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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.

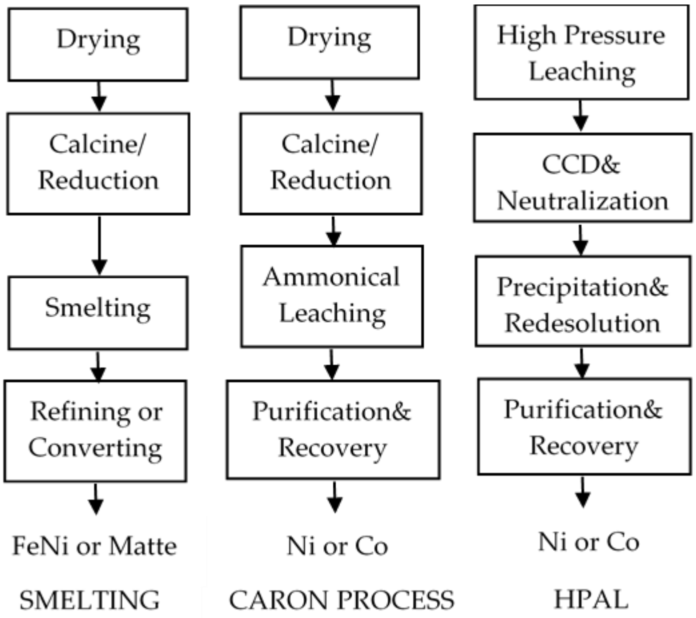

Figure 1. Pyrometallurgical and hydrometallurgical processes for lateritic nickel ore (Dalvi *et al*., 2004).

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 and Zedef, 2013; Ayanda *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 μm) for the experiments. Nickel and iron contents of each size fraction were given in Table 1.

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

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

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.

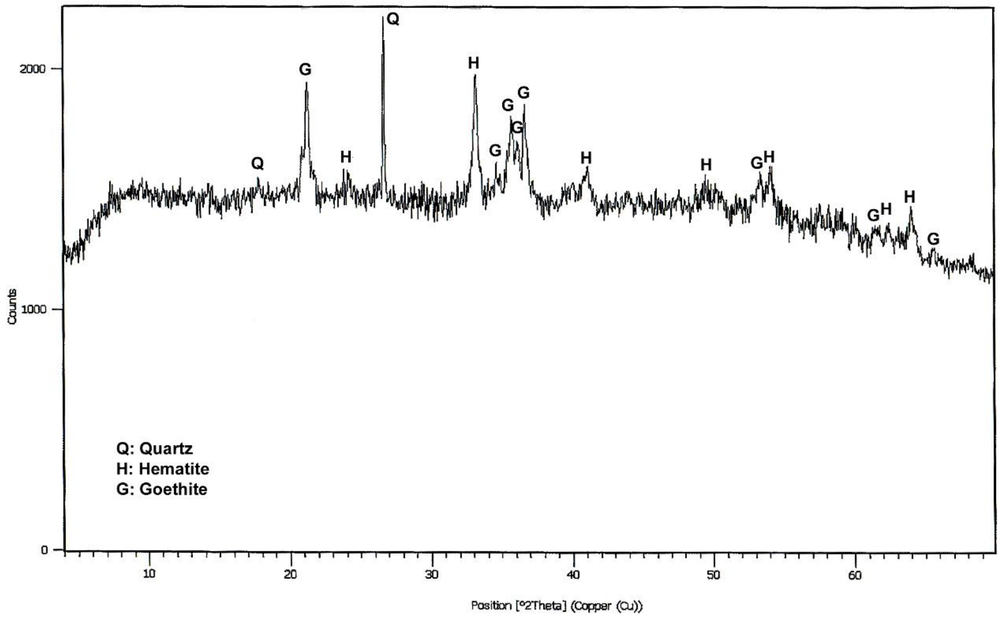

Figure 2. XRD pattern of the sample.

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 μm 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 H_2SO_4+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 H_2SO_4. 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.

The nickel extraction recovery increased for 3 hours of leaching time from 30.89% to 72.63% for 40 °C and 80 °C, respectively.

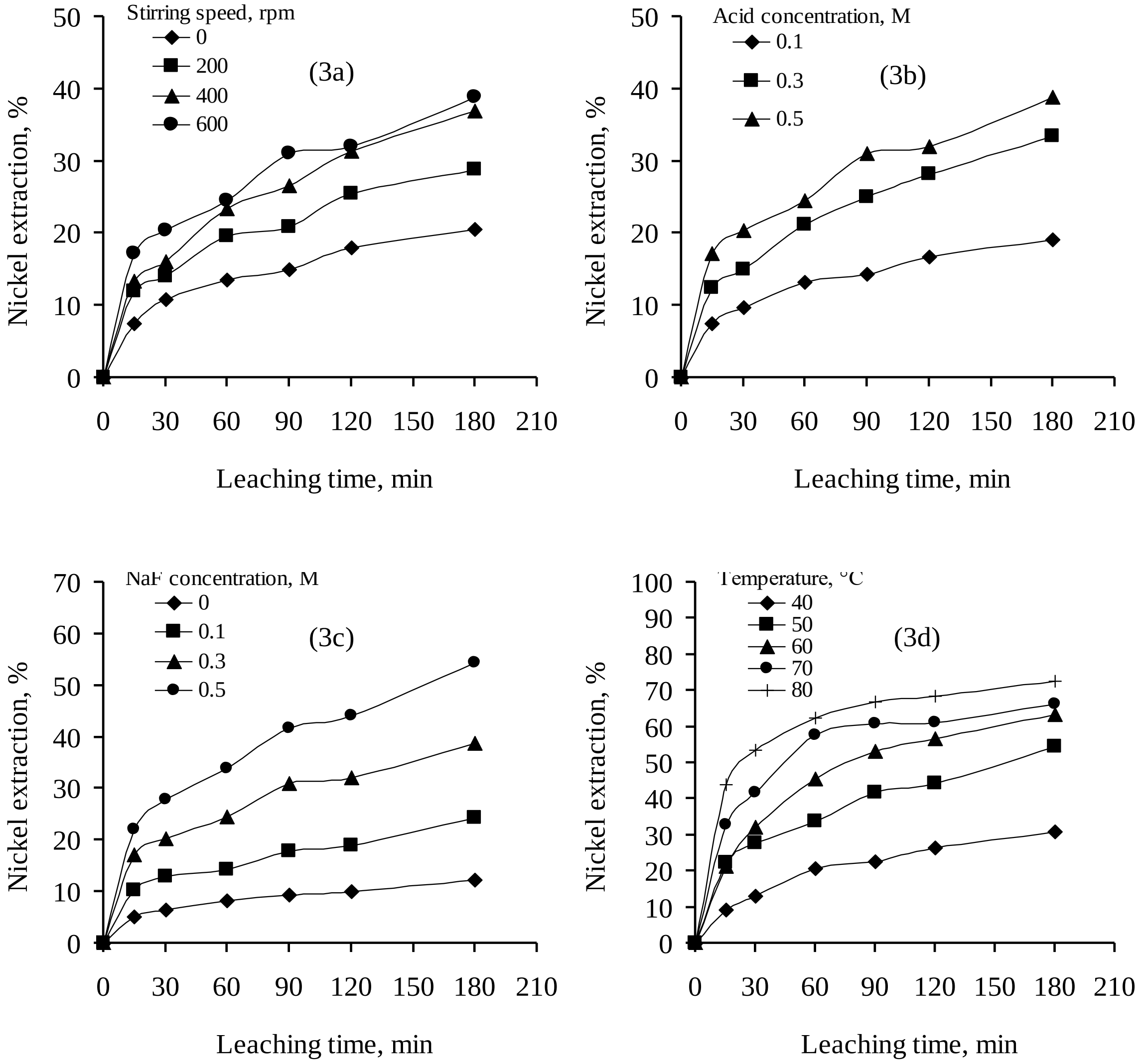

Figure 3. Effects of parameters on the nickel extraction

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).

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

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,

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

if the reaction is controlled by film diffusion,

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

if the reaction is controlled by diffusion from product layer

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

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

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

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.

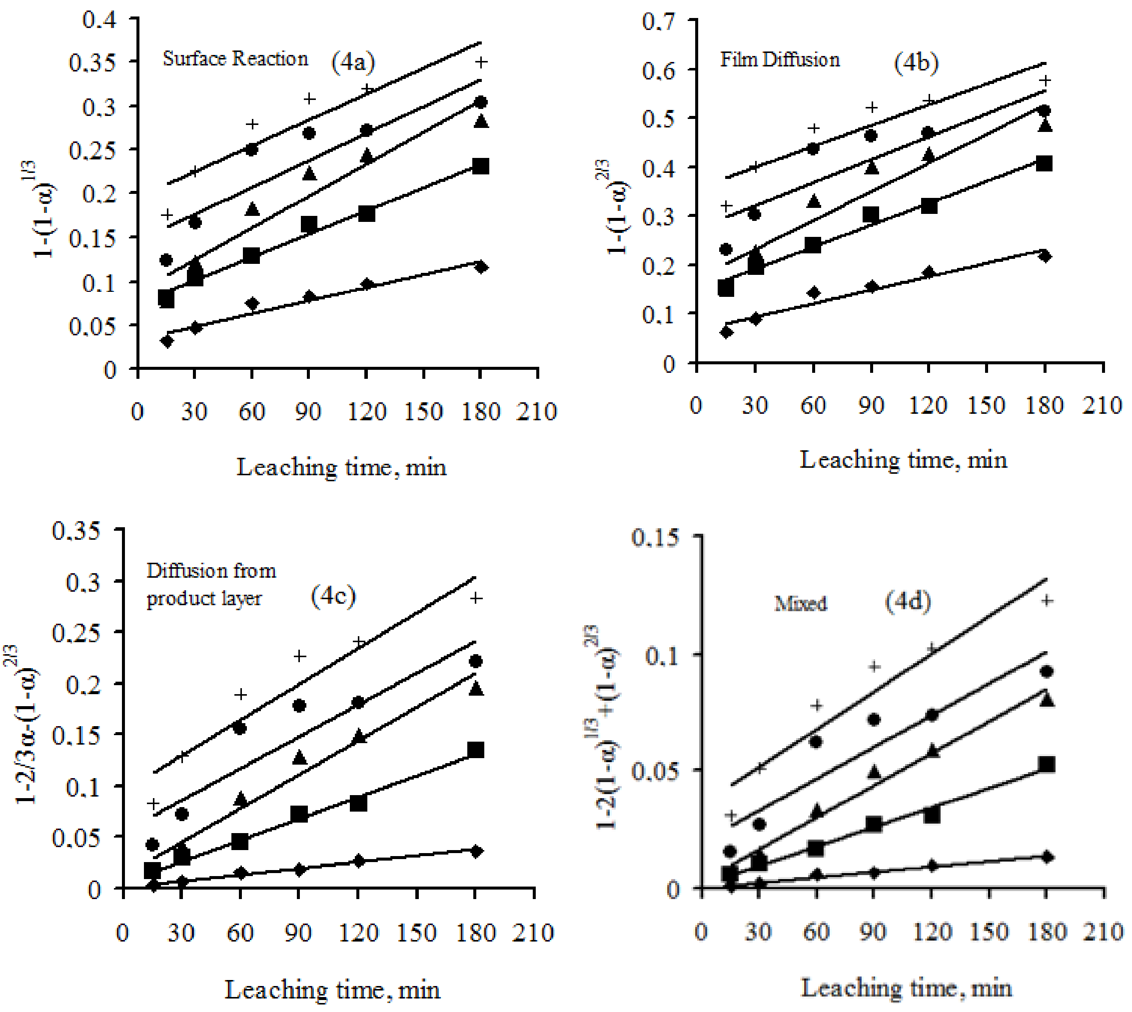

Figure 4. Plots of the shrinking core model vs leaching time for different temperatures.

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.

Table 2. Values of k_s, k_f, k_d, k_m and correlation coefficients for different temperatures.

Temperature °C	Surface Reaction $1-(1-\alpha)^{1/3}$		Film Diffusion $1-(1-\alpha)^{2/3}$	
	Apparent rate constant (k_s)x10^{-3}	Correlation coefficient, (R^2)	Apparent rate constant (k_s)x10^{-3}	Correlation coefficient, (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
Temperature °C	**Diffusion from Product Layer** $1-2/3\alpha-(1-\alpha)^{2/3}$		**Mixed Model** $1-2(1-\alpha)^{1/3}+(1-\alpha)^{2/3}$	
	Apparent rate constant (k_s)x10^{-3}	**Correlation coefficient, (R^2)**	**Apparent rate constant (k_s)x10^{-3}**	**Correlation coefficient, (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

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).

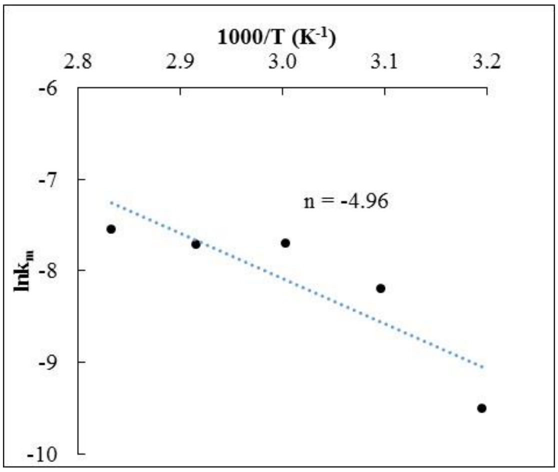

Figure 5. Arrhenius plot of data presented in Fig. 4d.

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 μm). 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.

REFERENCES

Agacayak, T., Zedef, V., Aydogan, S., 2011, "Leaching of Lateritic Nickel Ores of Karacam (Eskisehir-Turkey) with Hydrochloric Acid", 11th International Multidisciplinary Scientific Geo-Conference&EXPO SGEM, Modern Management of Mine Producing, Geology and Environmental Protection, Albena-Varna/Bulgaria. Vol. 1, pp. 1155–1162, 19-25 June 2011.

Agacayak, T., Zedef, V., 2012, "Dissolution Kinetics of a Lateritic Nickel Ore in Sulphuric Acid Medium", Acta Montanistica Slovaca, Vol. 17 (1), pp. 33–41.

Agacayak, T., Zedef, V., 2013, "Leaching of a Turkish Lateritic Nickel Ore in Nitric Acid Solution", Mine Planning and Equipment Selection, Proceedings of the 22nd MPES Conference, Dresden, Germany, 14 – 19 October 2013.

Agatzini-Leonardou, S., Zafiratos, I. G., 2004, "Beneficiation of a Greek Serpentinic Nickeliferous Ore Part II. Sulfuric Acid Heap and Agitation Leaching", Hydrometallurgy, Vol. 74, pp. 267–275.

Ayanda, O. S., Adekola, F. A., Baba, A. A., Fatoki, O. S., Ximba, B. J., 2011, "Comparative Study of the Kinetics of Dissolution of Laterite in Some Acidic Media", J. of Miner. & Mater. Character. & Eng., Vol. 10 (15), pp. 1457–1472.

Behera, S. K., Sukla, L. B., Mishra, B. K., 2010, "Leaching of Nickel Laterite Using Fungus Mediated Organic Acid and Synthetic Organic Acid: A Comparative Study", Proceedings of the XI International Seminar on Mineral Processing Technology, pp. 946–954.

Brand, N. W., Butt, C. R. M., Elias, M., 1998, "Nickel Laterites: Classification and Features", J. of Australian Geo. and Geoph., Vol. 17, pp. 81–88.

Chen, S., Guo, X., Shi, W., Li, D., 2010, "Extraction of Valuable Metals from Low-Grade Nickeliferous Laterite Ore by Reduction Roasting-Ammonia Leaching Method", Journal of Central South University of Technology, Vol. 17(4), pp. 765–769.

Dalvi, A. D., Bacon, W., Osborne, R. C., 2004, "The Past and The Future of Nickel Laterites", PDAC 2004 International Conference Trade Show and Investors Exchange, Toronto, CANADA.

Deepatana, A., Tang, J. A., Valix, M., 2006, "Comparative Study of Chelating Ion Exchange Resins for Metal Recovery from Bioleaching of Nickel Laterite Ores", Minerals Engineering, Vol. 19 (2), pp. 1280–1289.

Ekmekyapar, A., Oya, R., Kunkul, A., 2003, "Dissolution Kinetics of an Oxidized Copper Ore in Ammonium Chloride Solution", Chemical and Biochemical Engineering Quarterly, Vol. 17 (4), pp. 261–266.

Georgiou, D., Papangelakis, G. V., 1998, "Sulphuric Acid Pressure Leaching of a Limonitic Laterite: Chemistry and Kinetics", Hydrometallurgy, Vol. 49, pp. 23–46.

Gleeson, S. A., Butt, C. R. M., Elias, M., 2003, "Nickel Laterites: A Review. SEG Newsletter", Soc. of Econ. Geo., Vol. 54, pp. 12–18.

Golightly, J. P., 1981, "Nickeliferous Laterite Deposits", Economic Geology, Vol. 75 (1), pp. 710–735.

Guo, Q., Qu, J., Han, B., Zhang, P., Song, Y., Qi, T., 2015, "Innovative Technology for Processing Saprolitic Laterite Ores by Hydrochloric Acid Atmospheric Pressure Leaching", Minerals Engineering, Vol. 71, pp. 1–6.

Habashi, F., 1969, Principles of Extractive Metallurgy, New York: Gordon and Breach.

Harouiya, N., Oelkers, E. H., 2004, "An Experimental Study of The Effect of Aqueous Fluoride on Quartz and Alkali-Feldspar Dissolution Rates", Chemical Geology, Vol: 205, pp.155–167.

Kamberović, Ž., Korać, M., Anđić, Z., Uljarević, J., Mihajlović, A., Vučurović, D., 2014, "Technological and Environmental Aspects of Nickel Production in Serbia" Association of Metallurgical Engineers of Serbia, Vol. 20 (4), pp. 275-284.

Kursunoglu, S., Kaya, M., 2015, "Dissolution Behavior of Caldag Lateritic Nickel Ore Subjected to a Sequential Organic Acid Leaching Method", Journal of Minerals, Metallurgy, and Materials, Vol. 22 (11), pp. 1131–1140.

Levenspiel, O., 1999, Chemical reaction engineering, New York:John Wiley & Sons.

Li, J., Xiong, D., Chen, H., Wang, R., Liang, Y., 2012, "Physicochemical Factors Affecting Leaching of Laterite Ore in Hydrochloric Acid", Hydrometallurgy, Vol. 129 (130), pp. 14–18.

Luo, W., Feng, Q., Ou, L., Zhang, G., Chen, Y., 2010, "Kinetics of Saprolitic Laterite Leaching by Sulphuric Acid at Atmospheric Pressure", Minerals Engineering, Vol. 23 (6), pp. 458–462.

Ma, B., Wang, C., Yang, W., Yang, B., Zhang, Y., 2013, "Selective Pressure Leaching of Fe (II)-rich Limonitic Laterite Ores from Indonesia Using Nitric Acid", Minerals Engineering, Vol. 45, pp. 151–158.

McDonald, R. G., Whittington, B. I., 2008a, "Atmospheric Acid Leaching of Nickel Laterites Review (Part I). Sulphuric Acid Technologies", Hydrometallurgy, Vol. 91 (1/4), pp. 35−55.

McDonald, R. G., Whittington, B. I., 2008b, "Atmospheric Acid Leaching of Nickel Laterites Review, Part II. Chloride and Bio-Technologies", Hydrometallurgy, Vol. 91, pp. 56−69.

Mitra., A., Rimstidt, J. D., 2009, "Solubility and Dissolution Rate of Silica in Acid Fluoride Solutions" Geochimica et Cosmochimica Acta, Vol. 73, pp. 7045–7059.

Mohammadreza, F., Mohammad, N., Ziaeddin, S. S., 2014, "Nickel Extraction From Low Grade Laterite by Agitation Leaching at Atmospheric Pressure", International Journal of Mining Science and Technology, Vol. 24 (4), pp. 543–548.

Park, K. H., Nam, C. W., 2008, "Status and Prospect of Nickel Resources and Processing", Trending Metals Mater. Eng., Vol. 21, pp. 1–9.

Rezende, L., 2006, Chronology of Science, Fact on File, Inc., New York.

Rubisov, D. H., Krowinkel, J. M., Papangelakis, V. G., 2000, "Sulphuric Acid Pressure Leaching of Laterites Universal Kinetics of Nickel Dissolution for Limonites and Limonitic/Saprolitic Blends", Hydrometallurgy, Vol. 58 (1), pp. 1−11.

Sagapoa, C. V., Imai, A., Watanabe, K., 2011, "Laterization Process of Ultramafic Rocks in Siruka, Solomon Islands", Journal of Novel Carbon Resource Sciences, Vol. 3, pp. 32–39.

Sahu, S., Kavuri, N. C., Kundu, M., 2011, "Dissolution Kinetics of Nickel Laterite Ore Using Different Secondary Metabolic Acids", Brazilian Journal of Chemical Engineering, Vol. 28 (2), pp. 251−258.

Soler, J. M., Cama, J., Galí, S. Meléndez, W., Ramírez, A., Estanga, J., 2008, "Composition and Dissolution Kinetics of Garnierite from The Loma De Hierro Ni-Laterite Deposit, Venezuela", Chemical Geology, Vol. 249 (1/2), pp. 191−202.

Stopic, S., Friedrich, B., Fuchs, R., 2002, "Kinetics of Sulphuric Acid Leaching of The Serbian Nickel Laterite Ore Under Atmospheric Pressure", Metalurgica J. of Metall., Vol. 8 (3), pp. 235–244.

Sukla, L. B., Panchanadikar, V., 1993, "Bioleaching of Lateritic Nickel Ore Using A Heterotrophic Micro-Organism", Hydrometallurgy, Vol. 32, pp. 373–379.

Zhai, Y., Mu, W., Liu, Y., Xu, Q., 2010, "A Green Process for Recovering Nickel from Nickeliferous Laterite Ores", Transactions of Nonferrous Metals Society of China, Vol. 20, pp. 65–70.

Zuniga, M., Parada, F., Asselin, E., 2010, "Leaching of A Limonitic Laterite in Ammoniacal Solutions with Metallic Iron", Hydrometallurgy, Vol. 104, pp. 260–267.