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KINETICS OF SULPHURIC ACID LEACHING OF THE SERBIAN NICKEL LATERITIC ORE UNDER ATMOSPHERIC PRESSURE

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ABSTRACT

Kinetics of nickel leaching under atmospheric pressure from the Serbian nickel lateritic ore by sulphuric acid has been studied in this paper. Atmospheric leaching at temperatures as high as 90°C for 2 hrs generally resulted in nickel extraction up to 78%. Also the influence of reaction parameters: temperature, time, sulphuric acid concentration and stirring speed on the kinetics of metal extraction was presented. Kinetics analysis showed that the nickel dissolution from lateritic ore can be described by "diffusion model".

Key words: kinetics, nickel lateritic ore, atmospheric pressure

1. INTRODUCTION

As a result of the ever increasing costs of nickel production associated with traditional pyrometallurgical techniques and depletion of high-grade sulphide ores, renewed interest has recently developed for the production of nickel and cobalt from laterite deposits [1]. Today, 40 % of the world nickel production originates from laterites, which also present 54 % of the total reserves [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. E&MJ' 2002' s mine projects survey, compiled by Raw Materials Group (RMG) of Stockholm indicates that amongst 650 listings in the RMG project database 53 are nickel projects, such as acid pressure leach hydrometallurgical projects [3]. Because of the large presence of nickel laterite in South-East Europe and a small number of plants for hydrometallurgical production of nickel a need for studies of leaching under atmospheric and high pressure exists.

In this paper, we discuss the kinetics of the sulphuric acid leaching process for the Serbian nickel laterite under atmospheric pressure. The optimal conditions for leaching of nickel are prior determined and presented earliner [4]. The main aim was to understand the kinetics of leaching process of nickel from nickel lateritic ore.

2. METAL LEACHING SYSTEMS WITH SULPHURIC ACID

The main sulphuric acid leaching reaction for nickel lateritic ore under atmospheric conditions are presented in [4]. The dominant leaching reactions can be further identified from the corresponding (%) Me-pH diagrams with pH values between 0 and 2. In program "Stability calculation for aqueous system", USA four such diagrams for Ni, Mg, Al and Fe leaching systems (Figure 1a. - 1d) using following database [5-7] are designed.

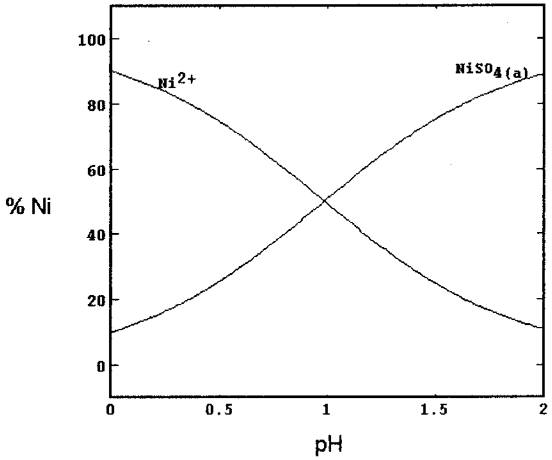

Figure 1a - % Ni - pH diagram of a nickel leaching system in 0.4 mol H_2SO_4 solution at temperature of 90° C

Nickel, cobalt and manganese in the assumed form of "oxides", remain in the aqueous phase as sulphates. Nickel and magnesium show the same behavior (Figure 1a. and 1b.). It is known that the solubility of metal sulphates in water increases as the temperature is raised above room temperature. Inverse solubility of many metals can occur at elevated temperatures. This trend exists also in acid leach conditions at atmospheric pressure.

Colović [8] reported that the solubility curves of magnesium sulphate and iron sulphate have maximum at 68 °C and 65 °C respectively. Chou et al. [9] confirmed the above mentioned values, adding the values for nickel sulphate and cobalt sulphate (100 °C and 70 °C, respectively).

Aluminum in the assumed form of bohemite dissolves remaining in the aqueous phase as sulphates (Figure 1.c).

Iron in the form of goethite FeOOH and nontronite $Fe_2Si_4O_{10}(OH)_2$ dissolves to ferric sulphates. If content of iron is very high (82-100 %), ferric cations can hydrolyze rapidly after the dissolution of goethite and nontronite forming hematite Fe_2O_3 or basic ferric sulphate $H_2Fe_3(SO_4)_2(OH)_7$ (Figure 1d).

Basic ferric sulphate formation depends upon leaching conditions and it is favored by very small pH values (pH=0.2).

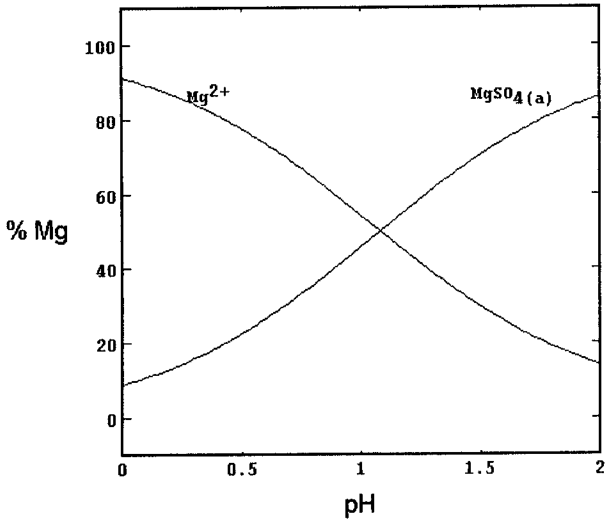

Figure 1b - % Mg - pH diagram of a magnesium leaching system in 0.4 mol H_2SO_4 solution at temperature of 90^0 C

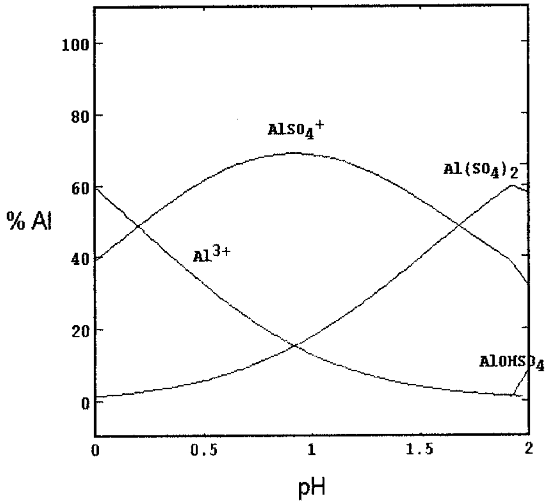

Figure 1c - % Al - pH diagram of an aluminum leaching system in 0.4 mol H_2SO_4 solution at temperature of 90^0 C

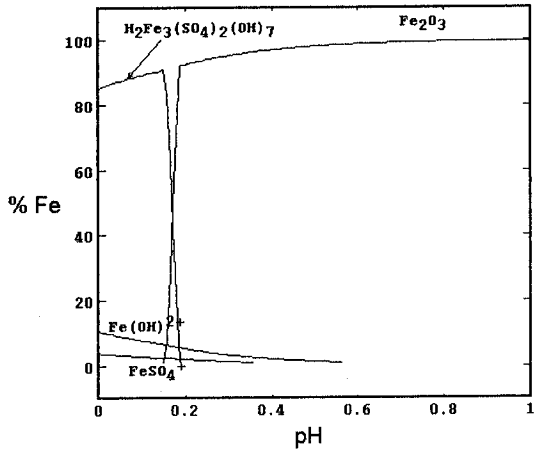

Figure 1.d - % Fe - pH diagram of an iron leaching system in 0.4 mol H_2SO_4 solution at temperature of 90°

High temperatures favor the formation of hematite. Ferric sulphate is present in an aqueous solution for a small content of iron up to 20 %.

The solubility of silica is not pH dependent. But silica is inorganically soluble only under high pHs. However organic acids can dissolve silica under low pHs. Terry reported [10] that the leaching of silicate laterites (garnierite) in 6 M HCl gives only a few mg/l of silica in solution, even after extensive exposure.

3. EXPERIMENTAL

3.1. 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 has a speed range from 50 to 1100 rpm. The temperature of the silumin heating plate of the instrument is set on the rotary knob "temp" with its corresponding dial (0-300 °C). 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 (α) of a given element in the field leached out over given period of time.

In our experiments the sample represents a pre-concentrate of previously homogenized "Rudjinci" ore. 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. The experiments were done at 45; 60; 75 and 90 °C in time up to 2 hours. Distilled water was used as a solution agent. The concentration of the used solutions amounted from 0.2 to 0.4 mol H_2SO_4 g/l with an constant ore-liquid ratio of 0.1. pH value of obtained solution after leaching amounted between 0 and 1. The stirring speed ω was from 700 to 900 rpm. The investigated particle size was between 50 and 160 μm.

The Microwave digestion system with HPR-1000/10 S Segment Rotor, MWS-Vetriebs GmbH, Germany was used for preparation of nickel ore samples for chemical analysis. Thermogravimetric TGA and differential thermal analysis DTA of nickel ore and solid products were carried out in an argon atmosphere in temperature range between 25 and 1000 °C using Derivatograph NETZSCH STA 409 with an α–Al_2O_3. The heating rate amounted 1 °C/min.

3.2. Results and discussion

Vučurović et al. [11, 12] have studied the optimal conditions for leaching of Serbian nickel lateric ore under atmospheric and high pressure conditions without a kinetics analysis of the process. They have obtained high degree of nickel and cobalt recovery in ammonium-carbonate and sulphuric acid leaching conditions.

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

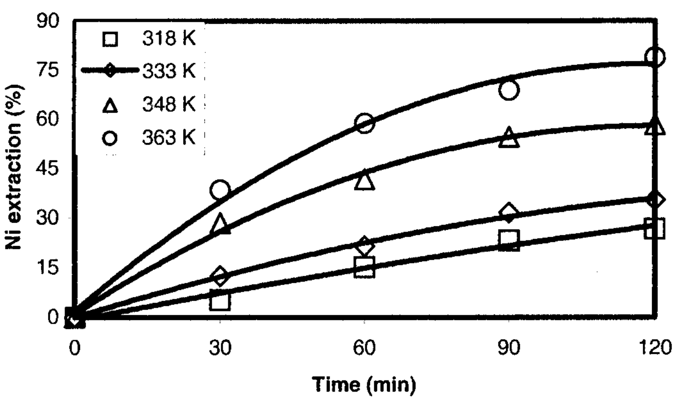

Figure 2 - Effect of temperature on nickel leaching kinetics. Leaching was performed in an approximately 10 % solid with sulphuric acid concentration of 0.2 mol/l

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 363 K in time of 120 min using sulphuric acid concentration of 0.2 mol/l. The required leaching time to reach the maximum increases with decreasing leaching temperature. The increasing of sulphuric acid concentration from 0.2 mol/l to 0.4 mol/l at 333 K increases extraction of nickel and magnesium for 20 %, and iron extraction for 10 %, respectively. The results show that extraction of nickel and magnesium is almost three times higher than for iron during leaching [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 [4].

3.3. Apparent activation energy of nickel leaching

To have 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 [13]. For an diffusion-controlled process of spherical particles, the kinetics equation is given by Eq. (1):

$$1-3\,(1-\alpha)^{1/3}+2\,(1-\alpha)=k\cdot t \qquad (1)$$

where:

α–the extraction at the given temperature and k-the rate constant.

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

$$1-(1-\alpha)^{1/3}=k\cdot t \qquad (2)$$

The absence of a linear relationship between $1-(1-\alpha)^{1/3}$ and leaching time suggests that the nickel leaching from nickel lateritic ore by sulphuric acid is not controlled by external diffusion and chemical reactions [4]. The nickel extraction data are plotted using the inner-diffusion model, as shown in Fig. 3, where the equations with values of rate constant (k (318 K)= 0,0002; k (333 K)= 0,0004; k (348 K)= 0,0014; and k (363 K)= 0,003 mol m^{-2} min^{-1} are situated.

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 which the sulphuric acid must pass to reach untreated lateritic ore. The leaching rate is therefore very fast, the leaching of Ni and Mg proceeds with the same rates, faster than the leaching ofFe and Al. At a certain thickness of the layer, diffusion through the layer of SiO_2 is becoming the rate controlling step.

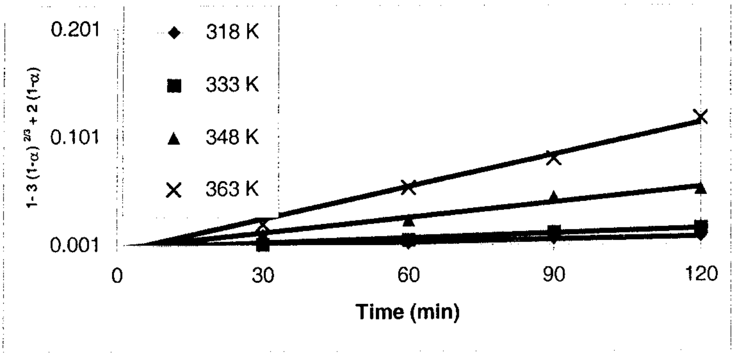

Figure 3 - Linear fit of nickel leaching kinetics to inner diffusion control model.

The experimentally determined rate constant (k) was plotted as a function of the reciprocal of the leaching temperature on a semi log scale, as shown in Figure 4, and a linear relationship was observed.

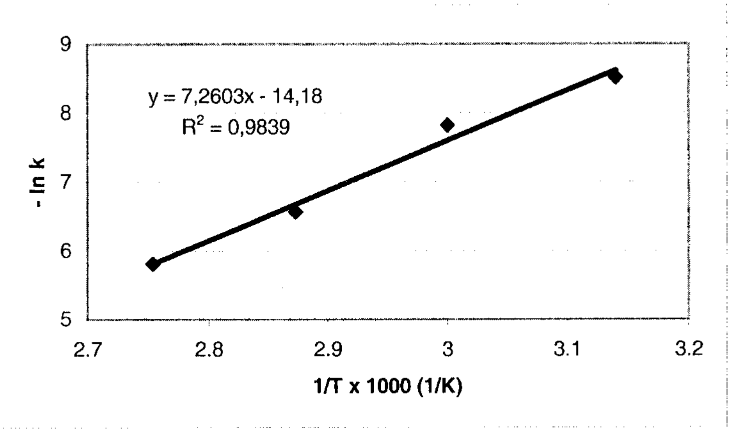

Figure 4 - Arhennius plot of leaching of nickel laterite by sulphuric acid

Following the Arrhenius equation (ln k = ln A – E/RT), an apparent activation energy of 60 kJ/mol was obtained (Figure 4).

Rinn and Fetting [14] calculated the energy activation of E_a = 40, 2 kJ/mol for leaching of nickel from a serpentine with particle size <160 μm in hydrochloric acid. They observed that the process is divided into two parts. In the first a high rate of nickel dissolution is controlled by chemical reaction and then a porous layer controls the process.

Halikia [15] mentioned the 44-150 μm fraction of a pre-reduced garnieritic laterite with sulphuric acid solution (5-50 g/l) and simultaneous feeding of air at low temperatures (30-40°C). She reported that the mechanism of dissolution of metallic nickel was electrochemical in nature and that nickel extraction followed a first-ordered rate equation with an activation energy E_a= 46 kJ/mol.

3.4. TGA and DTA analysis of solid product

TGA and DTA analyse of solid product in argon confirmed different behaviour of obtained solid products (Figure 5.a. and Figure 5.b).

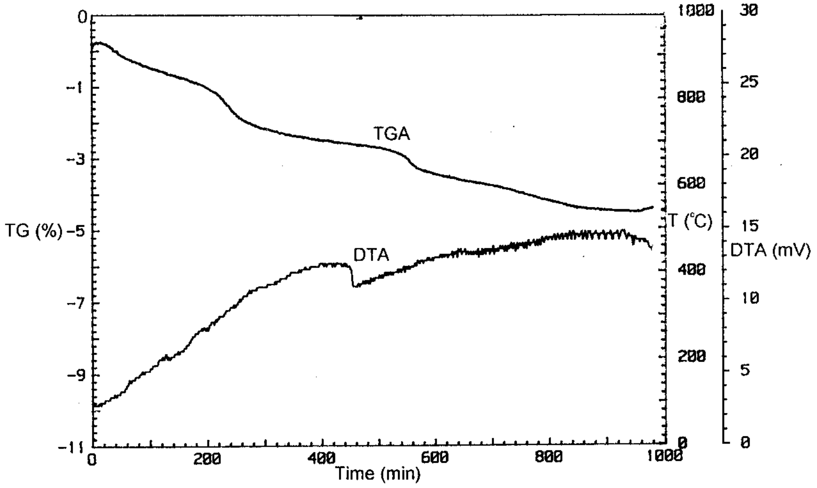

Figure 5a - DTA and TGA analysis in argon for products based on iron compounds obtained after leaching

After leaching of nickel lateritic ore and filtration, a SiO_2 based solid rest stayed with a small part of undissolved dark Fe_3O_4. These two parts are divided and dried at 100 °C over night before DTA and TGA analysis. The total mass loss of water amounted from 31 to 35 % during the above mentioned drying.

The mass loss for iron based product amounts about 5 %, and for SiO_2 based one 25 %. It is possible that air caused the oxidation of magnetite to maghemite, $\gamma\text{-}Fe_2O_3$, at about 450 °C.

$$4\,Fe_3O_4 + O_2 \rightarrow 6\,Fe_2O_3 \tag{3}$$

The mass loss for the rest had two times higher value than one for nickel lateritic ore under same conditions [4]. This is a consequence of decomposition of formed $Si(OH)_4$ to SiO_2.

It is known that because of the strength of Si-O bonds, infinitive silicates (chain, sheet and network) are not easily broken down into smaller silicate units and therefore most infinite silicates leave a siliceous residue acid attack [16].

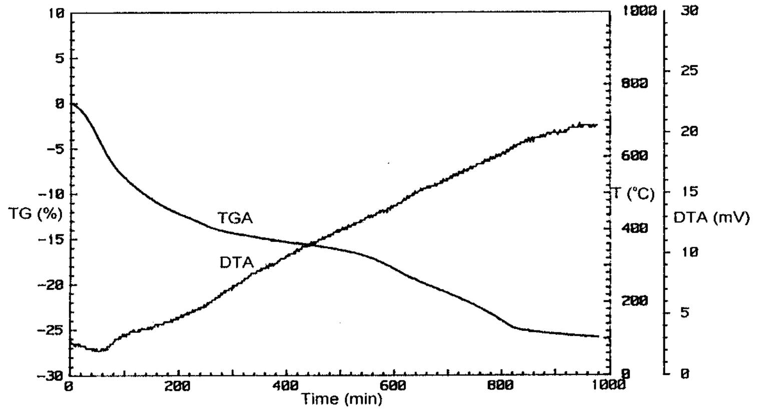

Figure 5b - DTA and TGA analysis in argon for product based on SiO_2 obtained after leaching

4. CONCLUSION

Leaching of the Serbian lateritic ore by sulphuric acid under atmospheric pressure at temperatures as high as 90°C generally resulted in nickel extraction up to 78 %. The nickel extraction increases with increasing leaching temperature and time. The increasing of sulphuric acid concentration from 0.2 mol/l to 0.4 mol/l at 333 K increases extraction of nickel and magnesium for 20 %, and iron extraction for 10 %. The increasing of stirring speed from 700 to 900 rpm had a negligible effect on the rate of Ni, Mg, Fe and Al dissolution. The results show that the nickel dissolution from lateritic ore is controlled by inner diffusion control model where diffusion through the layer of SiO_2 is the rate controlling step.

Acknowledgments

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