

Kinetics of High Pressure Leaching of the Serbian Nickel Lateritic Ore

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Abstract

The extraction of nickel from the Serbian lateritic ore by sulphuric acid leaching has been studied under high pressure conditions. A titanium autoclave equipped with acid injection and sample withdrawal unit was used in sulphuric acid pressure leaching (SAPL). The following parameters are tested: stirring rate, acid to ore ratio and reaction time and temperature. Studies are done with ore samples (1.1% Ni and 52.7 % SiO₂) from Rudjinci, Serbia which belongs to laterite-silicate group of deposits. These deposits have the great importance for nickel metallurgy, because of their large presence. The main aim was to study the kinetics of the SAPL process. The initial solids, as well the leach residues, are characterized by ICP analysis in order to determine the effects of investigated parameters on the nickel leaching degree. The reaction temperature, acid/ore ratio and stirring speed have showed a positive influence on the increasing of nickel extraction.

1 Introduction

Nickel demand has grown at an historic average annual rate of approximately 4 % per year and is expected to remain at that rate [1]. This strength has been driven primarily by a growing demand for nickel in stainless steel, whose production accounts for approximately two-thirds of primary nickel demand. Nickel is processed from two mineral sources, sulphides and oxides (laterite). Laterite ores are easily mined in comparison to sulphide ores, being close to the surface (10-100 m) [2]. Conservative forecasts for next 20 years indicate that leaching of nickel laterites will rise in the region of 40 % to 50 % of the actual total world nickel production [3]. Nickel processing from the laterite ores is either performed by pyrometallurgical methods producing ferro-nickel, or by leaching with ammonia or with the use of sulphuric acid under high pressure conditions. It is known that 54 % of the total reserves are found in laterites. Leaching from the laterite ore at atmospheric pressure is mentioned by many authors.

Stopić et al [4] showed that an atmospheric leaching of nickel lateritic ore "Rudjinci", Serbia at temperatures as high as 90°C generally resulted in nickel extraction up to 78 %. The influence of



reaction parameters 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 inner diffusion model.

Halikia [5] 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. Temperature had a marked influence on nickel extraction.

Vučurović et al. [6] have obtained the high degree of nickel and cobalt recovery in ammonium-carbonate and sulphuric acid leaching conditions at high pressure conditions.

Sulphuric acid pressure leaching of nickeliferous laterites has attracted considerable attention from the nickel industry during the last 5 years [7-9]. This process achieves a high nickel and cobalt extraction (more than 95 %) with a high selectivity due to simultaneous iron and aluminium dissolution and precipitation. Condition close to the industrial practice were tested: pulp density 30 %; acid to ore ratio 0.2 and temperature ranging from 230 to 270 °C. During leaching, goethite dissolves continuously liberating nickel whilst iron re-precipitates as dense hematite particles in solution by *ex situ* precipitation.

In this paper, favourite conditions for leaching of nickel from the Serbian nickel laterite under high temperature and high pressure are considered. A new equipment with acid injection and sample withdrawal unit on the autoclave is presented. The influence of reaction parameters such as temperature, time, sulphuric acid concentration and stirring speed on the kinetics of nickel recovery is determined. The aim was to understand the process chemistry and kinetics and to establish parameters of nickel laterite leaching from deposits in Serbia with a use of sulfuric acid in autoclave, namely, reaction time and temperature, total gas pressure, and acid concentration necessary for maximum transfer of nickel into solution. Because of the large presence of nickel laterite in South-East Europe and a small number of plants for hydrometallurgical production of nickel there exists a need for studies of leaching under high pressure.

2 Experimental

2.1 Material (Ore "Rudjinci", Serbia)

"Rudjinci" deposits, 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 SiO_2 . "Rudjinci" nickel ore deposits belong to a group of exogenous nickel deposits, a subgroup of laterite-silicate deposits. The deposits are represented with serpentine $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ variously decomposed into nontronite $\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. Therefore, silicates are the major and most important component of the deposits. The sample of ore "Rudjinci"

was previously homogenized with the following composition (%): 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.

2.2 Experimental procedures and analytical methods

Under high pressure leaching conditions tests were performed in a 2 l autoclave, manufactured by the Autoclave Engineers, USA. Figure 1 shows an overview presenting the autoclave at IME, Aachen, which is part of 3 reactor system from 1- 50 l. Temperature was controlled within ± 1 °C by a temperature control system, manipulating both an electrical heating mantle and a water cooling system. Agitation was provided by a titanium-made impeller that was magnetically driven. The autoclave was equipped with an acid injection device and a system to withdraw sample designed by IME. Only this allows a exact definition of the reaction starting point. A certain amount of laterite was mixed with a pre-calculated amount of deionised water and placed in an autoclave. The slurry was then heated up to a predetermined temperature in the range of 200 to 250 °C under continuous agitation. Upon temperature stabilisation, a certain amount of concentrated sulphuric acid (96 wt %) corresponding to different acid-to-ore ratios, was injected into the autoclave under pressure using the injection device made at IME. Using the sampling system 20 ml of almost clear liquid was periodically withdrawn through a dip tube and then rapidly cooled. After the end of experiments, solutions aliquots were filtered und analysed aiming Ni, Co, Mg, Al, Fe and Si by ICP spectrophotometry. Eh measurement were taken using a platinum electrode and Ag|AgCl reference electrode. pH measurement was done using universal pH probe. The pH was calibrated using pH standard (pH= 1 and pH=7).

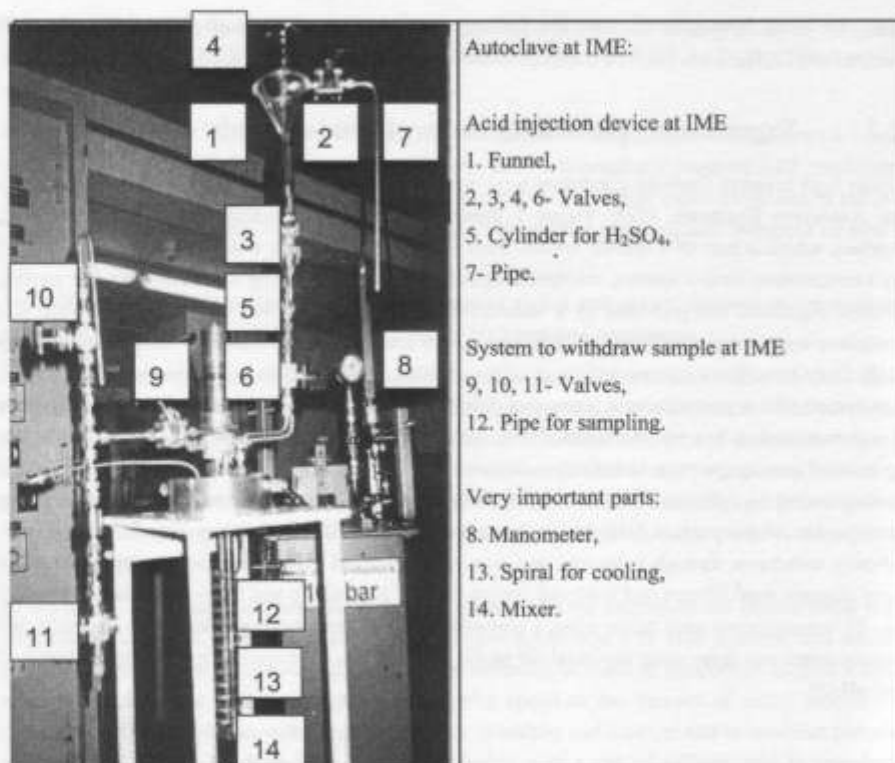


Figure 1: 2 l-Ti- autoclave at IME, RWTH Aachen

The leaching process was evaluated by metal extraction coefficient, defined as the fraction α of a given element leached out over given period of time. The experiments were done at 200; 230; and 250 °C in time up to 60 min. At these temperatures the equilibrium vapour pressure reaches 1.6 up to 4.1 MPa. The acid-to-ore rate (a/o) amounted from 0.24 to 0.40 g H₂SO₄/g ore.

2.3 New system with an acid injection device and system to withdraw sample

One aim of this work is to present a new injection device and a new system to withdraw samples during high pressure leaching. A sketch of two main system are presented in Fig. 2.a. and 2.b. Sulphuric acid is injected into funnel No.6 (Fig. 2.a). Then the valves No.5 and No.8 are slowly opened and concentrated sulphuric acid goes into cylinder. The valves No.5 and No.8 are closed. Firstly valve No.7 is opened, and then quite slowly the valve No.3 is opened. The sulphuric acid goes into solution in autoclave. Then the valves No.3 and No.7 are closed. Later on same way 20 ml

water is injected in autoclave. The injection of acid and water at 230 °C reduces the temperature of the solution inside reactor by a maximum of 10 °C. The controlling system regains the target temperature normally in less than 5 min.

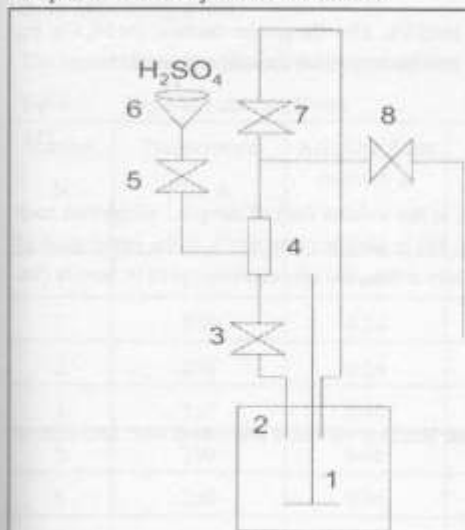


Fig. 2.a: Acid injection device at IME
(1-mixer; 2- pipe; 3, 5, 7, 8- valve; 4, cylinder for H_2SO_4 ; 6- funnel)

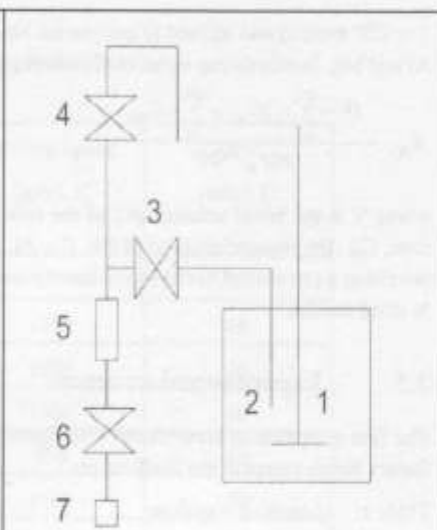


Fig. 2.b. System to withdraw sample at IME
(1- mixer; 2- pipe; 3, 4, 6- valve; 5- cylinder for sample; 7-glass)

Figure 2: System for acid injection device and to withdraw sample

Samples can be withdrawn using the sampling system in 2 min intervals (Fig. 2.b). Firstly the stirrer is shut down for 30 s aiming a separation of solid and liquid. Then the valve No.3 (Fig. 2.b) is slowly opened. 20 ml of the sample goes into the cylinder No.5 through pipe No.2 from the solution. Then valve No.3 is closed. After opening valve No.6, the sample goes into in glass No.7, where Eh and pH values are measured.

2.4 Chemical analysis of solution and calculation method of extraction yields

The ICP method was utilised to analyse the liquid samples, after the proper dilution, for Ni, Co, Fe, Al and Mg. In calculating metal extraction $X_{M,i}$, a volume correction formula was used:

$$X_{M,i} = \frac{(V - \sum_{i=1}^{i-1} v_i) C_{M,i} + \sum_{i=1}^{i-1} v_i C_{M,i}}{m(c_M / 100)} \quad (1)$$

where V is the initial volume (ml) of the solution, v_i the volume (ml) of sample i withdrawn each time, $C_{M,i}$ the concentration of M (Ni, Co, Al, Mg, Fe) in sample i (mg dm^{-3}), m the initial mass of laterite in g (on a dried basis) added into the autoclave and c_M the concentration of M in laterite (wt. % dried solids).

2.5 Experimental structure

The first campaign of experiments investigated four leaching variables associated with four critical factors for treatment of the Rudjinci ore.

Table 1: Leaching Variables

Variable	Parameter	Low Value	High Value
Temperature ($^{\circ}\text{C}$)	A	200	250
Acid to Ore Ratio (g H_2SO_4 / g ore)	B	0.24	0.40
Stirring speed (rpm)	C	250	1500
Time (min)	D	30	60

The significance of these variable was assessed by analysing the results in a 2^4 matrix. From the matrix data, mathematical algorithms will identify if the variation of a leach conditions alters process control, independently and in conjunction with other variables. The matrix values (A, B, C or D) can equal -1, 0 or 1. These data points represent low, median and high values. The number of experiments was defined by Wheeler's formula, Equation (2):

$$N = \left(\frac{7\sigma}{\Delta} \right)^2 \quad (2)$$

Where N =number of experiments, σ = estimated standard deviation, Δ = required degree of confidence (as a fraction). Thus it is necessary to include all experimental runs. Using the following values: $\sigma=4.7\%$; $\Delta=8\%$, it was calculated $N=17$.



3 Results and Discussion

3.1. Working plan

The experimental conditions (working plan) was presented in Tab. 2.

Table 2: Experimental conditions

Number N	Temperature (°C), A	Acid/Ore Ratio (wt/wt), B	Stirring Speed (rpm), C	Time (min), D
1	250	0.40	250	30
2	230	0.24	1500	60
3	230	0.24	1500	30
4	250	0.40	1500	60
5	230	0.40	250	60
6	250	0.40	1500	30
7	250	0.24	250	30
8	250	0.24	1500	30
9	230	0.40	1500	30
10	240	0.32	875	45
11	230	0.40	1500	60
12	250	0.24	1500	60
13	250	0.24	250	60
14	250	0.40	250	60
15	230	0.40	250	30
16	230	0.24	250	30
17	230	0.24	250	60

3.2 Effects of temperature

The temperature tested varies from 200 °C and 250 °C. The reaction temperature has a positive influence on nickel extraction. The increased temperature of 230°C and 250°C led to final nickel values 82 and 86 % (Fig. 3)

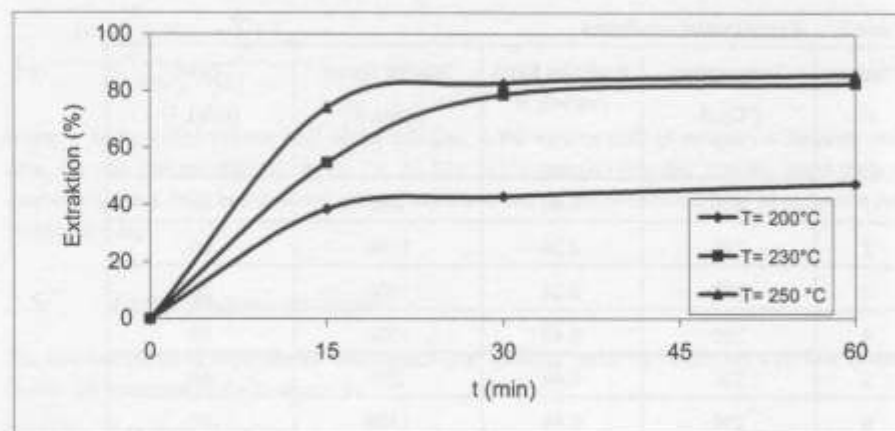


Figure 3: Effects of temperature on the leaching rate of nickel. Leaching was performed in an approximately 10 % pet solid with a/o ratio= 0.40 and $u=250$ rpm)

One-hour leaching tests was performed first at 10 % solid at the temperature of 200 °C with a stirring speed of 250 rpm. The obtained results in Figure 2 showed that about 48 % Ni and 68 % Co can be extracted in 60 min at 200 °C, while the extraction of magnesium amounted 63 %. A temperature of 200 °C apparently does not provide the driving force needed for rapid nickel extraction. By increasing of temperature up to 250 °C the nickel extraction and the initial rate of leaching can be improved (Fig. 3). An increased temperature influences on a separation of nickel from iron, that is the critical step of any nickel-laterite processing route. Nickel is incorporated into nontronite matrices within laterite ores, hence nickel release requires destruction of the host mineral by leaching. The ferric ion is sparingly soluble in dilute acids at temperatures above 230 °C, and precipitates from solution in the shell as an oxide or basic sulphate, depending upon the activity of the sulphate ion in solution, while nickel remains in solution

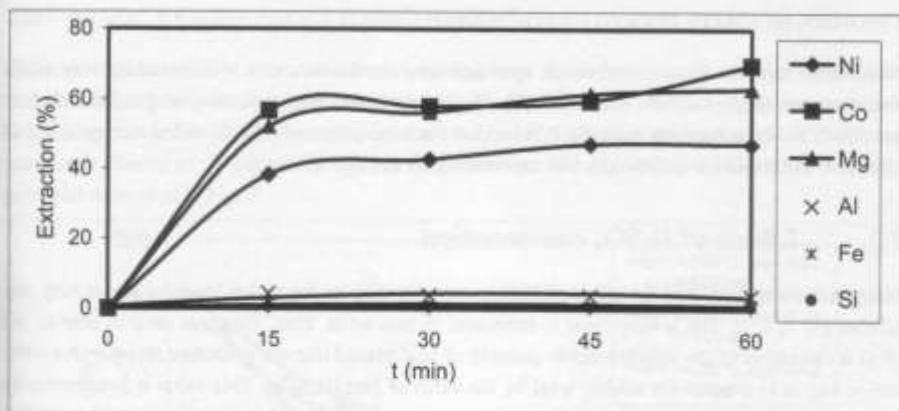


Figure 4: Dissolution kinetics of major metals in nickel lateritic ore at 200 °C. Leaching was performed in an approximately 10 % pct solid with a/o ratio= 0.40 and $u= 250$ rpm)

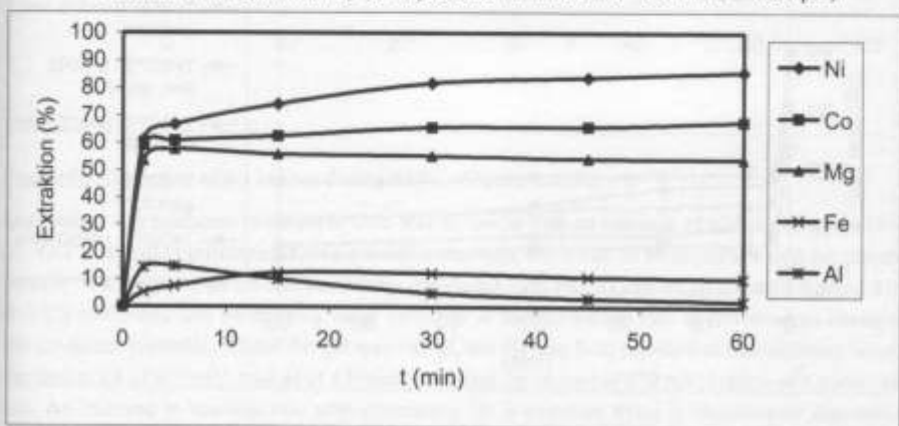
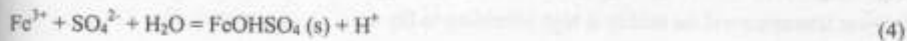
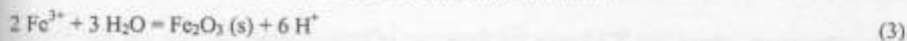
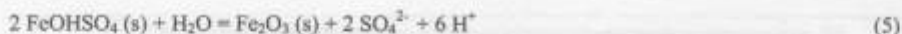


Figure 5: Dissolution kinetics of major metals in nickel lateritic ore at 250 °C. Leaching was performed in an approximately 10 % pct solid with a/o ratio= 0.40 and $u= 250$ rpm)

The reaction temperature, acid/ore ratio and reaction time have a big influence on iron extraction (Fig. 5). Ferric cations hydrolyse rapidly after the dissolution of iron compounds, forming directly hematite or basic ferric sulphate, which can transform to hematite.





Basic ferric sulphate formation depends upon leaching conditions and it is favoured by very acidic environments (high sulphate contents) [9]. High temperatures though, favour the formation of hematite. One-hour leaching tests at 10 % solid at the temperature of 250 °C with a stirring speed of 1500 rpm in 60 min have showed a iron extraction of 2 % (Tab. 2).

3.3 Effects of H_2SO_4 concentration

Many authors showed that the effect of H_2SO_4 concentration on the nickel leaching rate is very significant [4, 7, 8 9]. The acidity level is expressed in two ways. First, the mass ratio of acid-to ore (dry) is indicative of the stoichiometric quantity of acid placed into the autoclave initially. An alternative way is to express the acidity level by the value of free $[\text{H}_2\text{SO}_4]$. This value is fundamentally responsible for driving the dissolution and precipitation reactions which take place, and can be followed by ICP analysis during an experiment.

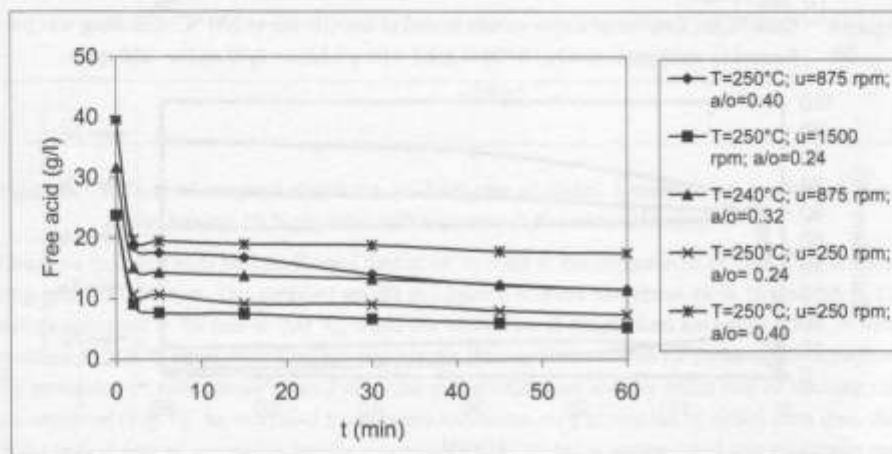
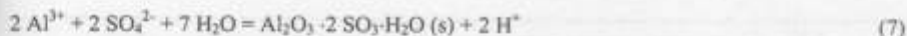


Figure 6: Variation of the free sulphuric acid in time during SAPL of Ni-laterite

Acidity was decreased during leaching. However, the hydrolytic precipitation of iron and aluminium regenerates, eventually leading to stabilisation of the acid concentration. Aluminium cations hydrolyse more slowly according to reaction (6) below 250 °C, leading to the formation of solid products.



High temperature (above 280 °C) favour the formation of basic sulphate, but this can also formed at lower temperature if the acidity is high according to Eq. 6.



Under process conditions, the concentration of dissolved aluminium usually exceeds its solubility and aluminium precipitates as hydronium alunite. As seen in Fig. 6, H_2SO_4 concentration initially drops very fast and essentially remains constant thereafter in all cases. Measurement of Eh of pregnant leach slurries of "Rudjinci" ore give a range between 580 and 630 mV. Variation in oxidation potential were seen in Fig. 7.

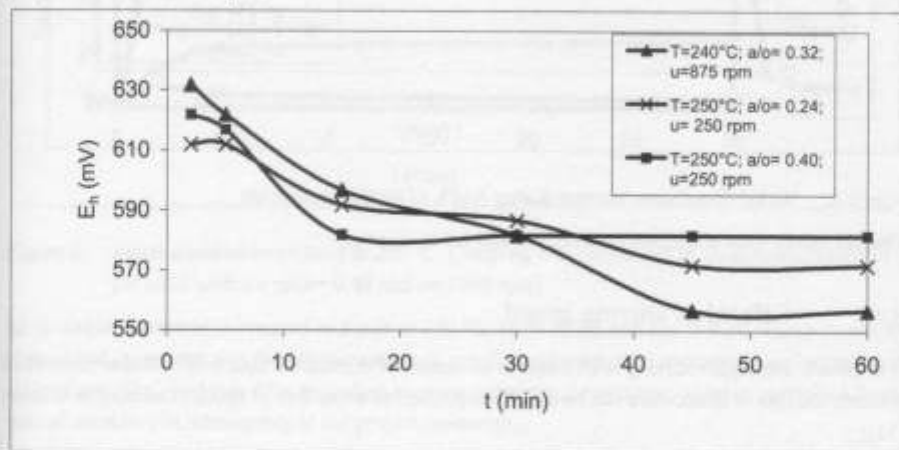


Figure 7: Variation of Eh in time during SAPL of nickel lateritic ore

Decreasing the oxidation potential in time was followed with an increase of nickel extraction (Fig. 8). This is no direct influence of Eh on nickel extraction, but it can be an important sign for process control. We suggest that Eh can be directly correlated with Fe (II) and Fe (III) concentration. Tindall [2] confirmed that remarkably large variation in transformation rate occurred when changing the oxidation potential. Whilst the pH was varied, the Eh was held constant at two different levels, the first at Eh of 850 mV, typical of a limonite ore and the second at 670 mV, typical of a nontronite ore. An increase in reaction rate with decreasing Eh is common trend in metal-oxide dissolution systems when the metal can assume different oxidation state. At low Eh, reduced species in solution (like Fe^{2+}) facilitate electron transfer into the oxide lattice which promotes the breakdown of the oxide lattice by dilute sulphuric acid.

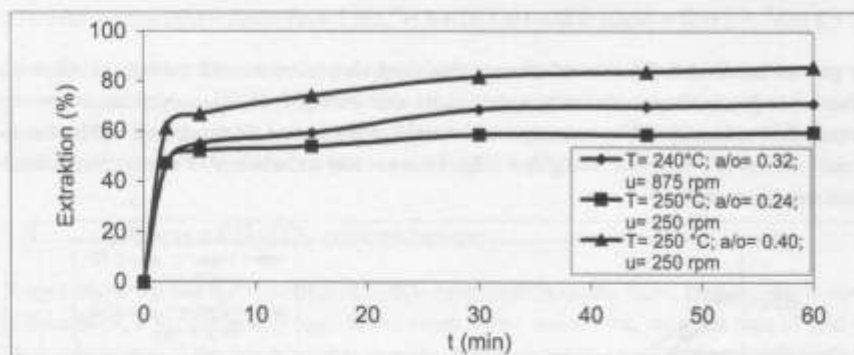


Figure 8: Nickel dissolution kinetics during SAPL of nickel lateritic ore

The pH values were amounted between 0.9 and 1.9 in all cases.

3.4 Effects of stirring speed

It is known that higher stirring rates result in an increased dissolution rate. In a diffusion-controlled process, the rate of dissolution can be usually expressed as a function of speed of stirring as follows [11]:

$$v_D \propto n^a \quad (8)$$

Where: v_D - the rate of dissolution (s^{-1}), n - the number of revolutions, and a - the constant with value of $a \leq 1$. Leaching tests conducted by Georgiou and Papangelakis [9] at various agitation rates between 450 and 650 rpm demonstrated that the agitation rate had a negligible effect of nickel dissolution. Chou et al. [12] showed that nickel extraction is independent of agitation after brief initial mixing period whereas two axial turbines provided ample mixing between 50 and 600 rpm. The same conclusions are presented by Tindall [2] in the agitation range between 130 and 410 rpm. As seen in Figs. 4 and 9, contrary the above mentioned the change from 250 to 1500 rpm increased extraction at 250 °C, 10 % solids and a/o of 0.40.

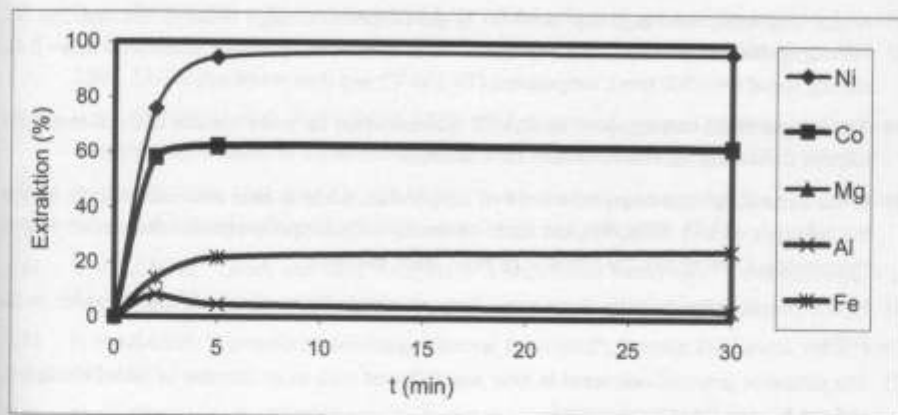


Figure 9: Metal dissolution kinetics at 250 °C. Leaching was performed in an approximately 10 % pct solid with a/o ratio= 0.40 and $u=1500$ rpm)

95 % nickel extraction is attained in 5 min at 250 °C, 10 % solids and a/o of 0.40. These results are unexpected due to the fact that an increasing of metal dissolution need necessarily an increased reaction time. The residence time is limited to some economical maximum volume controlled by the cost of autoclave in relationship to the project economic.

Under the above mentioned conditions an increasing of the stirring speed increased the mass transfer rate and metal extraction decreasing the residence time for leaching. Under these condition the thickness of interface layer is also decreased.

Additional experiments at high temperatures up to 275 °C and different agitation rate are planned to check this influence on nickel extraction for few different ore from Serbia and West Australia.

4 Conclusion

Sulphuric acid pressure leaching was employed for "Rudjinci" ore using a 2- liter titanium autoclave equipped with acid injection and sample withdrawal systems. Nontronite is the main host mineral for nickel in "Rudjinci" in Serbian laterites. The following points summarise the major findings:

- 1) A new system with an acid injection device and system to withdraw sample were successfully applied.
- 2) A temperature of 200 °C apparently does not provide the driving force needed for rapid nickel extraction. By increasing of temperature up to 250 °C the nickel extraction and the initial rate of leaching can be improved.



- 3) Nickel recoveries were high (up to 99 %) in the temperature range between 230 and 250 °C, indicating that nickel extracts from Rudjinci ore as long as there was sufficient acid ($a/o = 0.4$), stirring speed ($u = 1500$ rpm); temperature ($T = 250$ °C) and time ($t = 60$ min).
- 4) An increase of the stirring speed up to 1500 rpm increased the mass transfer rate und metal extraction decreasing the residence time for leaching.
- 5) In the same temperature range the reaction temperature, acid/ore ratio and reaction time have a big influence on iron extraction, but ferric cations hydrolyse rapidly after the dissolution of iron compounds, forming directly hematite or basic ferric sulphate.
- 6) H_2SO_4 concentration initially drops very fast and essentially remains constant thereafter in all cases.
- 7) The oxidation potential decreased in time was followed with an an increase of nickel extraction and can be used for process control.

5 Acknowledgments

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