Dissolution kinetics of a lateritic nickel ore in sulphuric acid medium

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The dissolution kinetics of a lateritic nickel ore in the sulphuric acid solution were investigated. The shrinking core model was applied to the results of experiments. The effects of stirring speed (100–600 rpm), H_2SO_4 concentration (0.1–2 mol l^1), leaching temperature (40-96 °C) and the particle size of the ore were studied on the nickel dissolution rate. The correlation coefficients for each different parameters were calculated. The results indicated that the dissolution rate of Ni is controlled by diffusion. The activation energy (Ea) for the dissolution reaction was determined to be 68.66 kJ mol^1. The Arrhenius constant was calculated to be 8.2578 s^{-1}. The order of reaction for the H_2SO_4 concentration and the particle size were also obtained. It was found that the stirring speed had no effect on the rate of nickel dissolution.

Key words: Nickel, leaching, dissolution kinetics, sulphuric acid, diffusion

Introduction

Nickel is a transition element and one of the demanded metal in the industry. Lateritic type nickel deposits are one of the significant sources of nickel and cobalt elements, but generally nickel is dominant [1]. Lateritic ores are widely distributed in the equatorial regions [2-3]. Oxidic nickel ores are products of weathered ultramafic rocks [4].

Lateritic ores can be classified into three main groups:
I. Hydrous silicate deposits: The Ni ore is found in the saprolite zone.
II. Clay silicate deposits: Ni is concentrated in smectite clays within the saprolite.
III. Oxide deposits: Ni is mostly associated with goethite [5-6].

The production of nickel from lateritic ores includes pyro-metallurgical and hydro-metallurgical processes [7]. Lateritic type ores are processed by ferronickel, smelting, matte smelting, Caron process and pressure acid leaching [8]. Several authors [3,7-15] have studied hydro-metallurgical methods of processing of lateritic nickel ores in various leach media.

Direct sulphuric acid pressure leaching is the process to recover nickel and cobalt from lateritic ores [3,9]. For that reason, in the literature, the majority of work [9-11] focused on the pressure acid leaching for nickel or cobalt extraction. Guo et al reported that 97 % Ni, 96 % Co, 93 % Mn, 95 % Mg and less than 1 % Fe are extracted from a laterite ore by high pressure acid leaching under optimum conditions. However, some authors [12-15]. studied the atmospheric pressure leaching of lateritic ores. The detailed review about atmospheric acid leaching was reviewed by McDonald and Whittington, 2008 [16,17] .During acid leaching with either atmospheric pressure or high pressure leaching, several acids (HCl, H_2SO_4, HNO_3, $HClO_4$, $H_2C_2O_4$, citric and lactic acids) can be used for extraction of metals from lateritic ores [18]. Nevertheless, sulphuric acid is mostly preferred due to its availability and low price.

In the present study, the dissolution kinetics of a lateritic nickel ore in the sulphuric acid medium were investigated. For this purpose, the effects of variables such as the stirring speed, temperature, sulphuric acid concentration and particle size were investigated.

Materials and Methods

Materials

In this study, lateritic nickel ore sample were taken from Karacam (Eskisehir) region of Turkey. Elemental analysis of the ore sample was performed with Atomic Absorption Spectrophotometer (AAS). The elemental composition of the sample is given in Tab. 1. Table also shows the element distribution according to size fractions of the sample. XRD pattern of the ore sample is given in Fig. 1. According to the mineralogical analysis of lateritic nickel ore sample, the main metallic ores are goethite, hematite and wustite. The gangues of the ore are composed of retgersite, gaspeite, quartz and clay type minerals.

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Tab. 1. Results of the elemental analysis of the lateritic nickel ore sample.

Particle size fractions [μm]	Elements [wt %]			
	Ni	**Fe**	**Mg**	**Co**
-106+75	1.88	17.80	1.22	0.048
-75+45	1.22	13.24	0.74	0.041
-45+38	1.24	11.00	0.58	0.038
-38	1.90	23.60	0.90	0.040
Total (-106)	1.84	23.14	1.58	0.030
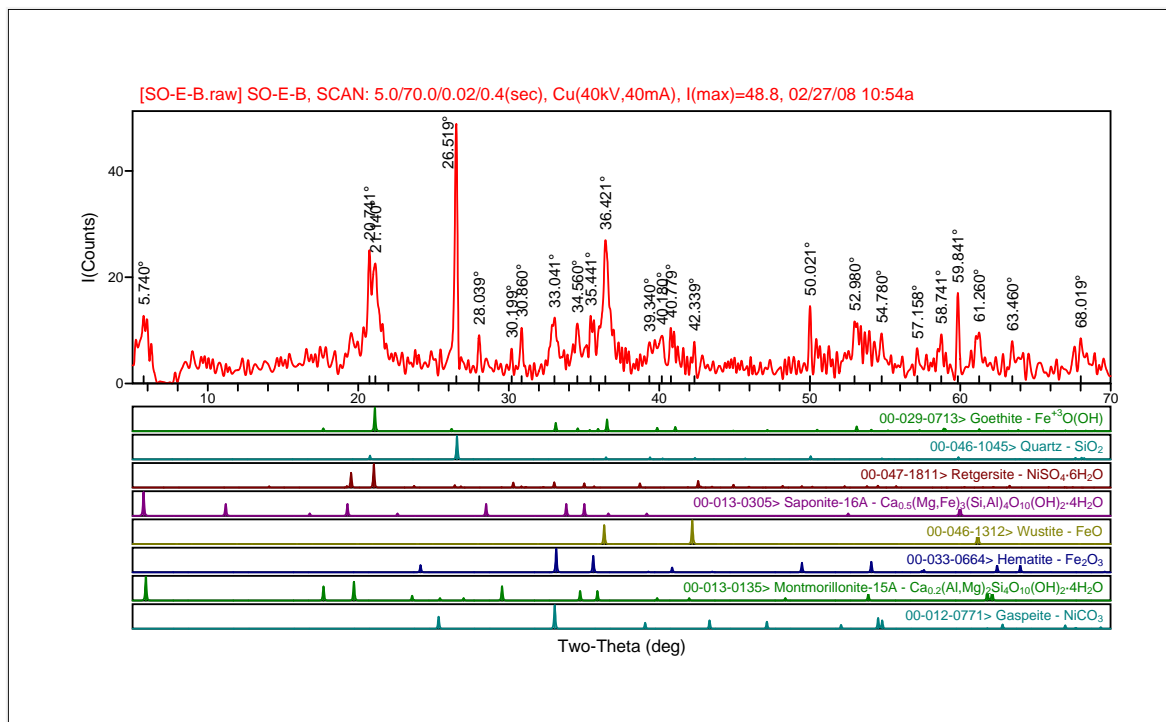
Fig. 1. XRD pattern of the lateritic nickel ore sample [19].

Methods

A glass vessel of 1 L was used as a leaching reactor put in a temperature-controlled water bath. Leaching reactor was closed by a rubber cover during experiment. The temperature ranged from 40 to 96 °C (± 0.2 °C) of the leach solution in the reactor was provided by a thermostatically controlled water bath. The solid liquid/ratio was 2.0 % by weight. The leach solution was stirred by Heidolph RZR 2021 model mechanical stirrer with teflon lined impeller. The amount of dissolved Ni in the leaching solution were determined by SensAA model AAS. Distilled water and reagent grade H_2SO_4 (Merck brand) were used to adjust the concentration of the leach solutions.

Results and Discussion

The effects of variables such as stirring speed, temperature, sulphuric acid concentration and particle size were investigated as dissolution parameters of nickel. The results of effects of those parameters were given below, separately. Besides dissolution of nickel, dissolution of iron were also analyzed and calculated. However, detailed results for iron extraction has not been presented in this study since the main focus of the work is nickel extraction. Results showed that iron and nickel was dissolved simultaneously. However, the effect of temperature on dissolution rate of iron is much pronounced than the nickel dissolution.

The effects of stirring speed

The effects of stirring speed on the nickel dissolution percentage from the lateritic nickel ore were investigated in 0.5 M H_2SO_4 solution at 60 °C in the range of 100 to 600 rpm. The results presented in Fig. 2 show that the dissolution percentage of nickel is independent of the stirring speed. Therefore, 200 rpm was selected optimum operating stirring speed in order to provide the stability of leach solution during sequent experiments to determine the effects of other parameters on dissolution of Ni.
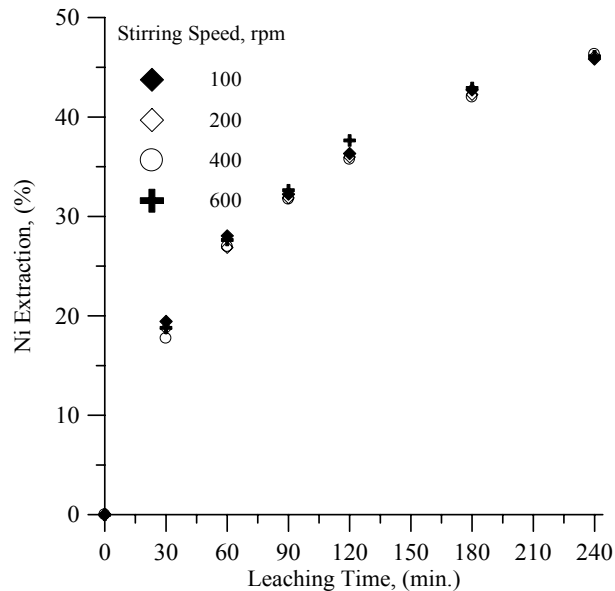
Fig. 2. Effects of stirring speed on the nickel dissolution ([H_2SO_4], 0.5 mol.l^{-1}; temperature, 60 °C; solid/liquid ratio, 2 % by weight; particle size, −106 μm).

The effects of H_2SO_4 concentration

The effects of sulphuric acid concentration on the dissolution of nickel were investigated from 0.1 to 2.0 M at 60 °C leaching temperature. The results given in Fig. 3 show that the percentage of nickel dissolved from the lateritic nickel ore increased with increasing sulphuric acid concentration. The nickel dissolution percentage after 240 min of leaching at 0.1 and 2.0 M sulphuric acid concentrations were found to be 23.8 % and 65.27 %, respectively.
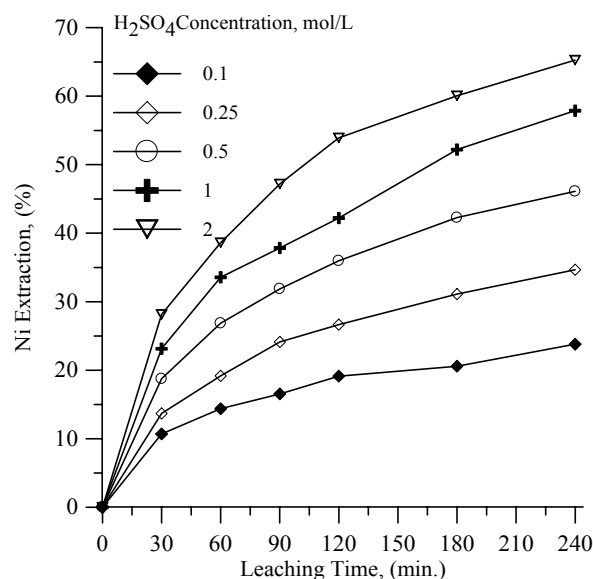
Fig. 3. Effects of H_2SO_4 concentration on the nickel dissolution (Stirring speed, 200 rpm; temperature, 60 °C; solid/liquid ratio, 2 % by weight; particle size, −106 μm)

The effects of leaching temperature

The leaching process was carried out in the temperature ranging from 40 to 96 °C with 2.0 M sulphuric acid solution at constant stirring speed of 200 rpm. The effects of temperature on nickel extraction from the lateritic nickel ore are presented in Fig. 4. It can be seen from the Fig. 4 that the extraction of Ni is increased with increased temperature. While, the extraction of Ni was 36.41 % at 40 °C after 240 min, it was increased to 100 % at about 80 °C. To determine the other leaching parameters, 80 °C was chosen as the optimum leaching temperature. The selection of 80 °C is also advantageous since it is lower than the boiling point of solution. By this way the leaching process will be more economic preventing the evaporation.
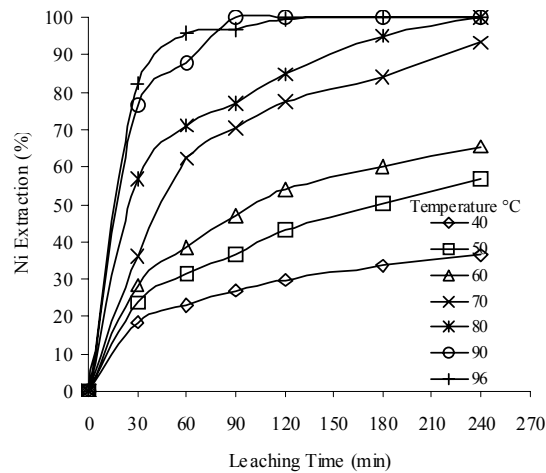

Fig. 4. Effects of temperature on the nickel dissolution ([H₂SO₄], 2.0 mol.l⁻¹; stirring speed, 200 rpm; solid/liquid ratio, 2 % by weight; particle size, −106 μm).

The effects of particle size

The experiments were carried out with the four different particle size fractions (-106+75, -75+45, -45+38 and -38 μm) in 2.0 M H₂SO₄ solution at 80 °C. The results are shown in Fig. 5. As shown in Fig. 5, the nickel dissolution percentage increases with decreasing particle size. Nickel extraction percentage reached to 46.7 % and 100 % after 240 minutes of leaching for −106+75 and −38 μm particle sizes, respectively. The reason of the higher dissolution percentage of the finer size fraction is due to the higher specific surface area of the ground sample. The higher the specific surface area of the ore is the higher the Ni extraction.
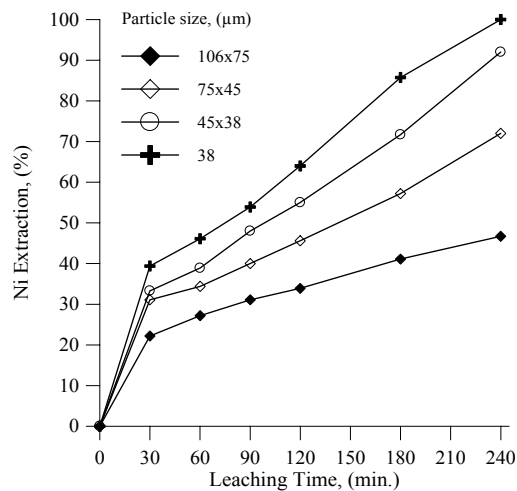

Fig. 5. Effects of particle size on the nickel dissolution ([H₂SO₄], 2.0 mol.l⁻¹; stirring speed, 200 rpm; temperature, 80 °C; solid/liquid ratio, 2 % by weight).

Kinetic analysis

The dissolution of Ni can be explained by the shrinking core model. Therefore, the diffusion and the surface reaction control models were investigated. If the reaction is controlled by diffusion the following equation can be used [20-21]:

$$1 - \frac{2}{3}x - (1-x)^{2/3} = k_{dif} \cdot t \tag{1}$$

If the reaction is controlled by the surface reaction [20-21]:

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

where x is the fraction reacted, t is the reaction time and k_{dif} and k_s are the rate constants. Eqs. (1) and (2) were applied to the experimental results and the correlation coefficients for each temperature are calculated and given in Tab. 2.

Tab. 2. k_{dif}, k_s and correlation coefficients for different temperatures.

Temperature [°C]	Apparent rate constants [10^{-3} h^{-1}] for Ni		Correlation coefficients [R^2] for Ni	
	k_{dif}	k_s	k_{dif}	k_s
40	0.0656	0.3494	0.99	0.96
50	0.2064	0.7442	0.99	0.99
60	0.2933	0.9075	0.98	0.96
70	0.8663	1.9585	0.98	0.96
80	1.3295	3.3966	0.99	0.95
90	2.7709	7.5741	0.90	0.92

These results indicate that the dissolution percentages of Ni is controlled by diffusion. The application of the diffusion model is shown in Fig. 6. Arrhenius plot (Fig. 7) considering the apparent rate constants were obtained by applying Eq (1) to the leaching experimental data. The calculated activation energy was for this lateritic type ore 68.66 kJ mol^{-1}.

The kinetics of nickel and magnesium leaching from the saprolitic laterite material was investigated by Luo et al. and the activation energies were determined to be 53.9 kJ mol^{-1} for nickel and 59.4 kJ mol^{-1} for magnesium respectively, which are characteristic for a chemical reaction controlled process [22] The activation energy of the overall reaction is calculated 41.1 kJ.mol^{-1} for the spent nickel oxide catalyst with sulfuric acid by Abdel-Aal and Rashad [23]. In another study, an activation energy of 47.34 kJ mol^{-1} after leaching of a lateritic nickel ore in acid media was determined by Arslan et al. [13]. In these studies about Nickel extraction, the dissolution reaction was found to be chemically controlled by some researchers while others found that the reaction was diffusion controlled.
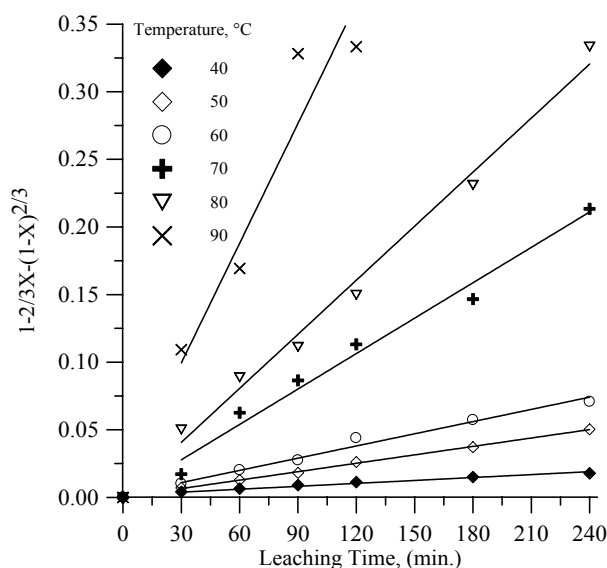

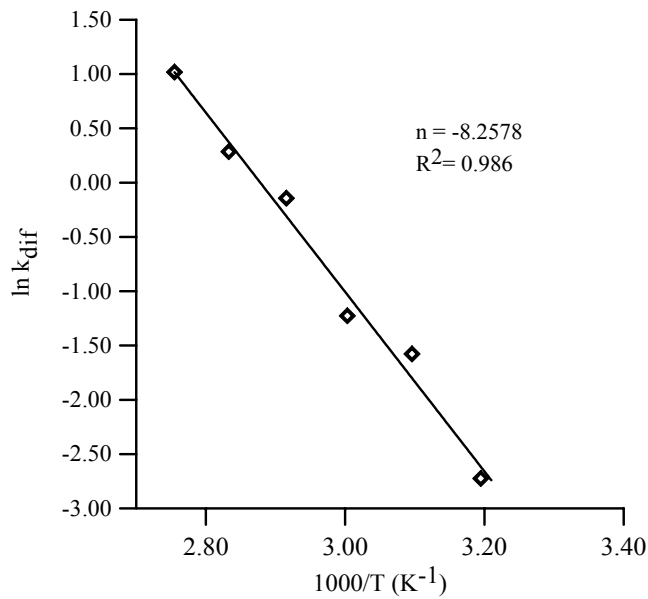*Fig. 6. Plot of Eq (1) vs. leaching time for different temperatures.*

Fig. 7. Arrhenius plot obtained for the dissolution of lateritic nickel ore.

Eqs (1) and (2) were applied to the obtained results from each acid concentration value. The k_s and k_{dif} values for each H_2SO_4 concentrations were determined (Tab. 3).

Tab. 3. k_{dif}, k_s and correlation coefficients for different acid concentrations.

Acid concentration [mol.l⁻¹]	Apparent rate constants [10^{-3} h⁻¹] **for Ni**		Correlation coefficients [R^2] **for Ni**	
	k_{dif}	k_s	k_{dif}	k_s
0.1	0.0259	0.2196	0.98	0.95
0.25	0.0648	0.3865	0.99	0.95
0.5	0.1243	0.5497	0.99	0.96
1.0	0.2168	0.7690	0.99	0.98
2.0	0.2889	0.8928	0.98	0.95

The application of the diffusion model for different acid concentrations is shown in Fig. 8. From the corresponding k_{dif} and H_2SO_4 concentration values, plots of $\ln k_{dif}$ versus $\ln[H_2SO_4]$ were obtained. As seen from Fig. 9, the order of the reaction was found proportional to the power of 0.823 of H_2SO_4 concentration ($[H_2SO_4]^{0.823}$).
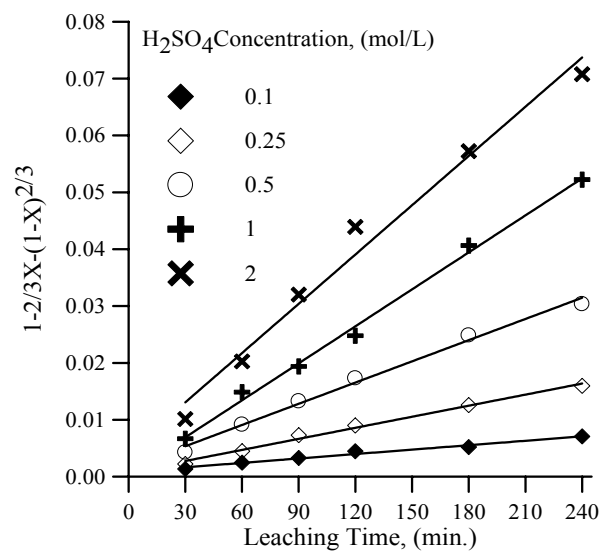

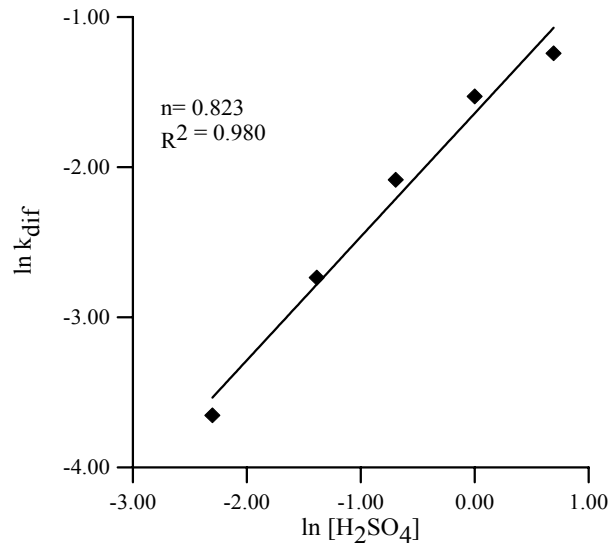*Fig. 8. Plot of Eq (1) vs. leaching time for different H_2SO_4 concentrations.*

Fig. 9. Dependence of the nickel dissolution to H₂SO₄ concentration.

Eqs (1) and (2) were applied to the obtained results from each particle size value. The k_s and k_{dif} values for each particle size were determined (Tab. 4).

The application of diffusion model for different particle size fractions is shown in Fig. 10. From the corresponding k_{dif} and particle size values, plots of $\ln k_{dif}$ versus $\ln r_0$ were obtained. As seen from Fig. 11, the order of the reaction was found inversely proportional to power 0.08 of particle size ($[r_0]^{-0.08}$).

Tab. 4. k_{dif}, k_s and correlation coefficients for different particle size fractions.

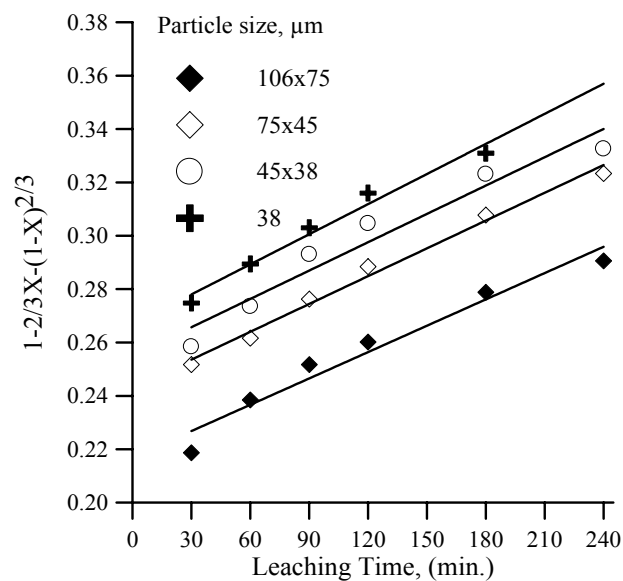| Particle Size [μm]	Apparent rate constants [10⁻³ h⁻¹] **for Ni**		Correlation coefficients [R²] **for Ni**	
	k_{dif}	k_s	k_{dif}	k_s
106x75	0.325	0.505	0.96	0.99
75x45	0.343	1.071	0.99	0.97
45x38	0.350	2.019	0.95	0.93
38	0.370	3.769	0.97	0.87

Fig. 10. Plot of Eq. (1) vs. leaching time for different particle size fractions.
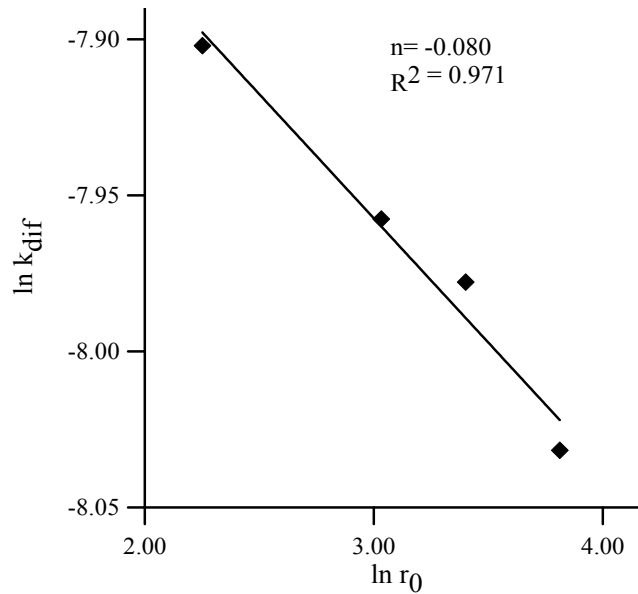
Fig. 11. Correlation of the nickel dissolution and the particle size.

Conclusions

In the present study, the dissolution kinetics of a lateritic nickel ore in the sulphuric acid medium was studied. It was determined that the nickel dissolution percentages increased with the increasing H_2SO_4 concentration and leaching temperature, and decreasing particle size. However, the stirring speed did not significantly affect the dissolution percentages. The correlation coefficients for each different parameter were calculated. These results indicate that the dissolution percentage of Ni is controlled by the diffusion model. The activation energy (Ea) for the dissolution reaction was calculated to be 68.66 kJ mol^{-1}. The Arrhenius constant was calculated to be 8.2578 s^{-1}. The order of the reaction for the H_2SO_4 concentration and the particle size were also obtained. The order of reaction was found proportional to the power of 0.823 of the H_2SO_4 concentration and the power of -0.08 of the particle size.

References

[1] Yongue-Fouateu R., Ghogomu R.T., Penaye J., Ekodeck G.E., Stendal H. and Colin F.: Nickel and cobalt distribution in the laterites of the Lomie´ region south-east Cameroon, *Journal of African Earth Sciences, 45 (2006), pp.33-47.*

[2] Golightly J.P.: Nickeliferous laterite deposits, *Economic. Geology, 75 (1981), pp.710–735.*

[3] Georgiou D. and Papangelakis G.V.: Sulphuric acid pressure leaching of a limonitic laterite: chemistry and kinetics, Hydrometallurgy *, 49(1998), pp.23-46.*

[4] Kotzè I.J.: Pilot plant production of ferronickel from nickel oxide ores and dusts in a DC arc furnace, *Minerals Engineering, 15(2002), pp.1017–1022.*

[5] Brand N.W., Butt C.R.M. and Elias M.: Nickel laterites: classification and features, *Journal of Australian Geology and Geophysic,. 17(1998), pp.81-88.*

[6] Gleeson S.A., Butt C.M.R. and Elias M.: Nickel laterites: a review, *SEG Newsletter Soc. Econ. Geosci.. 54(2003), pp.11-18.*

[7] Deepatana A., Tang J.A. and Valix M.: Comparative study of chelating ion exchange resins for metal recovery from bioleaching of nickel laterite ores, *Minerals Engineering, 19(2006), pp.1280–1289.*

[8] Zainol Z.: The development of a resin-in-pulp process for the recovery of nickel and cobalt from laterite leach slurries, *MSc thesis. Murdoch University. Western Australia, (2005).*

[9]   Rubisov D.H., Krowinkel J.M. and Papangelakis V.G.: Sulphuric acid pressure leaching of laterites-universal kinetics of nickel dissolution for limonites and limonitic/saprolitic blends, *Hydrometallurgy, 58 (2000), pp.1-11.*

[10]   Georgiou D. and Papangelakis G.V.: Behaviour of cobalt during sulphuric acid pressure leaching of a limonitic laterite, Hydrometallurgy, *100 (2009), pp.35-40.*

[11]   Guo X., Shi W., Li D., Tian Q.: Leaching behavior of metals from limonitic laterite ore by high pressure acid leaching, *Transactions of Nonferrous Metals Society of China, 21 (2011), pp.191-195.*

[12]   Büyükakinci E. and Topkaya Y.A.: Extraction of nickel from lateritic ores at atmospheric pressure with agitation leaching, *Hydrometallurgy, 97 (2009), pp.33-38.*

[13]   Arslan F., Özer Ö., Perek K.T, Gürkan V., Önal G.: Dissolution of lateritic ore in acidic media, *Proceedings of International Mineral Processing Congress, IMPC 2006, Istanbul, Turkey, 3–8 Sept, pp. 1500-1504.*

[14]   Agatzini-Leonardou S., Zafiratos I.G.: Beneficiation of a Greek serpentinic nickeliferous ore Part II. Sulfuric acid heap and agitation leaching, *Hydrometallurgy, 74 (2004), pp. 267-275.*

[15]   Curlook W.: Direct atmospheric leaching of saprolitic nickel laterites with sulfuric acid, In: Imrie, W.P., Lane, D.M. (Eds.), *International Laterite Nickel Symposium. TMS, Warrendale, 2004. pp. 385–398.*

[16]   McDonald R.G., Whittington B.I.: Atmospheric acid leaching of nickel laterites review. Part I. Sulphuric acid technologies, *Hydrometallurgy, 91 (2008),pp. 35-55.*

[17]   McDonald R.G., Whittington B.I.: Atmospheric acid leaching of nickel laterites review. Part II. *Chloride and bio-technologies, Hydrometallurgy, 91 (2008),pp. 56-69.*

[18]   Chander S.: Atmospheric pressure leaching of nickeliferous laterites in acidic media. *Transactions of the Indian Institute of Metals, 35 (1982) 4, pp.366–371.*

[19]   Agacayak T.: Beneficiation of Karacam (Eskisehir) Lateritic Nickel Ore By Physical and Chemical Methods, *PhD thesis, Selcuk University. Turkey, 2008, p.215.*

[20]   Habashi F.: Principles of Extractive Metallurgy, *Gordon and Breach, New York, 1,(1969), pp.153–163.*

[21]   Levenspiel O.: Chemical Reaction Engineering, *3rd ed. John Wiley and Sons, New York, USA. (1999), pp. 566-586.*

[22]   Luo W., Feng Q., Ou L., Zhang G., Chen Y.: Kinetics of saprolitic laterite leaching by sulphuric acid at atmospheric pressure, *Minerals Engineering, 23(2010), pp.458–462.*

[23]   Abdel-Aal E.A., Rashad M.M.: Kinetic study on the leaching of spent nickel oxide catalyst with sulfuric acid, *Hydrometallurgy, 74 (2004),pp. 189-194.*