KINETIC MODELS OF NICKEL LATERITE ORE LEACHING PROCESS

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Abstract: The subject of this study is leaching process of nickel-bearing laterite ore from Ržanovo, R. Macedonia. The influence of sulfuric acid concentration (0.5, 1 and 3 M H2SO4) on the extracted Ni (%, wt.) was studied. The leaching process intensified by magnetic stirring at different temperatures (298, 323, 348 and 363 K) in the time interval of 120 min. was performed. The results were used for kinetic analysis of the leaching process. It was found that for 3 M H_2SO_4, the best fitting has shown the Jander and Ginstling-Braunshtein models, which point out that limiting step of the process is diffusion. Activation energy was calculated to be 42,67 $kJ \cdot mol^{-1}$ (Jander model) 40,28 $kJ \cdot mol^{-1}$ (Ginstling – Brousthein model), which confirm the diffusion controlled process.

Keywords: NICKEL LATERITE ORE, LEACHING, KINETIC MODELS, ACTIVATION ENERGY

1. Introduction

Nickel is a silver white metal, with face centered cubic cell (FCC) showing good mechanical properties and corrosive resistance. Due to this, it is used as alloying element in steels as an austenitic stabilizer, forming variety of stainless steel with excellent mechanical properties [1, 2]. Nickel-bearing ores significant for industrial production are classified as sulfides and laterites (oxide) ores. Laterite ores are the major source of nickel (72 % of the reserves), much lower negative impact to environment and lower mining cost. But their contribution in the world's nickel production is only 42 % [3]. Industrial nickel production from laterite ores is based on both pyro- and hydrometallurgical processes. The pyrometallurgical processes are based on ferronickel smelting in the rotary kiln-electric furnace and nickel matte smelting. There are two main hydrometallurgical processes: high pressure acid leaching (HPAL) and the Caron process. HPAL technique needs expensive leaching aggregates – autoclaves, while in the Caron process, high-temperature reductive roasting is included before the leaching. Hydrometallurgical processes could be acid or alkaline [3].

This research work is focused on development of leaching method under atmospheric pressure (atmospheric leaching, AL). According to the periodic literature data, research studies of AL are oriented to use different acid solvents such as sulfuric acid [4], nitric acid [5], hydrochloric acid [6], acetic, citric and oxalic acid [7, 8]. The aim of this work is to optimize the AL process in sulphuric acid using magnetic stirring, with modeling the kinetic of the process at different temperatures.

2. Materials and methods

Ore

Low-grade nickel laterite ore from Ržanovo mining area in R. Macedonia was subject of leaching. It belongs to intermediate type Saprolitic ores (class C), with increased content of MgO (12–16 %, wt.) and Fe in the range of 25–33 %, wt.. Mechanical preparation of the ore with Ni content of 0.85 %,wt., was performed within the production line of the FENI INDUSTRI, Kavadarci. After sieving (0.200 mm, 0.104 mm, 0.074 mm, 0.043 mm and 0.037 mm) the major fraction with the highest content of Ni (0.92 %, wt.) was chosen for further study. Before the leaching, magnetic separation of this fraction was done in order to reduce the amount of Fe, and to increase the Ni content. Ni content was increased to 1.04 %, wt. According to the XRD analysis [9], dominant mineral is hematite (Fe_2O_3), while less, but considerable amount have shown talc ($Mg_3Si_4O_{10}(OH)_2$) and clinochlore ((Mg_5Al)(Al,Si)$_4O_{10}(OH)_8$). Quartz (SiO_2), magnetite (Fe_3O_4) and stilpnomelane ($Fe_2(Si_3O_9)$) have been shown as minor phases.

Leaching`

Sulfuric acid with different concentration (0.5, 1 and 3 M) was used as a solvent. The ratio of solid vs. liquid phase was 1:50 (5g

ore in 250 ml aqueous solution 25 of H_2SO_4). The leaching was performed under atmospheric pressure, using magnetic stirring with 600 rpm, at different temperatures: 298, 323, 348 and 363 K. For each leaching experiment, the samples of 5 ml were taken at the following time interval: 15, 30, 60 and 120 minutes. Concentration of the leached Ni was determined by atomic absorption spectroscopy (AAS) using a spectrometer, model PinAAcle 900F (PINAACLE900F).

3. Results and discussions

Leaching process

The first step in the study of the nickel laterite ore leaching process was determination of the influence of solvent (H_2SO_4) concentration at the ambient temperature (298 K). In Fig. 1 is shown dependence of yield of the leached fraction (α) on the time. As can be seen, the yield of the leached fraction increases during the time. Diffusion region of the curve is not reached within the experimental time. Also, with the increasing of the solvent concentration, the maximum yield of the leached fraction increased from 16.37 % (wt.) in 0.5M H_2SO_4, 22 % in 0.5M H_2SO_4 to 28 % in 3M H_2SO_4.
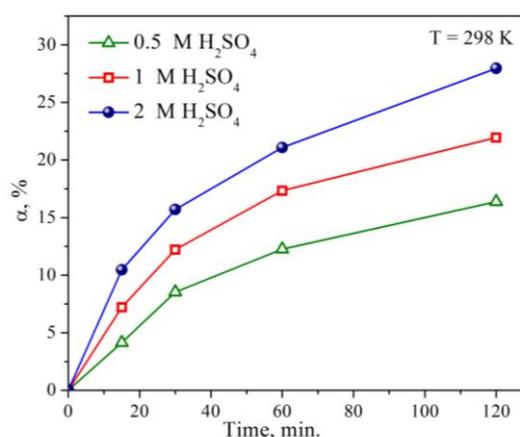

Fig. 1 *Diagram of yield of leached fraction (α) – time dependence for different concentrations of H_2SO_4 at 298 K.*

In Fig. 2, the dependence of the yield of the leached fraction (α) on the temperature is shown, for 3 M H_2SO_4. It is obvious that the temperature considerably intensifies the leaching process. After 120 minutes leaching in the 3 H_2SO_4, the yield of the leached fraction increased from 28 % at 298 K to 84 % at 363 K.

In Fig. 3, the change of the relative leaching rate (the yield of the leached fraction per time unit) during the experimental time is shown. During the time of leaching, as the yield of the leached fraction increases, the relative leaching rate decreases. The relative

leaching rate is higher at higher temperatures, but after 2 h, the leaching rates for all temperatures approach each other. At lower temperatures, the change of the relative leaching rate with time is slight, pointing out that the leaching process is limited by the chemical reaction. As the temperature of the process increases, the chemical reaction rate increases causing intensive change of the relative leaching rate indicating that reaction zone of the process occurs in the middle of the reacting ore particles. This points out on the diffusion control of the leaching process.
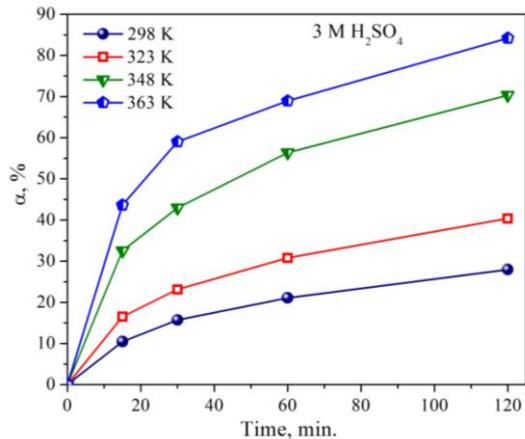

Fig. 2 *Diagram of yield of leached fraction α – time dependence for different temperatures in 3 M H₂SO₄.*
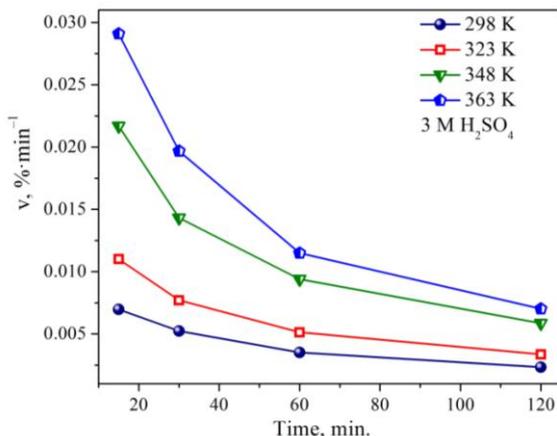

Fig. 3 *Diagram of relative leaching rate – time dependence for different temperatures in 3 M H₂SO₄.*

Kinetic models of the leaching process

The leaching process of nickel laterite ores can be expressed by the shrinking core model (Fig. 4), where the rate-determining step could be the chemical reaction on the core surface or diffusion process [10]. The model analysis was performed for leaching process in 3M H2SO4, at different temperatures (298, 323, 348 and 363 K).
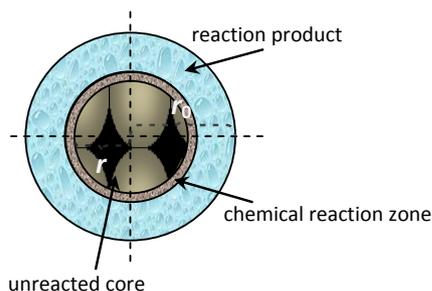

Fig. 4 *Schematic view of the shrinking core model: r_0- starting radius of the reacting ore particle; r- radius of the reacting ore particle after some time t.*

In the case when leaching process is limited by the chemical reaction, the process could be described by the Spenser-Topley-Kewan model [11]:

$$1-(1-\alpha)^{\frac{1}{3}} = k_S \cdot t$$

where α is yield of reacted fraction, k_S is Spenser-Topley-Kewan rate constant, defined by the following equation:

$$k_S = \frac{k \cdot C}{r_0 \cdot \rho}$$

where k is reaction rate constant, C is concentration of the solid reactant (ore particle), r_0 is a radius of the solid reactant, ρ is density of the solid reactant and t time of duration of the chemical reaction.

If the leaching process is limited by the diffusion, it can be described by the Ginstling-Braunshtein [12] or Jander model [13]. The Ginstling-Braunshtein model is given by the following equation:

$$1-\frac{2}{3} \cdot \alpha - (1-\alpha)^{\frac{2}{3}} = k_G \cdot t$$

where k_G is Ginstling-Braunshtein rate constant, defined as:

$$k_G = \frac{2 \cdot M \cdot D \cdot C}{a \cdot \rho \cdot r_0^2}$$

where M is molecular weight of the solid reactant, D is diffusion coefficient and a is a stoichiometric coefficient.

The Jander model is given by the following equation:

$$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2 = k_J \cdot t$$

where k_J is Jander rate constant, defined as:

$$k_G = \frac{2 \cdot S \cdot D \cdot K}{r_0^2}$$

where S is surface of the solid reactant layer and K is proportionality coefficient.

The experimental data from the diagram in Fig. 2 were included in the each model given above, and the corresponding straight-lines are shown in Fig. 5, 6 and 7, respectively.
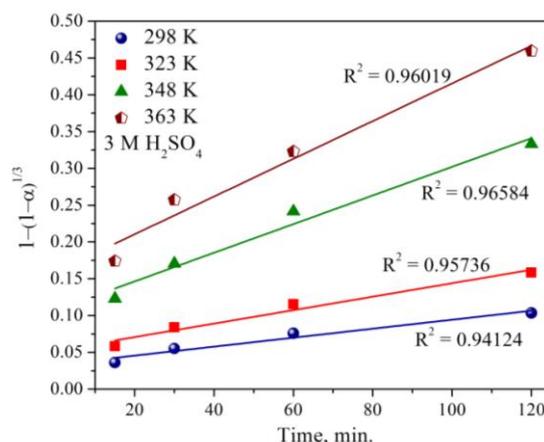

Fig. 5 *Linear fit of nickel leaching process in 3 M H₂SO₄ described by Spenser-Topley-Kewan model*
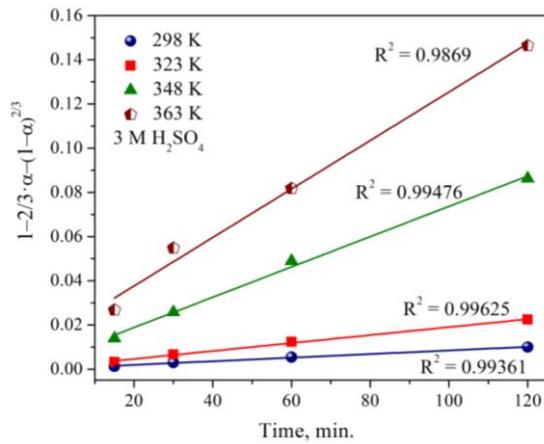
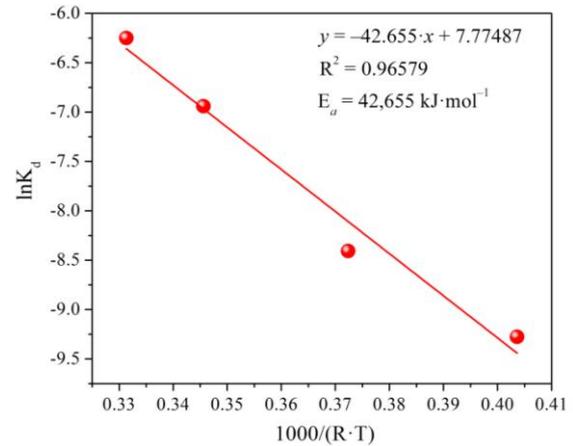**Fig. 6** *Linear fit of nickel leaching process in 3 M H_2SO_4 described by Ginstling-Braunshtein model*

Fig. 8 *Arrhenius plots of nickel leaching processs in 3 M H_2SO_4 described by Jander model*
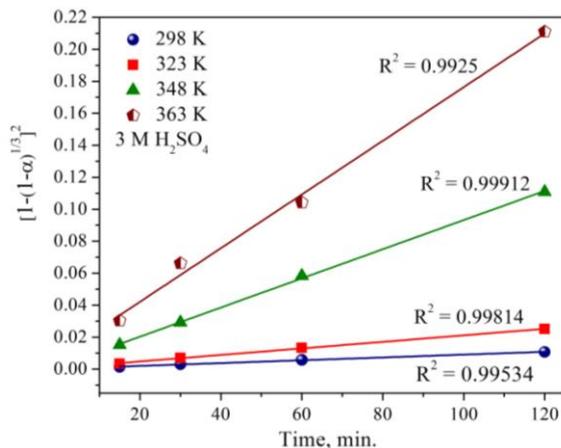

Fig. 7 *Linear fit of nickel leaching process in 3 M H_2SO_4 described by Jander model*
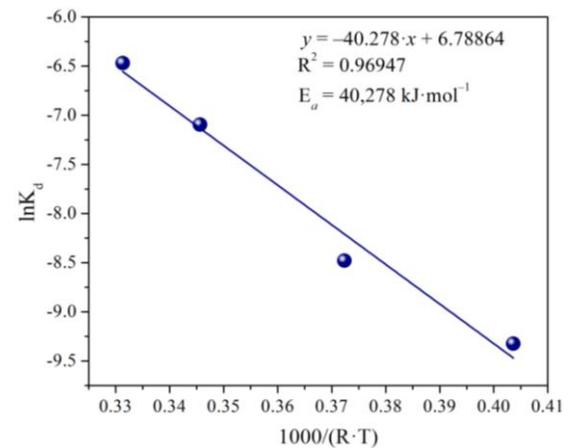

Fig. 9 *Arrhenius plots of nickel leaching processs in 3 M H_2SO_4 described by Ginstling-Braunshtein model*

It is obvious that diffusion-based models (Jander and Ginstling-Braunshtein) have shown much better fiting than the Spenser-Topley-Kewan model which assumes that the process is limited by the chemical reaction. The fitting of the Jander and Ginstling-Braunshtein models is very close, where Jander model describes the leaching process the best. This is an experimental proof that the leaching process of the nickel laterite ore is diffusionally controlled.

Activation energy analysis

Using the Arrhenius equation:

$$\ln k = -\frac{E_a}{R \cdot T} + \ln A$$

where k could be be Jander (k_J) or Ginstling-Braunshtein (k_G) rate constant, R is universal gas constant, T is temperature, A is the Arrhenius constant and E_a is an activation energy of the leaching process. E_a can be determined by further derivation of the previous experimental data and results with Arrhenius equation. The corresponding calculated values are shown in Fig. 8 and Fi. 9, for Jander and Ginstling-Braunshtein model, respectively. The calculated values of Ea of 42.65 kJ·mol^{-1} (by Jander model) and 40.28 kJ·mol^{-1} (by Ginstling-Braunshtein model) are in good mutual agreement, but also in good agreement with the literature data for activation energies characteristic for diffusion controled leaching processes [14-16].

4. Conclusions

According to the above presented results, we can draw the follow conclusions:

1. Increase of the temperature and concentration of the solvent (H_2SO_4) significantly intensifies the leaching process intenisfied with magnetic stirring.

2. The leaching process in 3M H_2SO_4 in the whole studied temperature range is the best described by Jander and Ginstling-Braunshtein model , which points out that the leaching process is diffusionally controled.

3. Activation energy for nickel laterite ore leaching process in 3M H_2SO_4 was determined to be 42.65 kJ·mol^{-1} (by Jander model) and 40.28 kJ·mol^{-1} (by Ginstling-Braunshtein model),which is in good agreement with similar leaching processes diffusionally controled.

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