

Sulphuric Acid Leaching of the Serbian Nickel Lateritic Ore

Srećko Stopić, Bernd Friedrich, Reinhard Fuchs

The extraction of nickel from the Serbian nickel lateritic ore by sulphuric acid leaching has been studied. Atmospheric leaching at temperatures as high as 363 K generally resulted in nickel extraction of up to 78 %. The influence of the reaction parameters of temperature, time, sulphuric acid concentration and stirring speed on the kinetics of metal extraction was determined. The results showed that the nickel dissolution from lateritic ore is controlled by

the "inner diffusion" model. Techniques such as ICP spectrometry, DTA and TGA analysis have been used to investigate the ore after various treatments.

Keywords:

Leaching – Lateritic ore – Nickel – Kinetics – Sulphuric acid

Schwefelsaure Laugung serbischer Nickellateriterze

Die Extraktion von Nickel durch Laugung mit Schwefelsäure aus dem serbischen Nickellateriterz wurde untersucht. Bei einer Temperatur von 363 K wird ein Nickelausbringen von bis zu 78 % unter Atmosphärendruck erreicht. Der Einfluß der Reaktionsparameter Temperatur, Zeit, Konzentration der Schwefelsäure und Umdrehungsgeschwindigkeit des Rührers auf die Kinetik der Nickelauslösung wird bestimmt. Die Ergebnisse haben

gezeigt, daß die Nickelextraktion durch das Modell „Innerer Stofftransport“ gesteuert wird. ICP-Spektrometrie, DTA- und TGA-Analyse wurden für die Untersuchungen der Erze und Laugerückstände nach den verschiedenen Behandlungen angewendet.

Schlüsselwörter:

Laugung – Lateriterz – Nickel – Kinetik – Schwefelsäure

Lixiviation sulfurique des minerais latéritiques de nickel

Lixiviación ácido sulfúrico de minerales lateríticos de níquel de Serbia

Laterites are oxide ores widely distributed in the equatorial regions. Lateritic deposits usually consist of three layers, namely the limonitic, the saprolitic and garnieritic layer. It is known that 54 % of the total reserves of nickel are found in laterites [1]. Conservative forecasts for the next 20 years indicate that leaching of nickel laterites will rise from 40 % to about 50 % of the total world nickel production.

HALIKIA [2] examined the influence of kinetic parameters on the extraction of nickel from a Greek hematite type laterite during leaching with sulphuric acid at atmospheric pressure mild conditions. The concentration of sulphuric acid in the leaching solutions influences nickel extraction in the initial stages of reaction at all molarities investigated. During the later stages of leaching the influence is more intense at low concentrations and less at higher concentration. Temperature has a marked influence on nickel extraction.

KONTOPOULOS [3] has studied the extraction of nickel and cobalt from low-grade Greek laterites by sulphuric acid leaching at atmospheric pressure at temperatures as high as 368 K on a continuous mini plant. An extraction of 82 %

of Ni and 75 % Co has achieved by leaching for 4 h at 95 °C with 3 N sulphuric acid, and 25 % pulp density.

In this paper, the optimal conditions for leaching of nickel from the Serbian nickel laterite under atmospheric pressure are determined and discussed. Here the influence of reaction parameters such as temperature, time, sulphuric acid concentration and stirring speed on the kinetics of nickel recovery have been studied. The main aim is to understand the process chemistry and present the nickel resource in Serbia which is of great importance for further investigations in high pressure leaching conditions.

1 Resources of the nickel ore in Serbia

Although there are enormous resources of nickel ore in Serbia, production of the very important metal Ni does not exist. In the past nickel in Serbia was imported from the European countries. Substantial reserves of nickel ore in Serbia are situated in four main zones amounting:

- | | |
|-----------------------------------|-----------|
| 1) Zlatibor (Mokra Gora) | 150 mio t |
| 2) West Morava (Rudjinci, and Ba) | 35 mio t |

3) Sumadija (Lipovac)	11 mio t
4) Kosovo (Goles, and Čikatovo)	24 mio t

The nickel ore in Serbia has the following characteristics: the nickel content dependent on location changes from 0.7 to 1.42 % (Table 1), the water content from 28 to 42 % and the high SiO₂ content is about 57 %. The ore bodies 1), 2) and 3) are situated in an area approx. 200 km around Belgrade. Conventional physical processing methods such as flotation, magnetic, gravity, and electrostatic separation were found to be ineffective to perform an enrichment of these ores [4].

Table 1: Chemical analysis of nickel ores in Serbia

Chemical composition [%]	Types of nickel deposits in Serbia				
	Rudjinci	Ba	Mokra Gora	Goles	Lipovac
Fe	14.90	30.66	18.55	12.20	31.70
SiO ₂	52.68	33.61	39.11	56.63	13.95
Al ₂ O ₃	5.17	8.59	6.30	2.50	7.22
Cr ₂ O ₃	0.54	2.41	2.40	1.70	4.16
MgO	4.40	1.58	11.50	5.25	0.05
CaO	1.30	0.90	0.80	0.24	5.16
NiO	1.44	1.43	0.77	1.50	1.29
CoO	0.06	0.05	0.05	0.05	0.04

VUČUROVIĆ et al. [4, 5] have studied the optimal conditions for leaching of the above mentioned ores under atmospheric and high pressure conditions without kinetic analysis of process. They have obtained the high degree of nickel and cobalt recovery in ammonium-carbonate and sulphuric acid leaching conditions.

2 Experiments

2.1 Experimental procedures and analytical methods

The leaching kinetics experiments were carried out in a glass reactor using IKA laboratory instrument, IKAMAG RCT basic, IKA Labortechnik, Germany. The motor speed is set on the rotary knob "mot" with its dial from 1 to 10, with a speed range from 50 to 1100 rpm. A 20 g ore sample of laterite is dispersed in 200 ml of determined water solution heated to a specified temperature. Later the sulphuric acid is injected into the solution at the investigated temperature. After a certain reaction time 1 ml of suspension is taken with a micropipette and placed immediately in a 100 ml volumetric flask containing a sufficient amount of distilled water to quench reaction. The suspension is then diluted to the 100 ml mark. After filtration the concentration of metals in the filtrate is determined by an inductively coupled plasma spectrophotometry. The leaching process is evaluated by the extraction of metal, defined as the fraction α of a given element in the field leached out over a certain reaction time.

The experiments were done at 318, 333, 348 and 363 K in time up to two hours. Distilled water is used as a solution agent. The concentration of H₂SO₄ is amounted from 0.2 to 0.4 mol/L with a constant ore-liquid ratio of 0.1. The pH-value of obtained solution after leaching had a value between 0 and 1. The stirring speed ω is between 700 to 900 rpm.

Thermogravimetric TGA and differential thermal analysis DTA of nickel ore is carried out in an argon atmosphere with temperature range between 298 and 1273 K using Derivatograph NETZSCH STA 409 with an α -Al₂O₃. The heating rate amounts to 1 K/min.

2.2 Material (Ore Rudjinci, Serbia)

Rudjinci deposits, situated near by Vrnjacka Banja (about 200 km southern from Belgrade) are the most abundant ones in Serbia. The sample of Rudjinci ore is a clay-like, loose material. The ore has a low level of metal components and high level of SiO₂.

Rudjinci nickel ore deposits belong to a group of exogenous nickel deposits, a subgroup of laterite-silicate deposits. The deposits consist of nontronite Fe₂Si₄O₁₀(OH)₂, a decomposed serpentine Mg₃Si₂O₅(OH)₄. Therefore, silicates are the major and most important components of the deposits.

In our experiments the sample represents a pre-concentrate of Rudjinci ore previously homogenized. The composition of pre-concentrate in %: 54.20 SiO₂, 14.90 Fe, 4.00 Al₂O₃, 1.09 Cr₂O₃, 1.13 Ni, 0.06 CoO, 1.40 CaO, 3.22 Mg, 0.48 MnO, 0.05 Na₂O and 0.05 K₂O. The rest represents the loss during calcinations. Using the sieving method the granulometric distribution of particles is determined. An analysis of each fraction is given in Table 2.

DTA and TGA analysis of nickel ore is presented in Figure 1. DTA and TGA analysis of nickel lateritic ore confirmed an existence of following chemical reactions up to 1273 K:

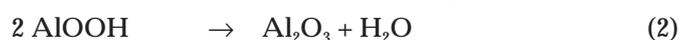


Table 2: Granulometric analysis of nickel lateritic ore

Fraction [μm]	Proportion [wt %]
200 - 160	50.97
160 - 100	10.94
100 - 80	6.48
80 - 71	9.37
71 - 63	6.18
63 - 50	7.60
50 - 32	7.31
< 32	1.12

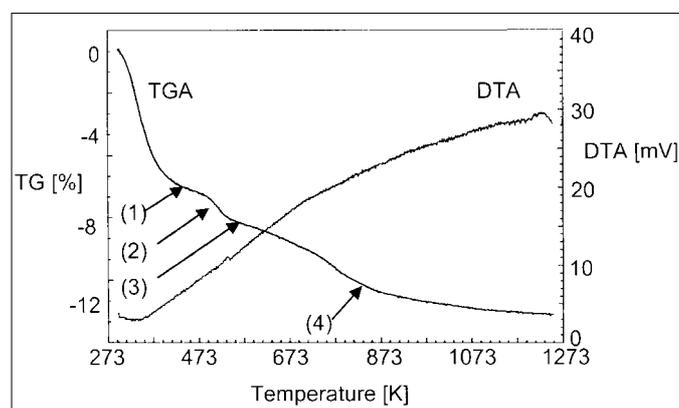
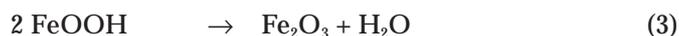


Fig. 1: DTA and TGA analysis of nickel lateritic ore in argon atmosphere



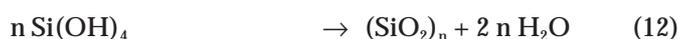
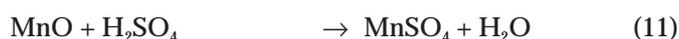
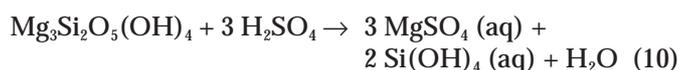
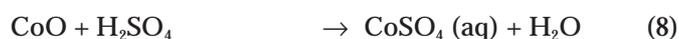
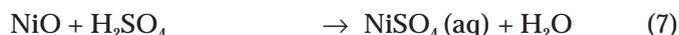
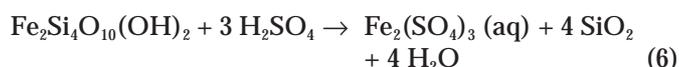
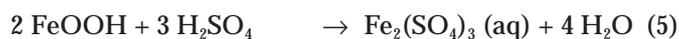
The calculated loss of chemically combined water in the above mentioned reactions (1), (2), (3) and (4) amounts to [%]: 40.9, 15.0, 10.6 and 12.9, respectively. The TGA analysis of the sample of nickel lateritic ore determines a total weight loss of 12.9 %.

The first weight loss occurring up to 393 K corresponds to the removal of the free water within the ore sample. A second minor weight loss is recorded at about 513 K indicating the removal of the crystalline water and OH- group from goethite structure and also formation of hematite (3).

The following major weight loss is observed at 833 K, indicating a significant transformation with a break down of the serpentine lattice and the formation of forsterite MgSiO_3 . During this transformation it is very likely that there is a rearrangement followed by a reaction of the type (4). The nickel oxide present in the lattice is probably liberated at this stage, making it readily available for further treatment.

3 Leaching reactions

The main sulphuric acid leaching reaction for nickel lateritic ore in the atmospheric conditions are presented below:



As shown in reaction (5) to (11) leaching of nickel ore consumes sulphuric acid. SiO_2 represents a main compound in a solid product after leaching. WHITTINGTON [6] proposed the same leaching mechanism studying scales formed during the leaching of Western Australian ore, from an acid environment in hypersaline process water. He indicated that the serpentine and nontronite present in the Western Australian ore ultimately react to an amorphous silica.

The dominant leaching reactions can be further identified from the corresponding % Me/pH diagrams with pH values between 0 and 2. In the program "Stability calculation for aqueous system", USA, such a diagram was designed for Ni, Mg, Al and Fe leaching system using following database [7]. The typical diagram for nickel solubility is shown in Figure 2.

Nickel, cobalt and manganese in the assumed form of "oxides" dissolve according to reactions 7, 8 and 11 respec-

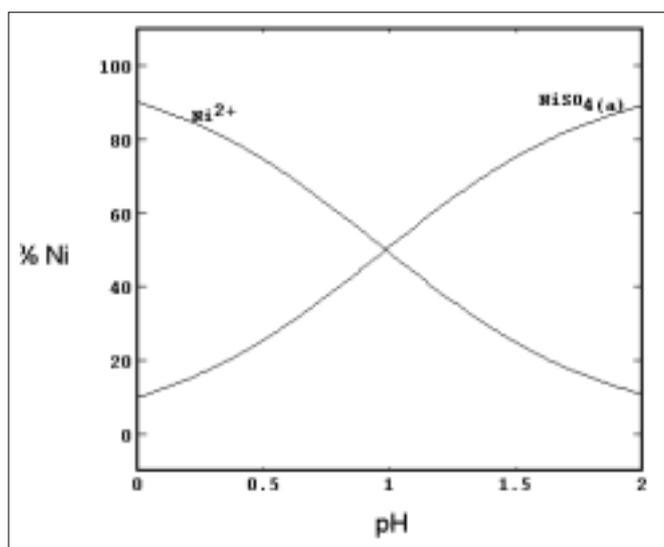


Fig. 2: % Ni/pH diagram of nickel leaching system in 0.4 mol H_2SO_4 solution at a temperature of 363 K [7]

tively and remain in the aqueous phase as sulphates. Nickel and magnesium showed same behavior. It is known that the solubility of metal sulphates in water increases as the temperature is raised above room temperature. Inverse solubilities of many metals can occur at elevated temperatures. This trend also occurs in acid leach conditions at atmospheric pressure.

Aluminum in the assumed form of boehmite dissolves according to reaction (9) and remains in the aqueous phase as sulphate.

Iron in the form of goethite FeOOH and nontronite $\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ dissolves to ferric sulphate respectively according to reaction 5 and 6. If content of iron is very high (82 to 100 %), ferric cations can hydrolyze rapidly after the dissolution of goethite and nontronite forming hematite Fe_2O_3 or basic ferric sulphate $\text{H}_2\text{Fe}_3(\text{SO}_4)_2(\text{OH})_7$. Basic ferric sulphate formation depends upon leaching conditions and it is favored by very small pH-values ($\text{pH} = 0.2$). High temperatures favor the formation of hematite.

The solubility of silica is not pH dependent. But silica is inorganically soluble only under high pH values.

4 Results and discussion

4.1 Effect of leaching temperature

The effect of temperature on nickel leaching from nickel laterite is shown in Figure 3.

It can be seen that the nickel extraction increases with increasing leaching time. The maximal obtained value of nickel extraction amounts to $a = 78\%$ at temperature of 363 K and a leaching time of 120 min using sulphuric acid concentration of 0.2 mol/L. The previously mentioned value is to be about to an extraction of 82 % of Ni achieved by KONTOPOULOS [3] during leaching for 4 h at 95 °C with 3 N sulphuric acid. The required leaching time to reach the maximum increases with decrease in leaching temperature.

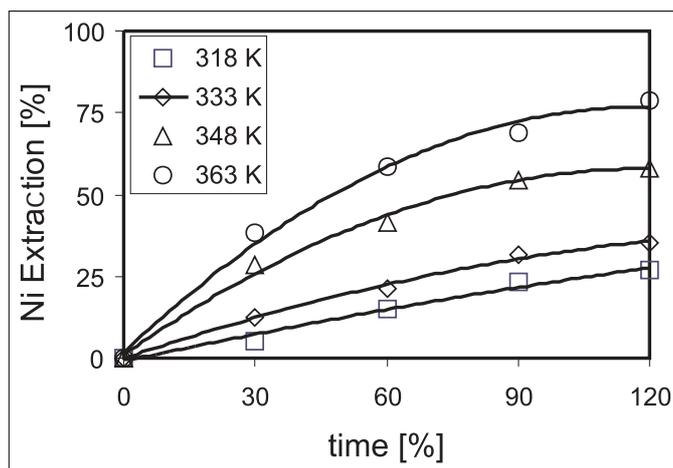


Fig. 3: Effect of temperature on nickel leaching kinetics. Leaching was performed in an approximately 10 % nickel lateritic ore with H_2SO_4 acid concentration 0.2 mol/L.

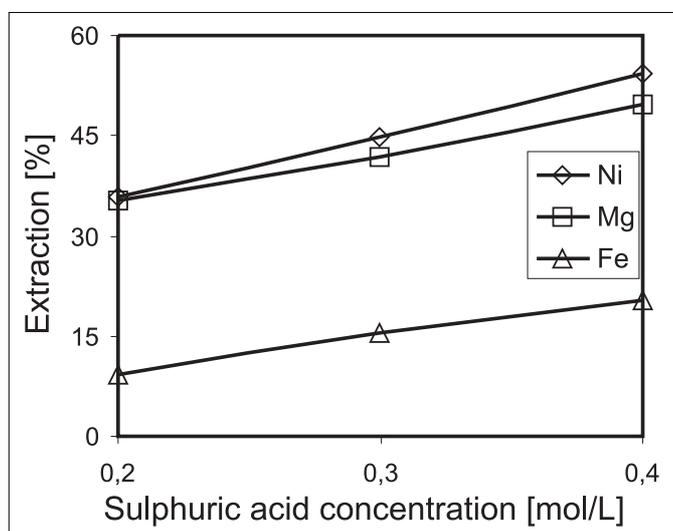


Fig. 4: Effect of H_2SO_4 dosage on the extraction of nickel, magnesium and iron. Leaching was performed at 333 K in an approximately 10 % nickel lateritic ore suspension during 120 min.

4.2 Effect of sulphuric acid concentration

As mentioned previously [3, 5, 8] leaching of nickel laterite under atmospheric pressure is an acid consuming process. The results in Figure 4 show that extraction of metals increases with increase of sulphuric acid dosage.

The increase of sulphuric acid concentration from 0.2 mol/L to 0.4 mol/L at 333 K increases the extraction of nickel and magnesium about 20 % and iron extraction about 10 %, respectively. The results show that the extraction of nickel and magnesium is almost three times higher than iron during leaching.

4.3 Effect of stirring rate

To eliminate the effect of external diffusion (diffusion through the liquid boundary layer), a minimum stirring rate is expected to disperse and suspend the lateritic ore in a liquid medium. The effect of stirring rate on extraction of Ni, Mg, Fe and Al is investigated in the range of 700 to 900 rpm (Figure 5).

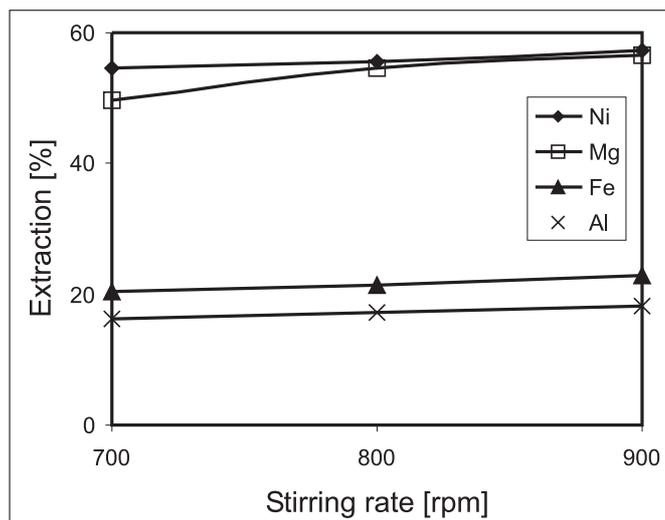


Fig. 5: Effect of stirring rate on Ni, Mg, Fe and Al extraction. Leaching was performed at 333 K in an approximately 10 % nickel lateritic ore with H_2SO_4 concentration of 0.4 mol/L during 120 min.

The increase in stirring speed from 700 to 900 rpm had a negligible effect on the rate of Ni, Mg, Fe and Al dissolution. Under these conditions the dissolution of Al is the smallest, and that of Ni is the highest. There is a difference in dissolution of Ni, Mg, Fe and Al, however a selectivity in this conditions is not demonstrated.

4.4 Apparent activation energy of nickel leaching

For a better control of the leaching process, it is important to establish a quantitative measurement of the leaching kinetics and mechanism. Various kinetics models have been proposed to describe the leaching process [9]. For a diffusion-controlled process of spherical particles (shrinking core model), the kinetics equation is given by Eq. 13:

$$1 - 3 \cdot (1-a)^{2/3} + 2 \cdot (1-a) = k \cdot t \quad (13)$$

(a: extraction at the given temperature; k: rate constant)

Should a leaching process be controlled by external diffusion or chemical reaction, the leaching process can be described by:

$$1 - (1-a)^{1/3} = k \cdot t \quad (14)$$

Using experimental values in Eq. 14 it is present that the nonlinear relationship between the values $1 - (1-a)^{1/3}$ and leaching time suggests that the nickel leaching from nickel lateritic ore by sulphuric acid is not controlled by external diffusion and chemical reactions. The nickel extraction data is plotted using the inner-diffusion model (Figure 6), where the equations with values of rate constant $k_{318\text{K}} = 0.0002$, $k_{333\text{K}} = 0.0004$, $k_{348\text{K}} = 0.0014$, and $k_{363\text{K}} = 0.003 \text{ mol m}^{-2} \text{ min}^{-1}$.

The former confirms that leaching of lateritic ore of nickel in current study is controlled by the diffusion of sulphuric acid and products through the ore matrix. The chemical reaction of nickel leaching is very fast producing a porous layer of SiO_2 at the particle surface through which the sulphuric acid must pass to reach untreated lateritic ore underneath. The leaching rate is therefore very high, leaching of Ni and Mg proceeds with the same rates faster than

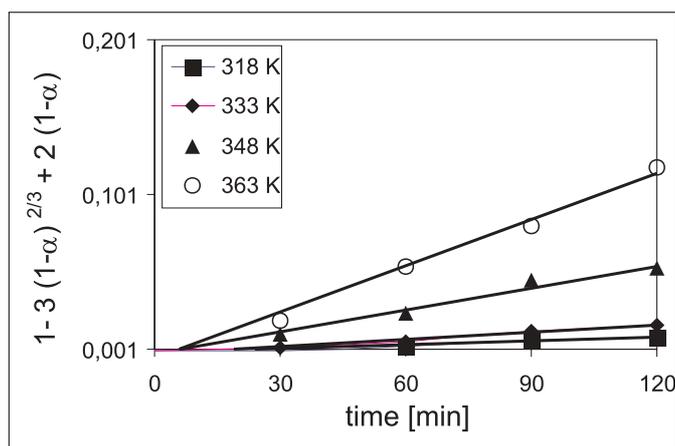


Fig. 6: Linear fit of nickel leaching kinetics to inner diffusion control model

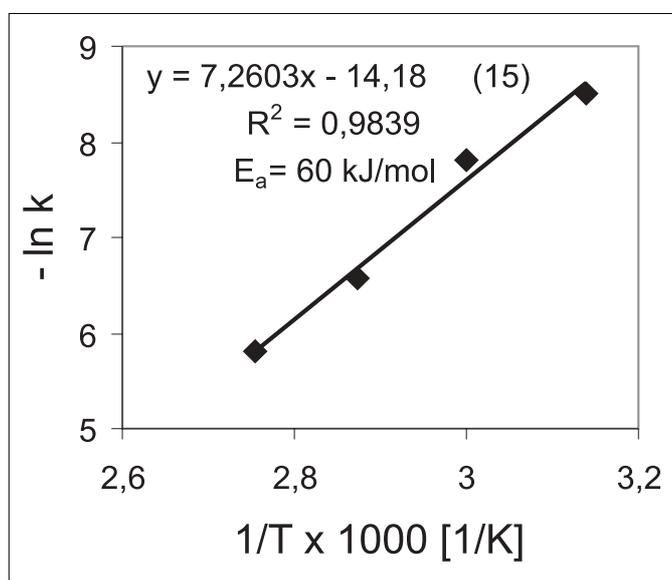


Fig. 7: Arrhenius plot of leaching of nickel lateritic ore by sulphuric acid

the leaching of Fe and Al. Diffusion through the layer of SiO_2 is becoming the rate controlling step at a certain thickness of the layer.

A linear relationship is observed and the experimentally determined rate constant k is plotted as a function of the reciprocal of the leaching temperature on a semi log scale, as shown in Figure 7. Following the Arrhenius equation ($\ln k = \ln A - E/RT$) an apparent activation energy of 60 kJ mol^{-1} is obtained (Figure 7).

RINN and FETTING [10] calculated the energy activation of $E_a = 40.2 \text{ kJ mol}^{-1}$ for leaching of nickel from a serpentine with particle size $< 160 \mu\text{m}$ in hydrochloric acid.

5 Conclusion

Leaching of the Serbian lateritic ore by sulphuric acid under the atmospheric pressure at temperatures as high as 363 K generally resulted in nickel extraction up to 78 %. The nickel extraction increases with increasing leaching temperature and time. The increase of sulphuric

acid concentration from 0.2 mol/L to 0.4 mol/L at 333 K increases the extraction of nickel and magnesium to about 20 %, and iron extraction to about 10 %, respectively. The increase in stirring speed from 700 to 900 rpm had a negligible effect on the dissolution rate of Ni, Mg, Fe and Al. The results showed that the nickel dissolution from lateritic ore is controlled by inner diffusion control model where the diffusion through the layer of SiO_2 is the rate controlling step. Above mentioned is of great importance for our further investigations in high pressure leaching conditions.

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