Kinetics of Leaching of the Serbian Nickel Lateritic Ore

[1]Dr.-Ing Srećko Stopić, [2]Prof. Dr.-Ing. Bernd Friedrich, [3]Dr.-Ing. Nikola Anastasijević

[1]Faculty of Technology and Metallurgy, Karnegijeva 4, 11001 Belgrade, Yugoslavia
[2]IME Process Metallurgy and Metal Recycling, Intzestraße 3, D-52056 Aachen, Germany
[3]Outokumpu Lurgi Metallurgy GmbH, Ludwig-Erhard Straße 21, D-61440 Oberursel, Germany

---

Abstract

The extraction of nickel from the Serbian lateritic ore by sulphuric acid leaching has been studied under atmospheric and high pressure conditions. Atmospheric leaching at temperatures as high as 90°C in 2 hours of time resulted in nickel extraction up to 78 %. It was determined the influence of reaction parameters: temperature, time, sulphuric acid concentration and stirring speed on the kinetics of metal extraction. A titanium autoclave equipped with acid injection and sample withdrawal unit was used in sulphuric acid pressure leaching SAPL. The following parameters are tested: reaction time, pressure, temperature, acid to ore ratio and stirring rate. Studies are done with ore samples (1.1% Ni and 52.7 % SiO_2) 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 optimal parameter of leaching process for nickel lateritic ore. The initial solids, as well the leach residues, are characterized by chemical and thermal techniques such as: Inductively Coupled Plasma ICP; thermal gravimetric analysis TGA in order to determine the effects of investigated parameters on the nickel leaching degree.

1 Introduction

Nickel demand has grown at an historic average annual rate of approximately 4 % 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 from 40 % to about 50 % of the 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 40 % of the world nickel production originates from, and 54 % of the total reserves are found in laterites.

Leaching from the laterite ore at atmospheric pressure is mentioned by many authors [4-6]. Halikia [4] 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 so at higher concentration. Temperature had a marked influence on nickel extraction.

Kontopoulos [5] has studied the extraction of nickel and cobalt from low-grade Greek laterites by sulphuric acid leaching at atmospheric pressure and temperatures as high as 95 ^{o}C on a continuous mini plant. An extraction of 82 % of Ni and 75 % Co was achieved by leaching for 4 h at 95 ^{o}C with 3 N sulphuric acid, and 25 % pulp density.

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

Sulphuric acid pressure leaching of nickeliferous laterites has attracted considerable attention from the nickel industry during the 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 ^{o}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, the optimal conditions for leaching of nickel from the Serbian nickel laterite under atmospheric pressure are 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. The main aim of this paper is to establish parameters of nickel laterite leaching from deposits in Yugoslavia with a use of sulphuric acid in autoclave, namely, reaction time and temperature, total gas pressure, and acid concentration necessary for maximum transfer of nickel into solution. It studies the influence of the above parameters on the total speed of the process. 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 $Mg_3Si_2O_5(OH)_4$ variously decomposed into nontronite $Fe_2Si_4O_{10}(OH)_2$. Therefore, silicates are the major and most important component of the deposits. In our experiments the sample represents a pre-concentrate of “Rudjinci” ore previously homogenized. The composition of pre-concentrate is (%): 54.2 SiO_2; 14.9 Fe; 4.00 Al_2O_3; 1.09 Cr_2O_3; 1.13 Ni; 0.06 CoO; 1.40 CaO; 3.22 Mg; 0.48 MnO; 0.05 Na_2O and 0.05 K_2O.

2.2. Experimental procedures and analytical methods

The leaching kinetics experiments at atmospheric pressure 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 was dispersed in 200 ml of determined water solution, heated to a specified temperature. Then the sulphuric acid is injected in solution at the investigated temperature. After a given period of reaction 1 ml of suspension was 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 was then diluted to the 100 ml mark. After filtration, the concentration of metals in the filtrate was determined by an inductively coupled plasma spectrophotometry. The leaching process was evaluated by an extraction of metal, defined as the fraction of a given element in the field leached out over given period of time.

Under high pressure leaching conditions tests were performed in a 2l autoclave, manufactured by the Autoclave Engineers, USA. Figure 1 shows overview the present autoclave plant at IME, Aachen.

Figure 1: Autoclave at the IME, RWTH Aachen

Temperature was controlled within ± 1 ^{o}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. A 90 g ore sample 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 predeterminated temperature in the range of 200 to 250 ^{o}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 IME injection device. Using the new sampling system 20 ml of liquid was periodically withdrawn through a dip tube and then rapidly cooled. After the end of experiments, solutions aliquots were filtered and analysed aiming Ni, Co, Mg, Al, Fe and Si by an inductively coupled plasma ICP spectrophotometry. 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 ^{o}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 0.48 g H_2SO_4/g ore. After leaching the pH and Eh values of the obtained solution were measured. Eh measurements were taken using a platinum electrode and reference Ag/AgCl electrode. The pH was calibrated using pH standards (pH 1 and 7)

3 Results und discussion

3.1. Leaching of laterite ore “Rudjinci”, Serbia under an atmospheric pressure

The effect of temperature on nickel leaching from nickel laterite is shown in Figure 2.

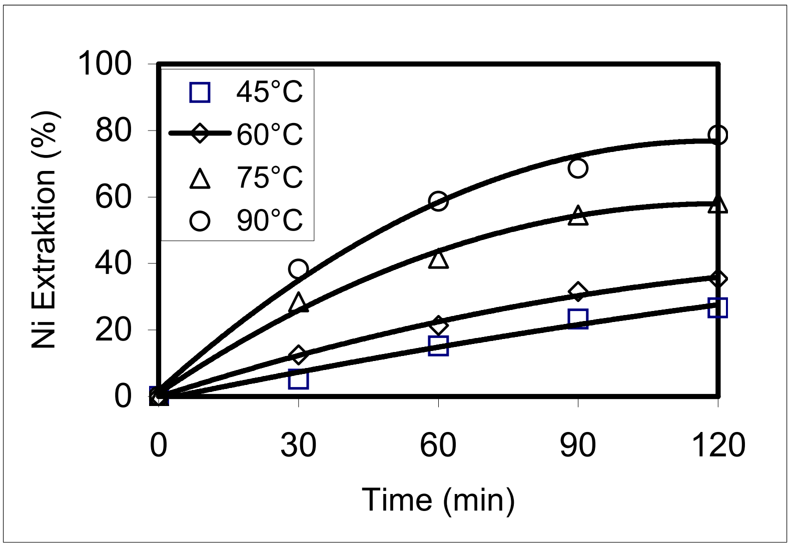

Figure 2: Effect temperature on nickel leaching kinetics

As it can be seen the nickel extraction increases with increasing leaching time. The maximal obtained value of nickel extraction amounts α= 78 % at temperature of 90^{o}C in time of 120 min using sulphuric acid concentration of 0.2 mol/l. As shown in Fig. 2 leaching of nickel ore consumes sulphuric acid. SiO_2 represents a main compound in a solid product after leaching. The required leaching time to reach the maximum increases with decreasing leaching temperature.

The results in Figure 3 show that extraction of metals increases with increasing of sulphuric acid dosage.

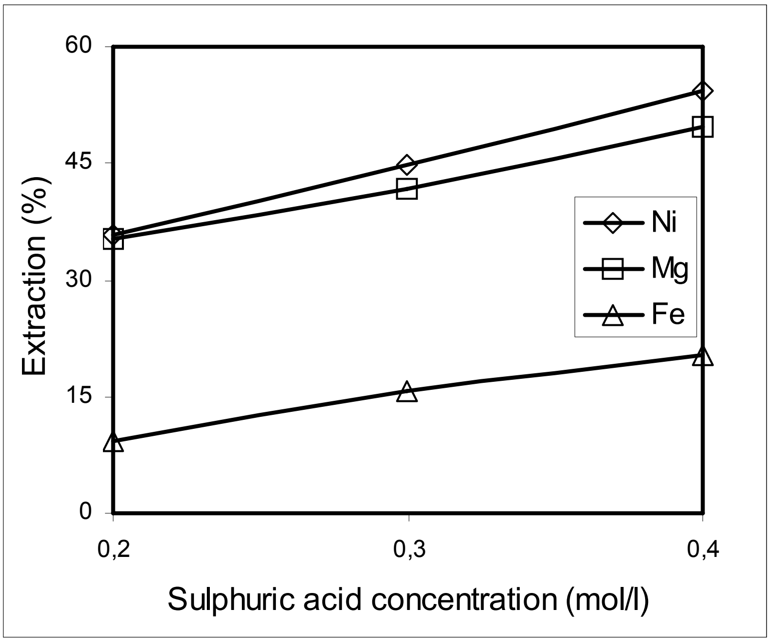

Figure 3: Effect of sulphuric acid dosage on the extraction of nickel, magnesium and iron

The increasing of sulphuric acid concentration from 0.2 mol/l to 0.4 mol/l at 60^{o}C increases an extraction of nickel and magnesium for 20 %, and iron extraction for 10 %, respectively. The results show that an extraction of nickel and magnesium is almost three times higher than iron during leaching.

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 range from 700 to 900 rpm (Fig. 4).

The increasing of 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 aluminium is the smallest, and nickel is the highest. There is a difference in dissolution of Ni, Mg, Fe and Al, however a selectivity in this conditions is not demonstrated. To have a better control of the leaching process, it is important to establish a quantitative measurement of the leaching kinetics and mechanism.

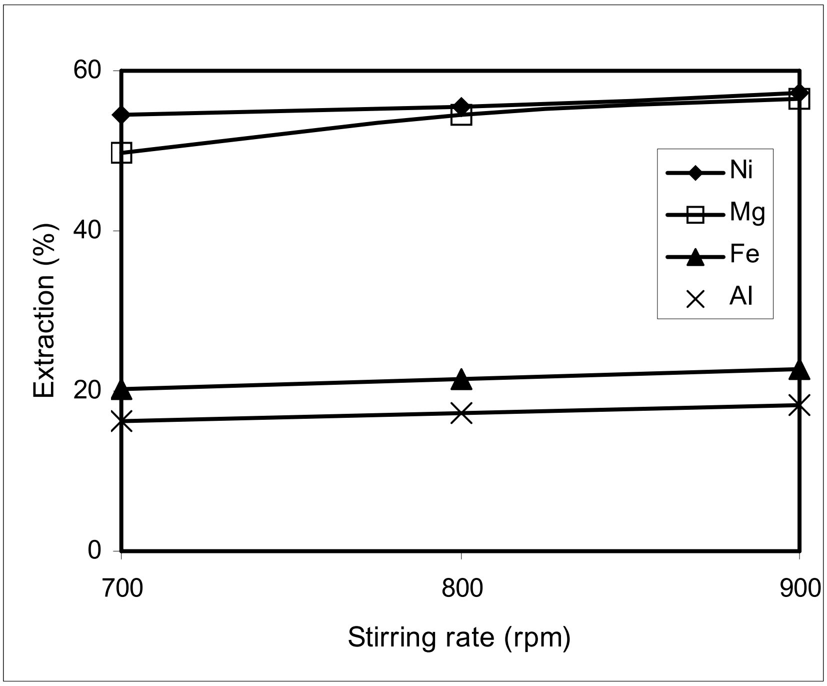

Figure 4: Effect of stirring speed on the metal extraction

3.2. Leaching of laterite ore “Rudjinci”, Serbia under high pressure conditions

One-hour leaching tests were performed first at 10 % solid in the temperature range between 200 and 250 °C with a stirring speed of 250 rpm. The obtained results in Figure 5 showed that about 48 % Ni and 68 % Co can be extracted in 60 min at 200 °C, while the extraction of magnesium amounted 63 %.

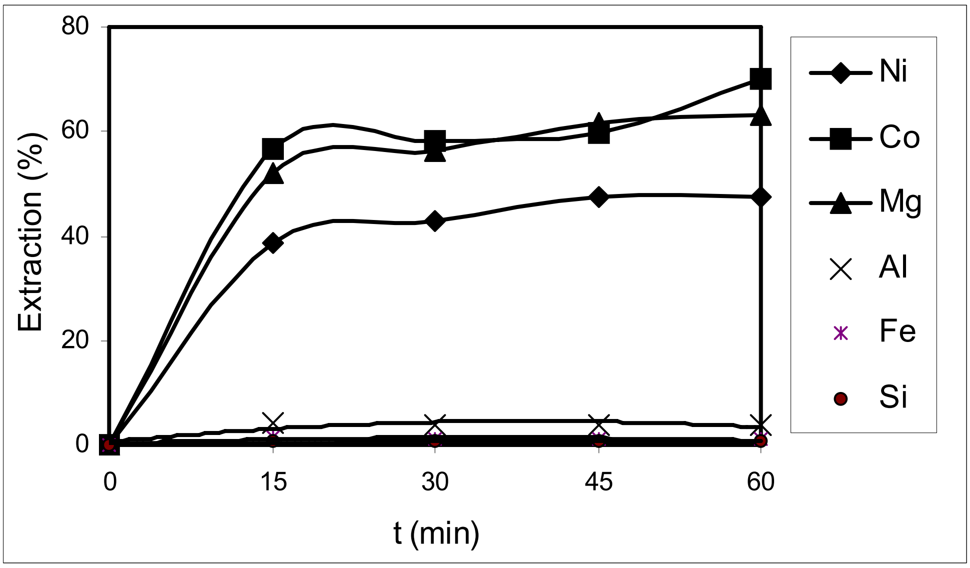

Figure 5: Metal dissolution kinetics at 200 °C (10 % solid; a/o= 0.40; u = 250 rpm)

The increased temperature of 230 °C led to final nickel, cobalt and magnesium extraction values of 93; 78 and 83 % (Fig. 6). Holding the temperature at 250 °C but increasing the acid to ore ratio (a/o) from 0.4 to 0.48 about 96 % Ni and 62 % Co is extracted in 30 min (Figure 7).

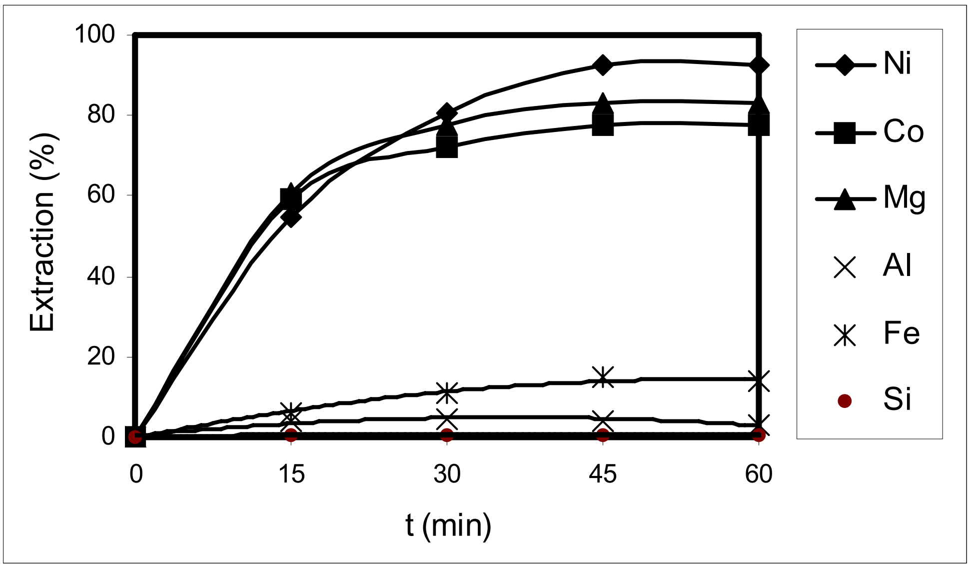

Figure 6: Metal dissolution kinetics at 230 °C (10 % solid; a/o= 0.40; u = 250 rpm)

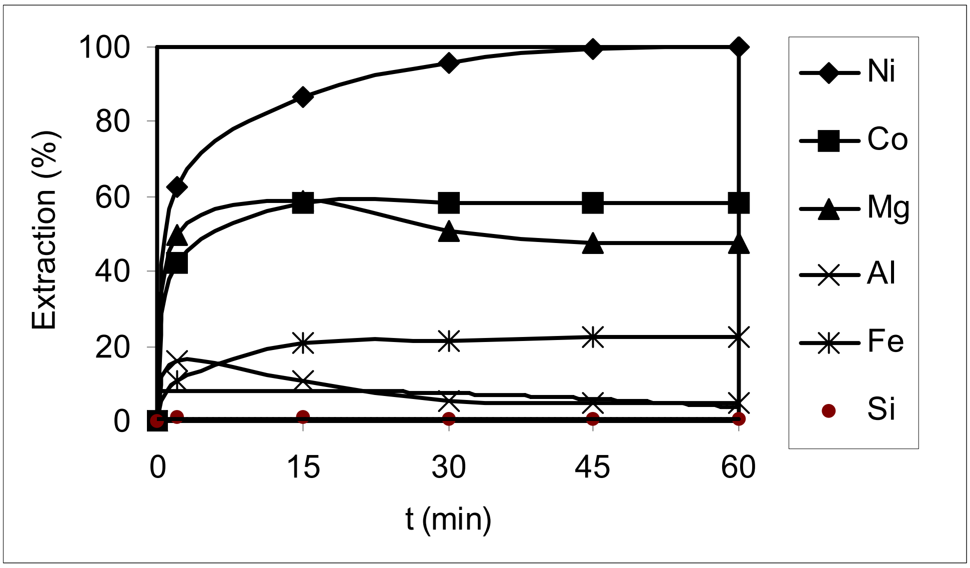

Figure 7. Metal dissolution kinetics at 250 °C (10 % solid; a/o= 0.48; u = 250 rpm)

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. Figure 8. summarizes that higher temperatures by allowing higher pressures in the autoclave the total nickel extraction increases.

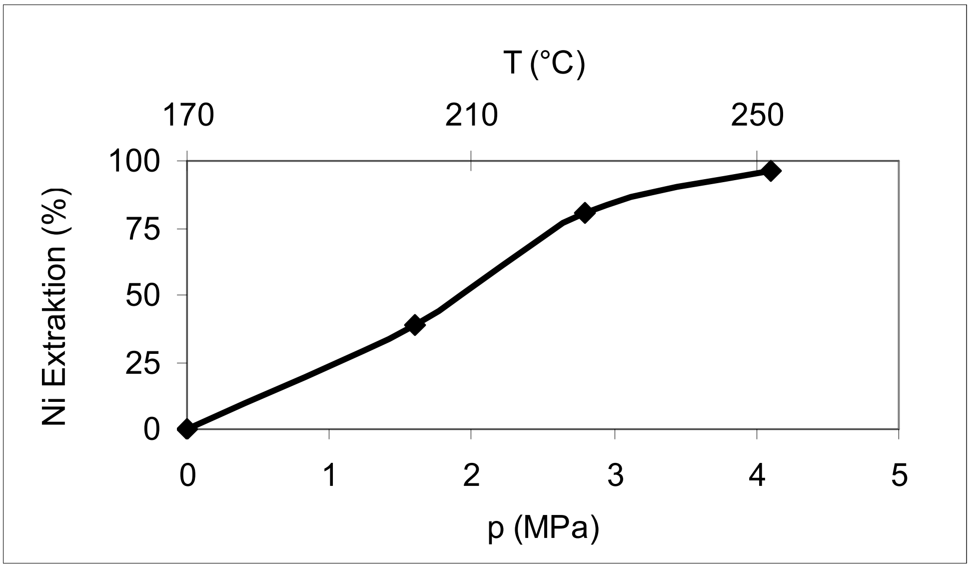

Fig. 8. Nickel extraction as a function of temperature/pressure in the autoclave
t = 30 min; a/o = 0.24 g H_2SO_4 / g Ni ore; and 10 % solid

One variable requiring careful control is the amount of acid added to a given weight of ore i.e., acid/ore (a/o) ratio, because it' s effects significantly the time required to attain a given level of nickel extraction. 56 % Ni extraction is attained in 5 min at 230 ^{o}C, 10 % solids and 0.24 a/o ratio. The change from 0.24 to 0.40 a/o ratio increased extraction of nickel from 56 % to 77 % Ni under same conditions (Fig. 9 and 10). Unfortunately, the same change increased the quantity of iron in pregnant liquor from 6 % to 12 % and the leach selectivity is decreased (Table 1).

Table 1: Effect of acid/ore ratio on metal extraction at 230 ^{o}C, 10 % solids in 5, 30 and 60 min

acid / ore ratio	Ni/Fe			Ni/Al		
	5 min	30 min	60 min	5 min	30 min	60 min
0.24	8.7	4.8	4.0	22.5	43.8	58.9
0.40	6.43	3.84	3.0	5.84	39.05	58.4

The Ni/Al ratio increases with time reflecting the relative rate of hydrolysis of this impurity. Additional experiments at high temperatures up to 275 °C are planned to check this influence on nickel extraction.

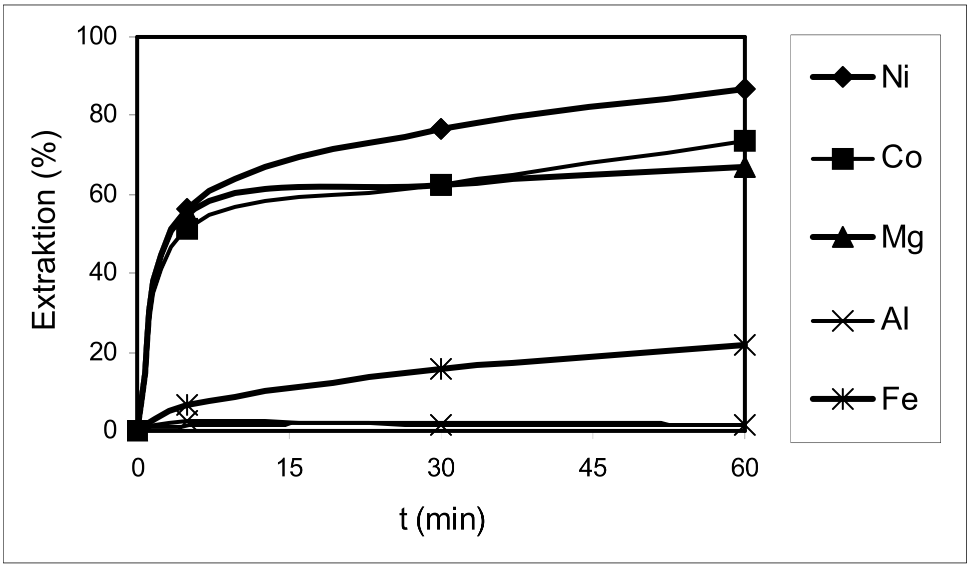

Figure 9: Metal extraction at 230 °C, 10 % solids, u> 250 rpm and 0.24 acid/ore ratio

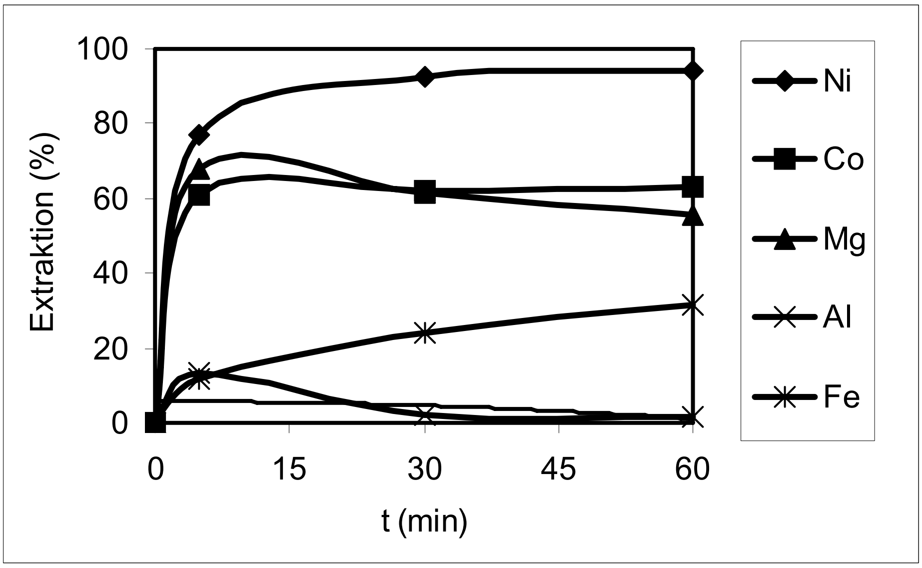

Figure 10: Metal extraction at 230 °C, 10 % solids, u> 250 rpm and 0.40 acid/ore ratio

Free sulphuric acid amounted between 8 g/l and 20 g/l.

3.2.1. TGA analysis of a solid product

After a leaching of nickel laterite ore and filtration, a solid rest is dried at 100 °C over night. TGA is performed in Argon and showed on Fig. 11. It is known that HPSAL of nontronite ore ends up with a the solid product that contains SiO_2, Fe_2O_3 and $(H_3O^+, Na^+)Al_3(SO_4)_2(OH)_6$ [5]. TGA showed that the mass loss obtained from 200 up to 250 °C and a/o ratio from 0.24 to 0.48 increased from 12 up to 28 %. The sample obtained under this conditions showed the biggest mass loss of Δ m = 28 %.

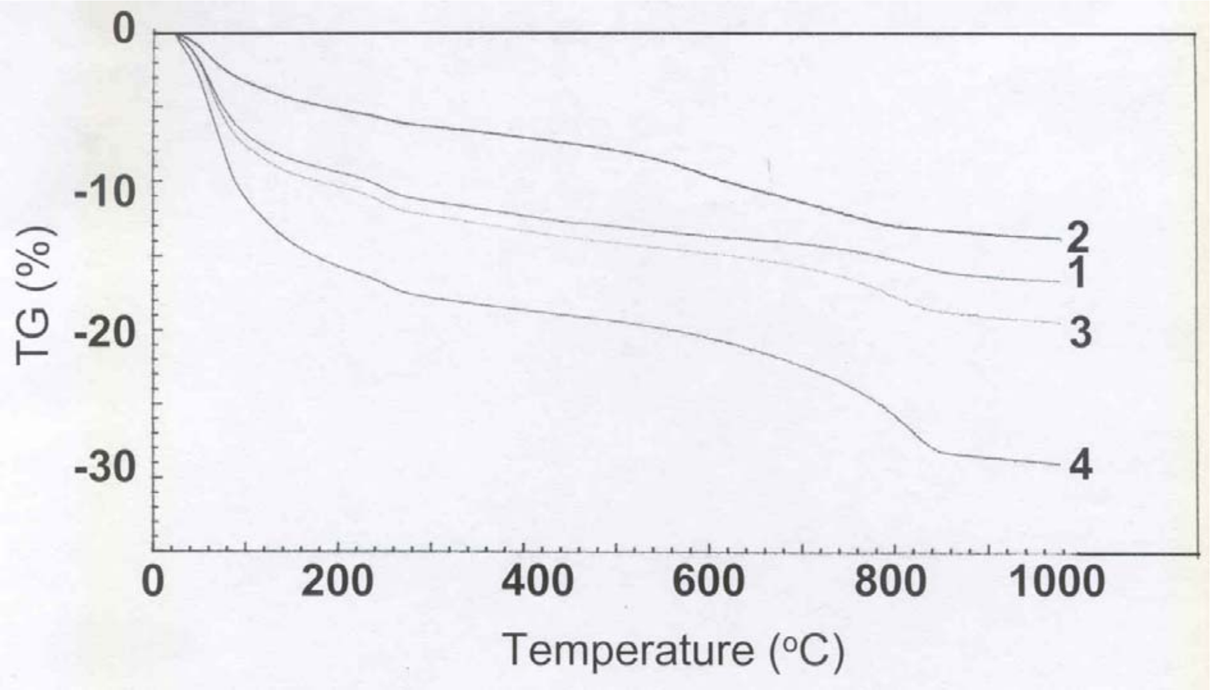

Fig. 11. TGA in argon for leach residue obtained by HPSAL of Ni lateritic ore under following conditions:

1) T = 230 °C; a/o = 0.24; Δm = 16 %; 2) T = 200 °C; a/o = 0.24; Δm = 12 %

3) T = 230 °C; a/o = 0.40; Δm = 20 %, 4)T = 250 °C; a/o = 0.48; Δm = 28 %

4. Conclusion

Leaching of the Serbian lateritic ore by sulphuric acid was firstly done under the atmospheric pressure. The following point summarise the finding:

1) The leaching at temperatures as high as 90°C generally resulted in nickel extraction up to 78 %.

2) The nickel extraction increases with increasing leaching temperature and time.
3) The increase of sulphuric acid concentration from 0.2 mol/l to 0.4 mol/l at 60 °C increases the extraction of nickel and magnesium to about 20 %, and iron extraction to about 10 %, respectively.
4) The increase in stirring speed from 700 to 900 rpm had a negligible effect on the dissolution rate of Ni, Mg, Fe and Al.
5) The diffusion through the layer of SiO_2 may be the rate controlling step.

Sulphuric acid pressure leaching was employed for “Rudjinci“ ore using a 2- liter titanium autoclave equipped with acid injection and sample withdrawal systems. It was concluded:

1) A temperature of 200 ^{o}C apparently does not provide the driving force needed for rapid nickel extraction. By increasing of temperature up to 250 ^{o}C the nickel extraction and the initial rate of leaching can be improved.
2) Nickel recoveries were high in temperature range between 230 and 250 °C, indicating that nickel readily extracts from Rudjinci ore as long as there was sufficient acid (a/o= 0.4), stirring speed (u>250 rpm); temperature (T= 250 ^{o}C) and time (t= 60 min).
3) 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.

5. Acknowledgments

We would like to thank the Alexander von Humboldt Foundation for its research fellowships for Dr. Srećko Stopić allowing a 15 month stay at IME Process Metallurgy and Metal Recycling, RWTH Aachen.

6. References

[1] W. G. BACON, A. D. DALVI, B. A. ROCHON: “Nickel Outlook- 2000 to 2010”, CIM Bulletin, Vol. 95, 2002, 47-52.

[2] G. P. TINDALL: “High Temperature Acid Leaching of Western Australian Laterites”, Doctoral Thesis, Murdoch University, 1998, 214.

[3] F. W. WELLMER: “Leachable supergene base and precious metal deposits worldwide”, Erzmetall, Vol. 55, 2002, 25-33.

[4] I. HALIKIA: “Parameters influencing kinetics of nickel extraction from a Greek laterite during leaching with sulphuric acid at atmospheric pressure”. Trans. Inst. Min. Metall. (Sect. C: Mineral Process. Extr. Metall), Vol. 100, 1991**,** 154-164.

[5] A. KONTOPOULOS: “Sulphuric acid leaching of laterites”, In: Extraction & Processing Division of TMS, Ed. Gaskell, D.R, (San Francisco: TMS, Warrendale, PA), 1991, 147-163.

[6] D. R. VUČUROVIĆ: “Study of possibility of nickel valorisation from its ore in Serbia,” Report, Faculty of Technology and Metallurgy, Belgrade, 1983, 271. (in Serbian)

[7] D. H. RUBISOV, V.G. PAPANGELAKIS: “Sulphuric acid pressure leaching of laterites-speciation and predication of metal solubilities at temperature,” Hydrometallurgy, Vol. 58, 2000, 13-26.

[8] D. H. RUBISOV, V.G. PAPANGELAKIS: “Sulphuric acid pressure leaching of laterites-a comprehensive model of a continuous autoclave”, Hydrometallurgy, Vol. 58, 2000, 89-101.

[9] D. GEORGIOU, V.G. PAPANGELAKIS: “Sulphuric acid pressure leaching of a limonite laterite: chemistry and kinetics”, Hydrometallurgy, Vol. 49, 1998, 23-46.