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DISSOLUTION KINETICS OF NICKEL FROM GÖRDES (MANİSA-TURKEY) LATERITIC ORE BY SULPHURIC ACID LEACHING UNDER EFFECT OF SODIUM FLUORIDE

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ABSTRACT: In this study, dissolution kinetics of nickel from Gördes (Manisa-Turkey) lateritic ore by sodium fluoride in sulphuric acid solution was investigated. The effects of stirring speed, sulphuric acid concentration, sodium fluoride concentration and temperature on nickel extraction were examined. To determine the dissolution kinetics of nickel in sulphuric acid medium under effect of sodium fluoride, shrinking core model was applied to dissolution recoveries. As a result of kinetic studies, it was determined that mixed kinetic model was appropriate. The activation energy (E_a) for the dissolution was calculated as 41.24 kJ/mol.

Key Words: Dissolution kinetics, Lateritic ore, Nickel, Sulphuric acid, Sodium fluoride, Activation energy

Sodyum Florür Etkisinde Sülfürik Asit Liçi ile Gördes (Manisa-Türkiye) Lateritik Cevherinden Nikelin Çözünme Kinetiği

ÖZ: Bu çalışmada, sodyum florür içeren sülfürik asit çözeltisinde Gördes (Manisa-Türkiye) lateritik cevherinden nikelin çözünme kinetiği araştırılmıştır. Karıştırma hızı, sülfürik asit ve sodyum florür derişimi ve sıcaklığın nikelin çözünmesine olan etkileri incelenmiştir. Sodyum florür etkisinde sülfürik asit ortamında nikelin çözünme kinetiğini belirlemek için elde edilen çözünme verimlerine küçülen çekirdek modeli uygulanmıştır. Kinetik çalışmalar sonucunda karışık modelin uygun olduğu belirlenmiştir. Nikelin çözünmesi için aktivasyon enerjisi 41.24 kJ/mol olarak hesaplanmıştır.

Anahtar Kelimeler: Çözünme kinetiği, Lateritik cevher, Nikel, Sülfürik asit, Sodyum florür, Aktivasyon enerjisi

INTRODUCTION

It is known that nickel was used in the production of coins at thousands of years ago. However, the use of nickel in the metal industry is based on two centuries ago. Nickel was discovered and isolated as an element by the Swedish scientist Axel Cronstedt in 1751 (Kamberović et al., 2014; Rezende, 2006).

Owing to its some properties, such as corrosion resistance, alloying, electrical, thermal and catalyst properties, nickel is used as an important metal in producing of stainless steel and super alloys. Laterites are oxide ores widely distributed in the equatorial regions. Lateritic nickel deposits occur during laterization, namely, a weathering process of ultramafic rocks containing minerals such as olivine, pyroxene and amphibole (Golightly, 1981). Ni-laterites can be classified in three main groups as oxide, hydrous silicate and clay silicate deposits (Golightly, 1981; Gleeson, *et al.*, 2003; Brand *et al.*, 1998; Sagapoa *et al.*, 2011; Georgiou and Papangelakis, 1998). It is known that nickel laterites are approximately composed 70 % of the world nickel reserves. However, about 40 % of world's nickel

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production is provided from lateritic ores (Dalvi *et al.*, 2004, Soler *et al.*, 2008). The production of nickel from lateritic ores includes pyrometallurgical and hydrometallurgical processes (Deepatana *et al.*, 2006). Pyrometallurgical and hydrometallurgical processes are given in Figure 1 for the recovery of nickel and cobalt from the lateritic nickel ores.



Figure 1. Pyrometallurgical and hydrometallurgical processes for lateritic nickel ore (Dalvi *et al.,* 2004).

In the literature, there are several studies related to lateritic nickel leaching in different solutions using high pressure or atmospheric pressure (agitation or heap leaching). The solutions used in these studies can be given as sulphuric acid (Georgiou and Papangelakis, 1998; Agacayak and Zedef, 2012; Luo *et al.*, 2010; Stopic *et al.*, 2002; Ayanda *et al.*, 2011; Rubisov *et al.*, 2000; Agatzini-Leonardou and Zafiratos, 2004; McDonald and Whittington, 2008a; Mohammadreza *et al.*, 2014), hydrochloric acid (Ayanda *et al.*, 2011; Park and Nam, 2008; Agacayak *et al.*, 2011; Guo *et al.*, 2015; McDonald and Whittington, 2008b; Li *et al.*, 2012), nitric acid (Agacayak *et al.*, 2011; Guo *et al.*, 2011; Ma *et al.*, 2013), ammonia (Zhai *et al.*, 2010; Chen *et al.*, 2010; Zuniga *et al.*, 2010), citric acid, oxalic acid and acetic acid (Sahu *et al.*, 2011; Behera *et al.*, 2010; Sukla and Panchanadikar, 1993; Kursunoglu and Kaya, 2015). In the present work, to investigate the effects of parameters such as stirring speed, sulphuric acid concentration, sodium fluoride concentration and temperature on the leaching of nickel from a limonitic laterite ore and to describe dissolution kinetics of nickel was aimed.

MATERIAL AND METHOD

The lateritic nickel ore used in this study was obtained from Manisa (Gördes) region in Turkey. The sample was ground and wet sieved into three particle size fractions (-150+106, -106+75 and -75+53 μ m) for the experiments. Nickel and iron contents of each size fraction were given in Table 1.

Particle size,	Ni %	Fe %
μm		
-150+106	1.02	37.03
-106+75	1.00	36.40
-75+53	1.01	38.25

Table 1. Nickel and iron contents of each size fraction.

An XRD analysis was carried out to find the mineralogic composition of the laterite ore. The main minerals were determined as goethite, hematite and quartz. XRD pattern of the sample was given in Figure 2.



Figure 2. XRD pattern of the sample.

The nickel leaching experiments were conducted in a 1000 mL vessel in a thermostatically-controlled water bath using 5/500 g/mL solid-liquid ratio. Since Ni and Fe contents of each size fraction of the lateritic ore were almost same, -150+106 μ m particle size fraction was used in the experiments. The leach solution was stirred by Heidolph brand RZR 2021 model mechanical stirrer with teflon lined impeller. Amount of the nickel in the solution was measured using flame atomic absorption spectrophotometer.

RESULT AND DISCUSSION

Effect of Parameters

The effect of variables such as stirring speed, sulphuric acid concentration, sodium fluoride concentration and leaching temperature on Ni extraction was investigated. The effect of stirring speed on the nickel extraction from lateritic nickel ore was investigated in 0.5 M H₂SO₄+0.3 M NaF solution at 50 °C in the range of 0–600 rpm stirring speed for 180 min. The experimental results were shown in Figure 3a. It was observed that the dissolution increased as the stirring speed increased. Therefore, 600 rpm was selected as optimum stirring speed to investigate the effect of other parameters on dissolution of nickel. To determine effect of the sulphuric acid concentration, leaching experiments were done using different sulphuric acid concentrations under effect of 0.3 M sodium fluoride at 50 °C. The experimental data were presented in Figure 3b. As shown from Figure 3b, nickel extraction increases with increasing leaching time and sulphuric acid concentration. To determine effect of sodium fluoride concentration, leaching experiments were carried out using different sodium fluoride concentrations at 50 °C in 0.5 M H₂SO₄. Figure 3c shows the effect of sodium fluoride concentration on the nickel dissolution. As shown from Figure 3c, nickel extraction increases with increasing sodium fluoride concentration. Thus, it can be concluded that some of nickel in the lateritic ore could be in silicate structure. Harouiya and Oelkers (2004) and Mitra and Rimstidt (2009) reported dissolution of quartz in fluoride solutions. Lateritic nickel ore was leached at different temperatures (40–80 °C). The obtained results were presented in Figure 3d.





Figure 3. Effects of parameters on the nickel extraction

Kinetic Models and Determination of Activation Energy

The kinetic of dissolution reactions is often described by the shrinking core model. According to the shrinking core model, it is thought that the reaction between solid and fluid reactants takes place on the outer surface of solid (Levenspiel, 1999).

$$aA_{\text{fluid}} + bB_{\text{particle}} \rightarrow \text{Product}$$
 (1)

Therefore, chemical reaction model, diffusion model and combination of both chemical control and diffusion model (mixed model) were investigated in this work. The dissolution of Ni from the lateritic nickel ore can be explained by a shrinking core model which can be expressed as follows (Habashi 1969; Levenspiel, 1999; Ekmekyapar *et al.*, 2003):

if the reaction is controlled by surface reaction,

$$1-(1-\alpha)^{1/3} = k_s t$$
 (2) if the reaction is controlled by film diffusion,

$$1 - (1 - \alpha)^{2/3} = k_f t$$
 (3)

if the reaction is controlled by diffusion from product layer

$$1-2/3\alpha - (1-\alpha)^{2/3} = k_d t$$
 (4)

if the reaction is controlled by combination of both chemical and diffusion

$$1-2(1-\alpha)^{1/3}+(1-\alpha)^{2/3}=k_{\rm m}t\tag{5}$$

where α is the fraction reacted, *t* is the reaction time, k_s, k_f, k_d and k_m are the rate constants. In this study, shrinking core model was applied to the dissolution recoveries obtained at different temperatures. Plots of the shrinking core model for various temperatures of Ni extraction were given in Figure 4.



Figure 4. Plots of the shrinking core model vs leaching time for different temperatures.

Apparent rate constants (*k*) at different temperatures were obtained from the slope of the linear plots in Figure 4 for nickel. The correlation coefficients and apparent rate constants for each temperature were given in Table 2.

	Surface Reaction $1-(1-\alpha)^{1/3}$		Film Diffusion 1-(1- α) ^{2/3}	•
Temperature °C				
	Apparent rate	Correlation	Apparent rate	Correlation
	constant (k_s) x10 ⁻³	coefficient,	constant (k_s) x10 ⁻³	coefficient,
		(R ²)		(R ²)
40	0.49521	0.94	0.91549	0.94
50	0.88494	0.99	1.49352	0.98
60	1.21441	0.91	1.97425	0.89
70	1.01943	0.80	1.59097	0.78
80	0.98306	0.86	1.43322	0.84
	Diffusion from		Mixed Model	
	Product Layer		$1-2(1-\alpha)^{1/3}+(1-\alpha)^{2/3}$	
Temperature °C	$1-2/3\alpha - (1-\alpha)^{2/3}$			
	Apparent rate	Correlation	Apparent rate	Correlation
	constant (k_s) x10 ⁻³	coefficient,	constant $(k_s)x10^{-3}$	coefficient,
		(R ²)		(R ²)
40	0.20633	0.99	0.07493	0.99
50	0.69124	0.99	0.27635	0.99
60	1.08712	0.97	0.45456	0.98
70	1.03451	0.84	0.44789	0.86
80	1.15299	0.90	0.53290	0.92

Table 2. Values of *k*_s, *k*_f, *k*_d, *k*_m and correlation coefficients for different temperatures.

These results indicate that the dissolution of nickel is combination of both chemical and diffusion controll. The application of the mixed model is shown in Figure 4d. Equation [5] is applied to the data obtained at each temperature to determine the rate constants used in the Arrhenius plot (Figure 5). The activation energy was calculated as 41.24 kJ/mol. The dissolution of nickel from lateritic ore in sulphuric acid solution was reported to be controlled by chemical or diffusion from product layer by different authors. In these studies, activation energies were given as 53.9 kJ/mol (Luo *et al.*, 2010), 68.66 kJ/mol (Agacayak and Zedef, 2012), 60.00 kJ/mol (Stopic *et al.*, 2002) and 67.53 kJ/mol (Ayanda *et al.*, 2011).



Figure 5. Arrhenius plot of data presented in Fig. 4d.

CONCLUSION

The contents of the lateritic nickel ore and dissolution kinetics results of nickel from the lateritic nickel ore were given as follows: The nickel and iron contents of the ore used in the experiments were determined as 1.02% and 37.03%, respectively. According to XRD results, the main minerals were determined as goethite, hematite and quartz. Dissolution kinetics of nickel from Gördes (Manisa-Turkey) lateritic ore using sodium fluoride in sulphuric acid solution was investigated. Experimental parameters used were stirring speed (0–600 rpm), temperature (40–80 °C), sulphuric acid concentration (0.1–0.5 mol/L), sodium fluoride concentration (0–0.5 mol/L) and particle size (-150+106 μ m). It was found that the dissolution rate increased with an increase in the leaching temperature, stirring speed, sulphuric acid and sodium fluoride concentration. In order to determine the dissolution kinetics of Ni, shrinking core model was applied to dissolution recoveries obtained at different temperatures. It was determined that, nickel dissolved in sulphuric acid solution under effect of sodium fluoride from the lateritic nickel ore by combination of both chemical and diffusion control (mixed model). Activation energy (E_a) was calculated for Ni as 41.24 kJ/mol.

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