Fig. 8. The k_r values and correlation coefficient obtained for various temperatures are given in Table 4. Plotting the natural logarithm of k_r versus the inverse absolute temperature gives an Arrhenius plot, the slope of that represents $-E_a/R$, where E_a is the apparent activation energy of sphalerite oxidation and R is the gas constant.

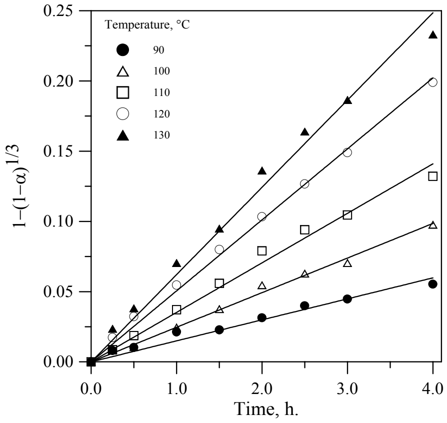

Figure 8. Plot of $1-(1-\alpha)^{1/3}$ again time oxygen partial pressure (Conditions as Fig. 7).

Şekil 8. *Farklı sıcaklıklar için zamana karşı* $1-(1-\alpha)^{1/3}$ *grafiği (Şartlar: Şekil 7'deki gibi).*

Table 4. The k_r values and correlation coefficients for each temperature.

Tablo 4. *Her sıcaklık için* k_r *değerleri ve korelasyon katsayıları.*

Temperature, °C	Apparent rate Constant, k_r (10^{-3} h^{-1})	Correlation coefficient (R^2)
90	14.946	0.989
100	24.622	0.998
110	35.231	0.996
120	50.529	0.999
130	62.118	0.996

The Arrhenius plot is given in Fig. 9 and the calculated apparent activation energy value was 43.59 kj/mol which supports the view that leaching reaction is controlled by chemical reaction at the particle surface.

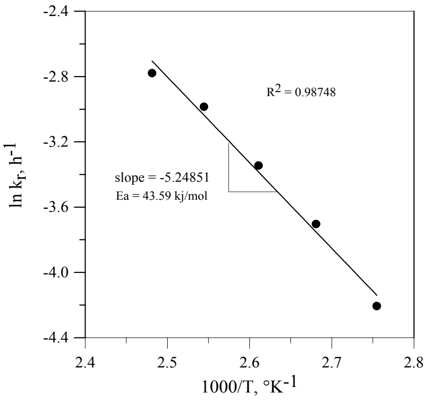

Figure 9. Arrhenius plot for sphalerite oxidation.

Şekil 9. *Sfalerit oksidasyonu için Arrhenius grafiği*

Effect of Particle Size

The kinetics of leaching was studied at varying particle size (from 106 µm to 38 µm). The effect of particle size on the Zn extraction is shown in Fig. 10. The rate of Zn extraction increased with decreasing particle size. The apparent rate constants were also determined and these showed an increasing trend with the decreasing particle sizes. Thus k_r were found to be 0.0242, 0.0369, 0.0395 and 0.0505 h^{-1} for the particle sizes -106 +75, -75 +63, -63 +45 and -45 +38 µm, respectively. As expected, the increase in rate constant values with the decrease in particle size of concentrate is due to higher surface energy thereby enhancing the rate of reaction.

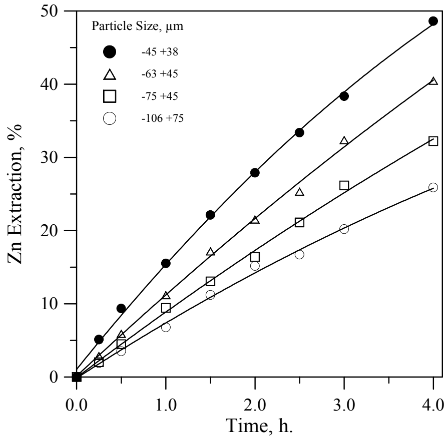

Figure 10. Effect of particle size on Zn extraction (Conditions: Temperature 120 °C, [NH_3] 3.0 M, P_{O_2} 2 atm, and pH 10.80).

Şekil 10. *Zn ekstraksiyonuna tane iriliğinin etkisi (Şartlar: Sıcaklık 120 °C, [*NH_3*]3.0 M,* P_{O_2} *2 atm, pH 10.80).*

Linear relation between the k_r values and the reciprocal of mean particle radius $1/r_0$ is shown in Fig 11. This relation is predicted by the shrinking core model for a reaction controlled process.

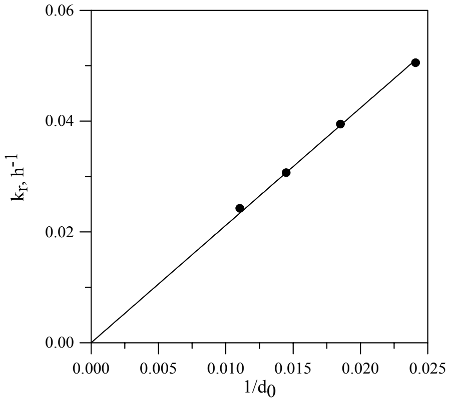

Figure 11. Plot of rate constant versus inverse of particle radius in support of surface reaction control.

Şekil 11. *Yüzey reaksiyon kontrolü desteğinde tane yarıçapının tersine karşı hız sabitinin grafiği.*

CONCLUSIONS

Oxidative ammonia leaching of sphalerite concentrate has been investigated. This study has been concerned with the kinetic model of sphalerite leaching in ammonia solution, assessing the effect of NH_3 concentration, oxygen partial pressure, reaction temperature and particle size. It was determined that the leaching rate increased with increasing NH_3 concentration, oxygen partial pressure and temperature and decreasing with particle size. The apparent activation energy was calculated as 43.53 kj/mol for the sphalerite concentrate in the temperature range of 90-130 °C. The empirical orders of reaction with respect to NH_3 concentration and O_2 partial pressure are 0.63 and 0.22, respectively. The kinetic studies showed that the leaching of sphalerite by shrinking core model and the leaching rate controlled by surface reaction under the studied conditions.

REFERENCES

Ablanov, A.D., Kabanova, L.M., Tkachenko, O.B. and Ermilov, V.V., 1960, *Tr. Inst. Met. Obogashch. Akad. Nauk. Kazakh. S.S.R.*, 90–104.

Akçıl, A. and Çiftçi, H., 2002, A study of the selective leaching of complex sulphides from the Eastern Black Sea Region; Turkey, Miner. Eng., **15**, 457–459.

Aras, A., Aydogan, S., Özkan, A. and Canbazoglu, M., 2003, Determination of leaching conditions of sphalerite concentrate in acidic ferric chloride solution; 18th Int. Mining Congress & Exhibition of Turkey-IMCET, 495-500.

Babu, M.N., Sahu, K.K. and Pandey, B.D., 2002, Zinc recovery from sphalerite concentrate by direct oxidative leaching with ammonium, sodium and potassium persulphates; Hydrometallurgy, **64**, 119–129.

Bobeck, G.E. and Su, H., 1985, The kinetics of dissolution of sphalerite in ferric chloride solution, Metall. Trans., **16,** B, 413-424.

Canbazoğlu, M. and Özkol, S., 1980, Leaching of Cayeli complex sulphide ore by HCl + $MgCl_2$ solution: recovery of Pb, Zn and $CuFeS_2$ concentrates, Complex Sulphide Ores Conference, Rome, Italy, 7-11.

Çopur, M., 2001, Solubility of ZnS concentrate containing pyrite and chalcopyrite in HNO_3 solutions, Chem. Biochem. Eng. Q., **15**, 4, 181-184.

Crundwell, F.K., 1987, Refractory behaviour of two sphalerite concentrates to dissolution in ferric sulphate solutions, Hydrometallurgy, **19**, 253–258.

Demopoulos, G.P. and Baldwin, S.A., 1999, Stoichiometric and kinetic aspects on the pressure leaching of zinc concentrates, In:Mishra, B.(Ed); TMS Annual Meeting, San Diego, 567-583.

Dutrizac, J.E. and MacDonald, R.J.C., 1974, Ferric ion as a leaching medium, Minerals Sci. Eng., **6**, 2, 59-100.

Dutrizac, J.E. and MacDonald, R.J.C., 1978, The dissolution of sphalerite in ferric chloride solutions, Metall. Trans., **9**, B, 543-551.

Evans, D.J.I. and Mackiw, S., 1964, Treatment of copper-zinc concentrates by pressure hydrometallurgy, Can. Min. Metall. Bull., **57**, 857-866.

Ghosh, M.K., Anand, S., Das, R.P., 1989, Effect of dissolved impurities during ammonia leaching of pure zinc sulphide, Hydrometallurgy, **21**, 207-221.

Ghosh, M.K., Das, R.P. and Biswas, A.K., 2002, Oxidative ammonia leaching of sphalerite 1: Noncatalytic kinetics, Int. J. Miner. Process., **66**, 241-254.

Habashi, F., 1980, Principles of Extractive Metallurgy; 2nd Ed., Gordon and Breach Science Publ., New York.

Habashi, F., 1999, Kinetics of Metallurgical Processes; 2nd Ed. Metallurgie Extractive Quebec, Quebec, Canada.

Levenspiel, O., 1972, Chemical Reaction Engineering; 2nd Ed., Wiley, New York, NY.

Majima, H. and Peters, E., 1966, Aqueous oxidation at elevated temperatures, Trans. Metall. Soc. AIME, ***236***, 1409-1413.

Majima, H., Awakura, Y. and Misaki, N., 1981, A kinetic study on nonoxidative dissolution of sphalerite in aqueous hydrochloric acid solutions, Metall. Trans., **12**, B, 645-649.

Mizoguchi, T. and Habashi, F., 1981, The aqueous oxidation of complex sulfide concentrates in hydrochloric acid, Int. J. Miner. Process., **8**, 177-193.

Nelen, I.M. and Sobol, S.I., 1959, Kinetics of the oxidation of sphalerite under conditions of ammonia leaching under pressure of sulphide concentrate, Sb. Tr., Gos. Nauchno-Issled. Inst. Tsvetn. Met. 15, 447- 475.

Parker, E.G., 1961, Oxidative pressure leaching of zinc concentrate, CIM Bull., **74,** 5, 145-150.

Perez, I.P. and Dutrizac, J.E, 1991, The effect of the iron content of sphalerite on its rate of dissolution in ferric sulphate and ferric chloride media, Hydrometallurgy, **26**, 211–232.

Rao, K.S., Paramguru, R.K., Das, R.P. and Ray, H.S., 1992, The role of galvanic interaction during ammonia leaching of multimetal sulphides, Miner Proces. Extr. M., **11**, 21-37.

Rao, K.S. and Ray, H.S., 1998, A new look at characterisation and oxidative ammonia leaching behaviour of multimetal sulphides, Miner. Eng., **11**, 11, 1011-1024.

Stanzyk, M.H. and Rampacek, C., 1966, Oxidation leaching of copper sulfides in ammoniacal pulps at elevated temperature and pressures, US. Bur. Mines, R.I. No. 6808.

Tozawa, K., Umetsu, Y. and Sato, K., 1976, Extractive Metallurgy of Copper-Vol II. Edt. Yannopoulos, J.C. and Agarwal, J.C., Met. Soc. AIME, 705-721.

Umetsu, Y., Tozawa, K. and Sasaki, K.J., 1967, Ammonia pressure leaching of complex copper/zinc sulphide concentrate, Nippon Kagaku Kaishi, **83**, 8, 1016-1022.

Warren, G.W., Kim, S.H. and Henein, H., 1987, The effect of chloride ion on the ferric chloride leaching of galena concentrate, Metall. Trans,. **18**, B, 59-69.