



Technical note

Effect of a thermal pretreatment on dissolution kinetics of a limonitic laterite ore in chloride media

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ARTICLE INFO

Keywords:

Nickel
Colombian laterites
Hydrochloric acid leaching
Atmospheric leaching
Dissolution kinetics

ABSTRACT

The effect of a thermal pretreatment on the kinetic parameters and rate-controlling step for nickel leaching dissolution in hydrochloric acid-sodium chloride solutions from a low – grade Colombian nickel laterite (1.15% Ni, 0.12% Co and 41.1% Fe), was evaluated. The mineralogical analysis showed that nickel is associated with iron in the form of hematite (Fe₂O₃) and goethite (FeOOH) within the calcined and uncalcined ore, respectively. The hydrochloric acid and total chloride ions concentrations, as well as the leaching temperature, were shown to have a direct effect on nickel extraction. The experiments showed that ~92% of nickel can be dissolved after only 25 min in a 3 M HCl and 2 M NaCl solution when the leaching temperature was increased to 60 °C, after the sample had been previously calcined at 430 °C for 1 h. Nickel dissolution can be described by the chemical reaction-controlled shrinking particle model for both the calcined and uncalcined sample with apparent activation energies of 98 kJ/mol and 103 kJ/mol, respectively. This result suggests that a thermal pretreatment stage does not affect the nickel reaction mechanism, although it may liberate the nickel within the laterite structure.

1. Introduction

Approximately 60% of the global nickel resources correspond to laterites (U.S. Geological Survey, 2018) however, by 2010, the total world nickel production from these minerals did not exceed 50% (Butt and Cluzel, 2013). However, the continuous depletion of sulfides in recent years, along with high demands for nickel have made laterites an attractive choice for nickel production.

Laterites are the result of soil degradation generated by climatic changes, water filtration and other factors (Wilman et al., 2009). Laterites can be classified into limonites or saprolites, depending on the iron and magnesium content (Dalvi et al., 2004; Oxley and Barcza, 2013; Thubakgale et al., 2013) and different treatments can be used (pyro or hydrometallurgical processes) to recover the nickel content, depending on its chemical composition.

Saprolites are characterized by a high nickel content (more than 1.8%), low percentages of iron (up to 25%), but with elevated magnesium content. On the other hand, limonites denote laterites with high iron contents (at least 40% by weight) and low magnesium grades (0.5–5.0%); in these minerals, nickel is mainly contained in hydrated iron oxides, with grades up to 1.5% (Apostolidis, 1974). In a typical

profile of nickel laterites, saprolites occur at greater depths than limonites (Oxley and Barcza, 2013). The chemical and mineralogical homogeneity of limonitic laterites, in addition to the great value of potential byproducts such as cobalt, chromium and iron, renders limonites an ideal material to be treated by hydrometallurgical processes (Girgin et al., 2011).

Based on the above considerations, an increasing number of studies have explored novel methods to exploit laterite resources, including sulfuric acid technologies, chloride and bio-technologies (McDonald and Whittington, 2008a, 2008b).

During last decades, atmospheric acid leaching has been considered a relevant research topic since pyrometallurgical processes and high pressure leaching have become economically marginal due to the elevated energy consumptions required for the processing of minerals with low nickel content (0.95% to 1.00%) (Agatzini-Leonardou and Zafiratos, 2004; Wang et al., 2012). In consequence, atmospheric pressure leaching has been proposed as a promising technology for processing lateritic deposits since significant amounts of nickel, cobalt, iron and magnesium can be recovered (Liu et al., 2009).

Process variables, such as particle size, acid concentration and leaching time, play an important role in nickel extraction (Büyükakinci

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and Topkaya, 2009; Girgin et al., 2011; Thubakgale et al., 2013). The mineralogical composition also has a significant effect, determining aspects, such as the selection of the leaching agent and the need for a pre-treatment or the recovery of nickel at a later stage.

Different publications (Landers and Gilkes, 2007; Landers et al., 2009; Li et al., 2013; Li et al., 2009; O'Connor et al., 2006) have described a significant enhancement of nickel extraction by atmospheric leaching, after simply heating nickel laterite at different temperatures, as a means of converting the hydrated iron oxides to hematite, thus avoiding the requirement for expensive autoclave technology. The metals dissolution from limonitic laterite ore is directly related to the mechanism of metal release during the acidic dissolution of iron oxides (Landers et al., 2009)

Fundamental studies have shown that hydrochloric acid is more effective for metal extraction from nickel laterite ores under atmospheric conditions (McDonald and Whittington, 2008b). Chloride-based processes for the treatment of low grade lateritic ore have several advantages over the conventional hydrometallurgical and smelting processes, including higher leachability of complex ores, greater stability of chloride complexes and regeneration of leaching reagents (Lakshmanan et al., 2013). Additionally, its leaching power increases the dissolution kinetics and, consequently, decreases equipment sizes and operating temperatures and extends the range of operating conditions (Harris et al., 2009; Taylor, 2013). However, among the known disadvantages, the need to recycle the acid implies a highly energetic process and more expensive building materials.

The positive effect of employing chloride solutions for nickel dissolution from lateritic ores can be explained by their physicochemical properties, mainly the increase in proton activity, the formation of stable complexes and greater nickel solubility (Harris and White, 2011).

It is important to note that chloride ions are not only generated with hydrochloric acid; they may be provided by the addition of chloride salts to an acid solution or by the direct use of ferric chloride as a leaching agent (McDonald and Whittington, 2008b; Moyes, 2005; Moyes et al., 2012; Munroe, 1997). The addition of salts to generate highly concentrated chloride solutions has a significant effect, since even small amounts of acid can act as if they were highly concentrated (Jansz, 1983). The increase in HCl activity has long been recognized when salts, such as NaCl, CaCl₂ or MgCl₂, are added to a dilute HCl solution (Jansz, 1983; Majima and Awakura, 1981). For example, (Majima and Awakura, 1981) reported that the activity of 1 M HCl is 3 times higher in 1 M NaCl and 20 times higher in 3 M NaCl than in the absence of the added salts.

Considering the above, in this research, the leaching conditions of uncalcined and calcined limonitic laterite using hydrochloric acid at atmospheric pressure was investigated. A kinetic analysis was performed, based on the shrinking core model in order to evaluate the effect of a thermal pretreatment on the kinetic parameters and rate-controlling step for nickel leaching dissolution. The effect of important parameters, including acid and total chloride ion concentrations, as well as temperature, was determined.

2. Experimental

2.1. Materials

In this study a low-grade Colombian nickel laterite ore was used for all experiments. The ore sample was screened at 37 μm (400 mesh) and part was calcined at 430 °C for 1 h (Garces-Granda et al., 2018).

An elemental analysis of the sample was performed with Atomic Absorption Spectrometry (AAS, Varian SpectraAA 220 fs), giving the elemental composition as is shown in Table 1. The large SiO₂/MgO ratio and high iron content indicate that the ore consists mainly of limonite-type laterites.

The XRD patterns of the raw ore and calcined sample are displayed in Fig. 1. According to the mineralogical analysis, within the limonitic

Table 1
Chemical Analysis results by AA.

%Ni	%Fe	%MgO	%SiO ₂	%Al ₂ O ₃	%Co	SiO ₂ /MgO
1.15	41.1	1.51	14.29	6.9	0.122	9.45

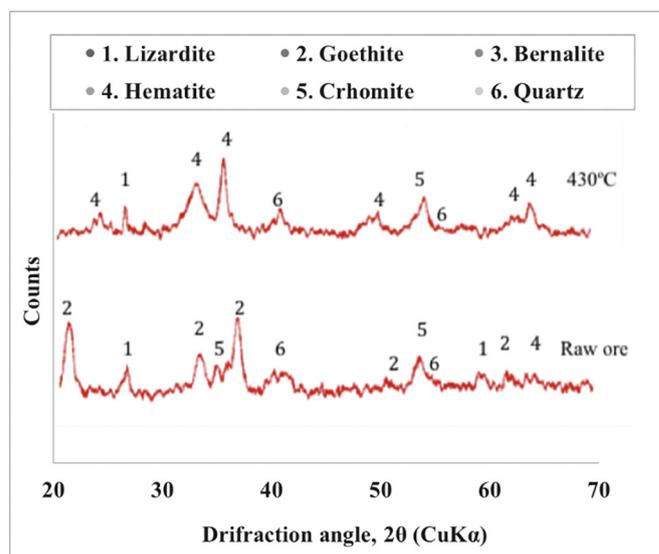


Fig. 1. XRD pattern of calcined sample at 430 °C for 1 h.

nickel laterite (raw ore), the iron is present in the form of goethite (FeOOH), however when the sample is calcined at 430 °C, the iron is present in the form of hematite (Fe₂O₃) and chromite (FeCr₂O₄); magnesium silicates in form of lizardite (Mg₃(Si₂O₅)(OH)₄) and silica contents as quartz. In addition, nickel was associated with the iron oxides and there was no evidence of the existence of a single nickel phase.

X-ray diffraction shows that the transformation of goethite into hematite occurs with increasing calcination temperature. On heating at 250 °C for 2 h, goethite started to alter to hematite, the peaks of goethite totally disappear when the sample is calcined at 430 °C (Garces-Granda et al., 2018). According to Kim et al. (2010) this transformation is almost completed at 800 °C.

2.2. Methods

The leaching experiments were carried out in a jacketed reactor, connected to a thermostatted bath with recirculation of a mixture of ethylene glycol (30% v/v) solution. Different authors have proposed that nickel extraction is independent of the stirring speed, i.e., the increasing of stirring speed had a negligible effect on the rate of nickel dissolution (Agacayak and Zedef, 2012; Agacayak et al., 2016; Ayanda et al., 2011). The ore-solution suspension was mechanically stirred at a constant velocity of 300 rpm in order to keep the particles in suspension and prevent agglomeration and inhomogeneities in solution. All experiments were performed under the ambient pressure of Mexico City (79 kPa) and 25 °C, except for those in which the influence of temperature was studied.

The effect of hydrochloric acid at three different concentrations (1, 2 and 3 M HCl) was evaluated, as well as the addition of sodium chloride (NaCl) as an enhancer for nickel extraction (1 and 2 M NaCl). The solid/liquid ratio was fixed at 10 g sample per liter of solution.

For the study of dissolution kinetics, the best combination of acid and salt (3 M HCl and 2 M NaCl) was used in order to evaluate three different leaching temperatures (25, 40 and 60 °C).

Successive aliquots of the suspension were withdrawn at set times

using a 3 mL plastic syringe and filtered through a 0.20 μm Millipore® filter. Dissolved nickel in leaching solutions was analyzed by AAS. At the end of each leaching test, the leached residue was filtered, rinsed with water and air-dried to be weighed.

For nickel extractions calculations, the following equation was used (Liu et al., 2012):

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

Where M represents the metal (Ni), V is the initial volume (mL) of the solution, v_i is the volume (mL) of the sample i withdrawn at each time, $C_{M,i}$ is the metal concentration (Ni) in sample i (mg/L), m is the initial mass (g) of tailing sample used in the test (feed sample) and C_M is the total content of the metal in the feed sample.

3. Results and discussion

In a previous publication, (Garcés-Granda et al., 2018) demonstrated that the use of calcination as a pretreatment can enhance the nickel extraction and significantly decrease the time required for the atmospheric acid leaching step, proving to have great potential for the extraction of nickel from low-grade laterites. The thermal pretreatment can increase the iron oxide particles surface area, reflecting the development of a greater porosity and the change in the reactivity of the mineral. The specific surface area practically doubled when the sample was calcined at 430 °C for 1 h, increasing from 84 m^2/g to 154 m^2/g .

The high density of structural defects in the newly transformed and poorly ordered hematite, make the resulting solid more amenable to leaching, even from the initial moments (Landers and Gilkes, 2007; Li et al., 2009; Olanipekun, 2000). However, higher temperatures are detrimental to iron, as well as nickel extraction. When the sample was calcined at 800 °C, the specific surface area decreased to 77 m^2/g as well as the nickel dissolution.

Considering these findings, a low-grade limonitic nickel laterite ore, calcined at 430 °C for 1 h was used to evaluate the effect of hydrochloric acid and total chloride ion concentration and leaching temperature.

3.1. Effect of hydrochloric acid (HCl) concentration

The effect of the acid concentration on nickel dissolution was studied from 1 to 3 M at 25 °C. According to the results shown in Fig. 2, an increase in hydrochloric acid concentration positively affects nickel extraction. The higher the acid concentration, the greater the metal extraction velocity, due to the increase in the hydrogen ion (H^+)

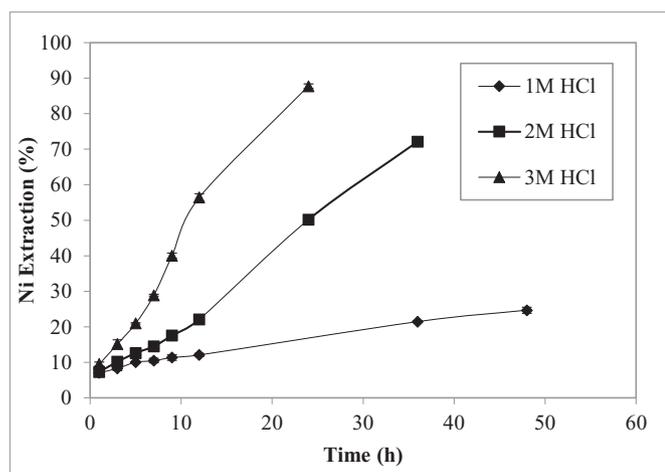


Fig. 2. Effect of the hydrochloric acid concentration on nickel dissolution at 25 °C. Operating conditions: 10 g of calcined sample per liter of solution; mechanical stirring at 300 rpm.

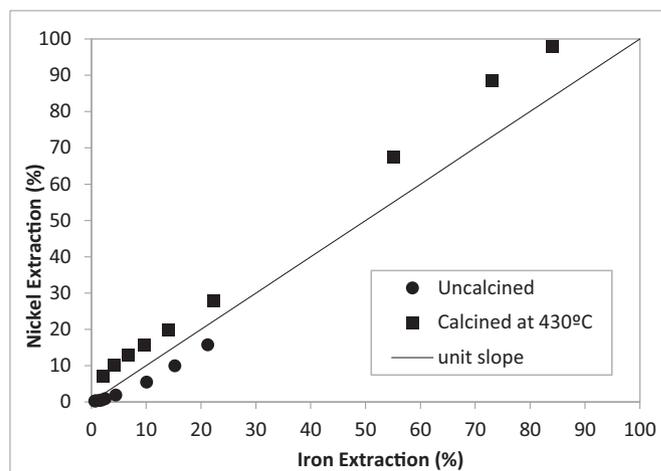


Fig. 3. The correlation between nickel and iron dissolution for calcined samples at 430 °C, and uncalcined (Garcés-Granda et al., 2018).

activity, which leads to dissolution of nickel-containing materials (Astuti et al., 2016).

From Fig. 2 it is evident that greater nickel extraction velocities are achieved as the concentration of hydrochloric acid concentrations is increased.

3.2. Effect of total chloride ion concentration

In a previous publication, Garcés-Granda et al. (2018) also reported that nickel dissolved congruently with iron (Fig. 3), indicating uniform incorporation of Ni in the iron oxide minerals, i.e., the release of nickel into the solution is associated with the leaching of iron. In that case, nickel bound within iron oxide grains will require a complete dissolution of the grain to achieve high nickel extraction (Senanayake and Das, 2004).

The leaching of iron oxides (hematite and goethite) from laterite by hydrochloric acid occurs according to the reaction eqs. (2) and (3), respectively (Cornell et al., 1976; Olanipekun, 2000):



Considering the above, the presence of protons (H^+) is required for iron oxide dissolution and, in an acidic medium, the addition of chloride ions can significantly accelerate the dissolution of nickel. However, Cornell et al. (1976) found that in the absence of protons, chloride ions are unable to attack goethite; suspensions of goethite in NaCl at its natural pH (~5.8) remained for months without showing signs of Fe(III) release. The effect of the total concentration of Cl^- , adjusted with NaCl and at a constant acid concentration (3 M HCl) was evaluated (Fig. 4). As can be observed, the addition of chloride ions to the hydrochloric acid solution accelerates the nickel dissolution. With the addition of 1 and 2 M of sodium chloride (NaCl) to the 3 M HCl solution, nickel extractions approximately 65% and 79% were obtained after 12 h of leaching, corresponding to an increase of 8% and 23%, respectively, when compared to the percentages obtained with a 3 M HCl solution without addition of NaCl. Therefore, an increase in the total Cl^- concentration, through the addition of NaCl, has a similar effect on nickel extraction as the increase in acid concentration, although not as pronounced.

When iron oxides are leached in the presence of chloride ions, (Bath, 1968; Cornell et al., 1976; Sidhu et al., 1981; Singh, 1969) suggested the formation of a complex (Fe-Cl) on the mineral surface. This complex formation, with a negatively charged chloride ion on a positively charged goethite surface, can sufficiently decrease the positive surface

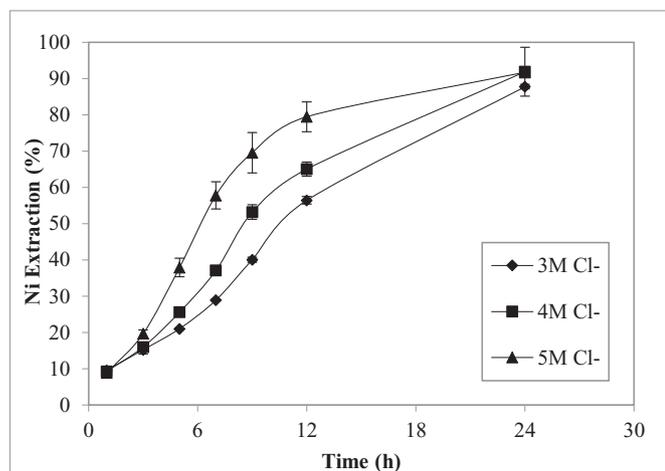


Fig. 4. Effect of the total concentration of Cl^- (3 M HCl + 0, 1 and 2 M NaCl) on nickel dissolution at 25 °C. Operating conditions: 10 g of calcined sample per liter of solution and mechanical stirring at 300 rpm.

charge, facilitating the reaction with the positively charged protons (H^+). Furthermore, this complex also weakens the attractive force between the surface Fe^{+3} or Fe^{+2} and the neighboring O^{-2} ions, enabling rupture of the Fe–O bonds. Consequently, (Cornell et al., 1976) states that the dissolution of an oxide is enhanced by the presence of an anion that forms complexes with the cation of the oxide. The effectiveness of the anion with respect to dissolution can often be correlated with its complexing ability. Although at the commencement of the leach, the nickel extraction rate increases with the chloride ion concentration, after 20 h when the nickel extraction is greater than 85%, the addition of NaCl does not have a significant effect. According to (Cornell et al., 1976), this situation is due to mineral surface saturation with adsorbed chloride ions and, therefore, can no longer form more complexes.

With these results it is possible to conclude then, that less leaching time is required to extract the nickel when a salt is added to the HCl solution. For this reason, the best leaching solution tested corresponded to 3 M HCl with addition of 2 M NaCl; this solution composition will be used for further studies.

3.3. Effect of leaching temperature

Different researchers have concluded that temperature is one of the most important factors affecting the nickel leaching process (Büyükkakinci and Topkaya, 2009; Girgin et al., 2011; Thubakgale et al., 2013). Nickel dissolution behavior was explored in leaching tests carried out at 25, 40 and 60 °C, using the acid-salt combination: 3 M HCl and 2 M NaCl (Fig. 5).

The results show that by elevating the temperature, nickel extraction significantly increases. While, the extraction of Ni was 9% at 25 °C after 1 h of treatment, it increased to 55% and 91% at 40 and 60 °C, respectively. To reach the maximum extraction of Ni (~ 92%) at 25 °C, it would take more than 12 h, whereas, at 60 °C, only 25 min.

On the other hand, the asymptotic shape nearing the maximum extraction of 92% implies that the leaching reagent directly attacks the metal that has been exposed by the pretreatment; consequently, the nickel leaching rate is initially high, but does not reach 100% probably because the undissolved nickel is encapsulated or in a phase that is insoluble at the working conditions. This effect is more evident at 40 and 60 °C.

3.4. Kinetic analysis

The substitution of nickel for iron in the crystalline structure of iron oxides, suggests that the decomposition of the latter is necessary for the

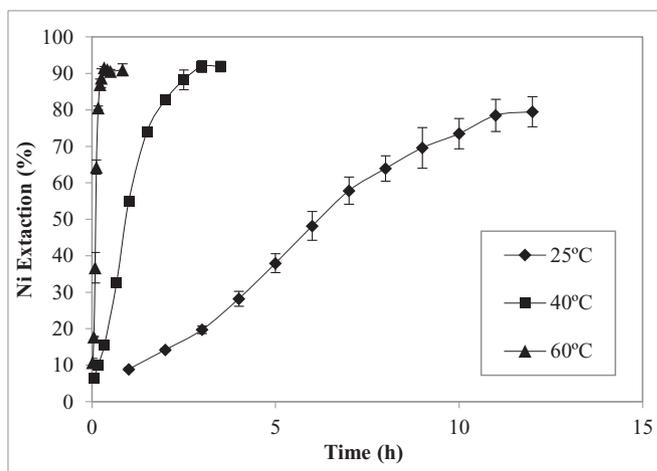


Fig. 5. Effect of the leaching temperature on the nickel dissolution in a 3 M HCl and 2 M NaCl solution. Operating conditions: 10 g of calcined sample per liter of solution and mechanical stirring at 300 rpm.

recovery of nickel. Furthermore, it implies that the nickel dissolution mechanism is similar to the mechanism of dissolution of the iron oxide, since a total dissolution of the iron oxides is required to achieve high nickel extraction.

The kinetics of nickel dissolution can be represented by the shrinking core model and its derivation (Safari et al., 2009), where the laterite structure forms the bulk of the particle. The rate of the process is controlled by the slowest of these sequential steps: diffusion through the fluid film surrounding the particle, diffusion through the inert solid structure or the chemical reaction at the surface of the unreacted core, where nickel is still present within the laterite particle (Levenspiel, 1987).

If the reaction is controlled by diffusion of the fluid reactant, in this case, the proton (H^+), the following equation can be used:

$$1 + \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = k_d t \quad (4)$$

But, if the reaction is controlled by the surface chemical reaction kinetics, then the following equation can be used:

$$1 - (1 - \alpha)^{1/3} = k_r t \quad (5)$$

Where α refers to the nickel fraction reacted, t is the time in minutes, k_r and k_d are the overall rate constants for chemical reaction and diffusion, respectively.

3.4.1. Rate-controlling step

In order to determine the effect of a thermal pretreatment on the kinetic parameters and rate-controlling step for the leaching of the limonitic nickel laterite ore in hydrochloric acid solutions, the experimental data were fitted using the above equations of shrinking core model. The correlation coefficients for each temperature were calculated and presented in Table 2.

According to the calculated regression correlation coefficients (Table 2) the experimental data best adjusted to the chemical reaction-controlled rate equation for both samples (Figs. 6 and 7). All the R^2 values for Eq. 5 are greater than 0.90, suggesting that the extraction rate is controlled by the chemical reaction, taking place on the surface of unreacted core, within the laterite particles, where nickel is still present.

As was mentioned above, for comparison purposes, the nickel dissolution kinetics from the uncalcined sample was also modeled.

Fig. 7 shows that the experimental data for the uncalcined laterite also gives very good straight-line fits for the chemical reaction-controlled kinetics, indicating that this is the rate controlling step for the

Table 2
Correlation coefficients of the shrinking core model for Ni leaching at different temperatures.

Leaching Temperature (°C)	Uncalcined		Calcined	
	[Diffusion] R ²	[Chemical Reaction] R ²	[Diffusion] R ²	[Chemical Reaction] R ²
25	0.76	0.97	0.84	0.97
40	0.79	0.97	0.91	0.99
60	0.88	0.91	0.55	0.96

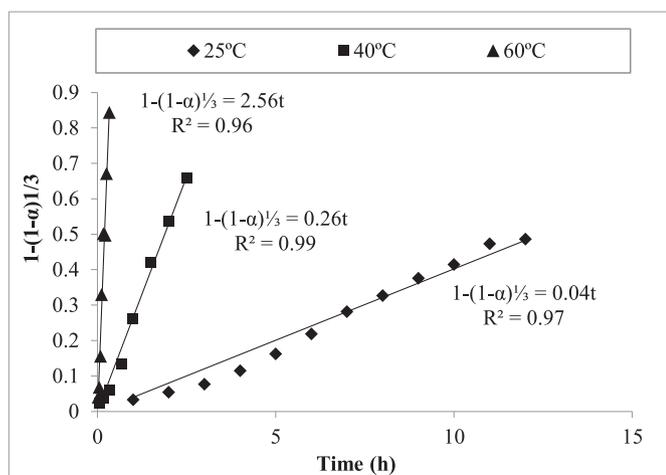


Fig. 6. Kinetic plots of chemical reaction controlled shrinking core model ($1 - (1 - \alpha)^{1/3}$) vs time for the nickel dissolution from a calcined limonitic nickel laterite ore.

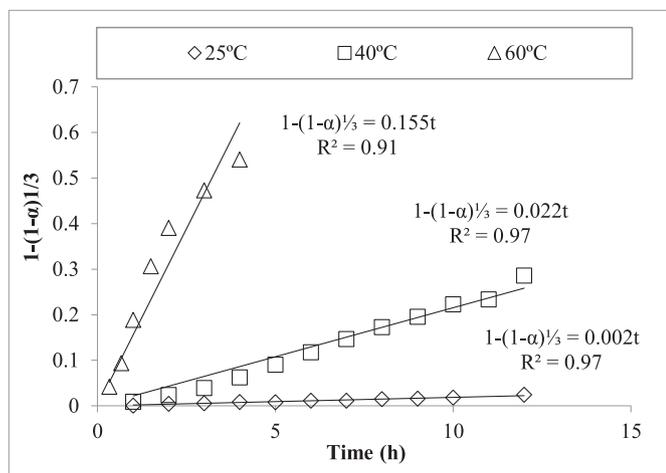


Fig. 7. Kinetic plots of chemical reaction control ($1 - (1 - \alpha)^{1/3}$) vs time for the nickel dissolution from a uncalcined limonitic nickel laterite ore.

nickel dissolution from the untreated material. In this manner, the results also suggest that a thermal pretreatment stage does not affect the reaction mechanism for the dissolution of nickel in chloride media.

The apparent rate constants (K), calculated from the slopes of the lines in Figs. 6 and 7, are presented in Table 3.

These results demonstrate that the new phase formed (hematite) after the thermal pretreatment, dissolves much more rapidly than the original goethite. Furthermore, the K -values show that at higher leaching temperatures, the dissolution rates considerably increase.

This significant effect of leaching temperature on rate dissolution

Table 3
Apparent rate constants for Ni at different leaching temperatures.

Leaching Temperature (°C)	K_c (h ⁻¹) Uncalcined sample	K_c (h ⁻¹) Calcined sample
25	1.9×10^{-3}	4.02×10^{-2}
40	2.15×10^{-2}	2.65×10^{-1}
60	1.55×10^{-1}	2.56

also, corroborates that the reaction rate is controlled by chemical reaction on the iron oxides surface. In general, a process controlled by diffusion is only slightly dependent on temperature, while chemically-controlled processes are very sensitive to temperature change (Havlík, 2008; Izquierdo et al., 2004; Liu et al., 2012).

3.4.2. Activation energy

On the other hand, activation energy for the reaction was calculated to clarify the rate-determining step. The Arrhenius equation (Eq. 6) was used to estimate the activation energy for the nickel dissolution from the calcined and uncalcined samples.

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

Where k is the reaction rate constant, A is called the frequency factor, R is the gas constant, T the temperature and E_a is the activation energy of the reaction.

By plotting the apparent rate constants for each experiment in an Arrhenius plot (Fig. 8), the activation energies calculated from the slopes of the lines were 98 kJ/mol and 103 kJ/mol for the calcined and uncalcined sample, respectively.

These high activation energy values confirm, once again, that, under these experiments conditions, the dissolution rate of nickel is controlled by the chemical reaction. This is in accordance with the values of 90 kJ/mol, 96 kJ/mol, 87.5 kJ/mol and 94 kJ/mol, obtained by (Bath, 1968; Cornell et al., 1976; Sidhu et al., 1981; Singh, 1969), respectively, for the dissolution of different iron oxides in HCl, since, Ni was uniformly incorporated into the iron oxides structure, as (Garces-Granda et al., 2018) showed in their previous publication.

Finally, scanning electron microscopy analysis was performed on the solid residues at different leaching times, in order to observe the product layer formation and/or the modification in particle size. SEM micrographs for solid residues after leaching for 2 and 6 h are presented in Fig. 9.

A drastic decrease in particle size is evident, which agrees well with the mass loss detected in solid leach residue. Losses of up to 70% were

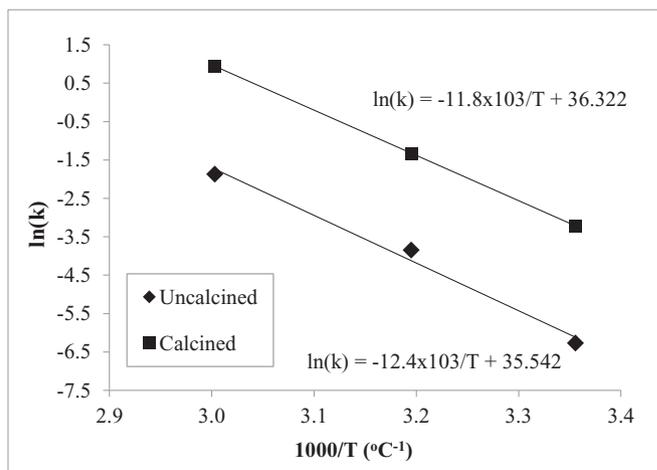


Fig. 8. Arrhenius plot for nickel dissolution from calcined and uncalcined sample.

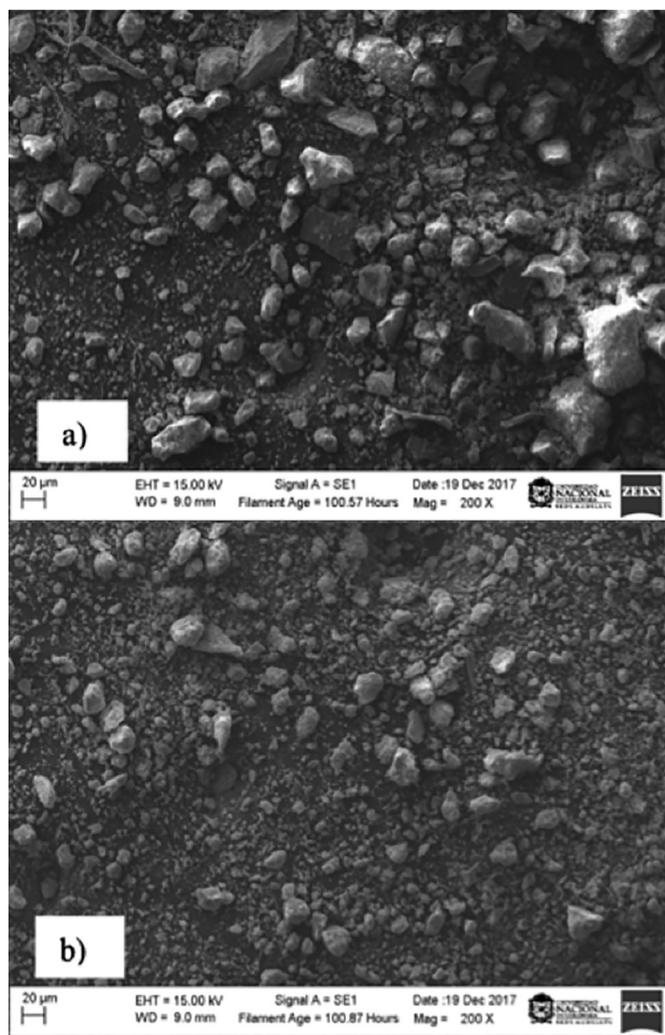


Fig. 9. SEM images of leach residues: a) after 2 h of leaching; b) after 6 h of leaching.

attained when the highest amount of nickel was extracted. The shrinking core model (SCM) with no product layer formation is equivalent to the shrinking particle model (Levenspiel, 1987; Safari et al., 2009) and is justified to describe the leaching process in this case, since the product completely dissolves and, consequently, the reaction takes place on the exposed surface of the particle.

4. Conclusions

The dissolution kinetics of a limonitic nickel laterite ore in chloride media was studied in this work. Variables, such as acid concentration, addition of chloride ions to the system and the leaching temperature, were shown to have a significant effect on the nickel extraction. Therefore, increasing hydrochloric acid and the total chloride ion concentrations, as well as the leaching temperature, noticeably increased the metal extraction rate.

The presence of protons (H^+) is required for the dissolution of the iron oxides. On the other hand, the addition of chloride ions is not essential, since, even without NaCl addition, the dissolution of nickel occurs at a substantial rate. However, its presence can significantly accelerate nickel dissolution, when acidic medium is used.

The nickel dissolution kinetics from a low-grade limonitic laterite was found to adjust well to the shrinking particle model with chemical reaction as the rate controlling step. The apparent rate constants for nickel from the calcined sample were an order of magnitude greater

than those for the uncalcined material at 25 °C and their magnitudes considerably increased by elevating the leaching temperature up to 60 °C.

The activation energies observed in a 3 M HCl and 2 M NaCl solution were similar (98 kJ/mol and 103 kJ/mol, respectively) for the calcined and uncalcined sample, which agrees with a chemical reaction control for the nickel dissolution. This result suggests that a thermal pretreatment stage does not affect the reaction mechanism.

Declaration of Competing Interest

None.

Acknowledgments

A. Garces-Granda is grateful to the Administrative Department of Science, Technology and Innovation (COLCIENCIAS) for the post-graduate scholarship received. The authors are grateful to the Hydrometallurgy laboratory at the Universidad Autónoma Metropolitana-Iztapalapa and the CIMEX Institute for the financial support and the technical assistance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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