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STUDY OF THE REDUCTION PROCESS OF IRON IN LEACHATE FROM NICKEL MINING WASTE

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Abstract - A mechanism to convert Fe(III) to Fe(II) by a reduction process could be a solution to the problem of selective separation of metals in extraction processes by using the ion-exchange process. The aim of this research was to reduce Fe(III) to Fe(II) present in leachate from nickel mining waste. Reducing agents used were sodium dithionite and sodium metabisulfite. The potential was decreased in order to quantify the minimum reducing agent that was necessary for conversion. Reaction time, pH, stirring speed and temperature were also studied. Results indicated dithionite was a better reducing agent than metabisulfite and complete conversion was possible by reducing the potential to 590mV at pH 0.5-2 and 240mV at pH 2.5. Stirring speed had no influence on the reduction process at 2 hours; however, conversion decreased after 24 hours, perhaps due to oxygen present in air. The analyses were conducted by ion chromatography and voltammetry.

Keywords: Sodium dithionite; Sodium metabisulfite; Reduction process; Ion exchange.

INTRODUCTION

Nickel is an important metal used in modern infrastructure. It plays a role in stainless steel (65%), metal alloys (~20%), electric batteries and chemical applications (~9%). Nickel is found mainly as two types of ores: sulfide and laterite. Approximately 60% of all production comes from sulfide ores, while 70% of nickel resources are from laterite ones. This is due to the complexity of treating lateritic nickel ores compared to sulfide ores (Dalvi et al., 2004; British Geological Survey, 2008; Mudd, 2009; Crundwell et al., 2011).

The characteristics of lateritic ores strongly depend on their geological formation. The layers creating the lateritic structure are: ferricrete, with approximately 35% Fe; limonite with nearly 45% Fe – the highest iron content among laterite layers -; nontronite, or smectite, presents in dryer climates, with almost 18%Fe; and saprolite, with almost 9% Fe in dry areas and 10-25% Fe in humid areas (Dalvi et al., 2004). The presence of iron content in lateritic nickel has great influence in terms of extraction processes (Crundwell et al., 2011).

As the nickel production rises annually, the amount of reserves has increased too, due to the improvement of mining technology, the extraction from new reserves, development of new process routes from known resources and the extraction of nickel from tailings or waste (Crowson, 2011; Miranda and Marques, 2016; Marta-Almeida et al., 2016; Kemp et al., 2016; Machado, 2007; Azam and Li, 2010).

Laterite processes used to extract metals are: the Caron process (pyrometallurgical process), HPAL or AL (high pressure acid leaching or acid leaching - hydrometallurgical process) and RKEF (rotary kiln electric furnaces – pyro- and hydrometallurgical process). The liquor obtained from hydrometallurgical process can be purified by techniques of precipitation, solvent extraction and ion exchange (Dalvi et al., 2004; McDonald and Whittington, 2008; Crundwell et al., 2011).

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An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchange resin, where cations and anions are fixed) and a solution phase, the ion exchanger being insoluble in the environment in which the exchange is carried out (Abrão 2014; Harland 1994). In recent years, researches have been carried out on ion-exchange process applied to hydrometallurgy (Coutinho et al., 1999; Alexandratos, 2009; Zainol and Nicol, 2009; Mendes and Martins, 2004; Mendes and Martins, 2005a; Mendes and Martins, 2005b; Riani, 2008).

Generally, extraction of nickel from laterites results in dissolution of iron compounds, which leads to a pregnant leach solution containing high concentrations of iron. Therefore, Fe(III) occupies more active sites of the resin than Fe(II), and the ion exchange is limited to pH 2, because above it the iron precipitates which causes co-precipitation of other metals, unless the iron in solution is in the form of Fe(II) (Jiménez Correa et al., 2016). In order to improve efficiency in recovery of metals, the chemical reduction of Fe(III) to Fe(II) could be a solution for techniques of precipitation, ion exchange and solvent extraction.

Pourbaix's Diagram as in Fig. 1 shows areas where Fe(II) or Fe(III) are stable, which could give the opportunity to predict the existence of Fe(II) depending on pH and potential. Another problem of ion exchange processes at pH below 2 is the high presence of H^+ ions. These ions compete with metal ions for the functional groups of the ion exchange resin. However, when the pH value increases, the increasing presence of OH^- ions cause formation of hydroxyl complexes with metals. In other words, metals begin to precipitate, which is strongly related to pH and composition of the solution (Inamuddin and Luqman, 2012; Zainol and Nicol, 2009; Gode and Pehlivan, 2003).

Sodium dithionite (DS) is used for this process in kaolin - $Al_2Si_2O_5(OH)_4$ – where brightness for use in paper coating is affected by Fe(III) (Cameselle et al., 1995; Ambikadevi and Lalithambika, 2000; Chandrasekhar and Ramaswamy, 2006; Bertolino et al., 2010). The species responsible for the reduction process is the bisulfite anion (HSO_3^{-1}), originated from dissociation of DS in aqueous solution. Bisulfite anion reacts with Fe(III) and, through a reduction process, results in Fe(II) (Cermak and Smutek, 1975).

The aim of this work is to develop a route to reduce Fe(III) to Fe(II) using sodium dithionite and sodium metabisulfite as reducing agents. During the study, synthetic iron sulfate solution was used. The parameters studied were: pH (0.5 to 2.5), reaction time (30 to 240 minutes and 96 hours), stirring speed (0 to 200 rpm), reducing agent concentration (0.1 to 1 $mol.L^{-1}$), and temperature (25 to 60°C). After conditions were determined, an experiment was performed using synthetic multi-element solution in order to simulate the reduction process in leachate from nickel mining waste. This solution simulates the metal concentration of liquor from limonite after the acid leaching process, that was considered before as a waste due to the high concentration of iron, which interfered in traditional processes.

MATERIALS AND METHODS

Solution Preparation

The solution was prepared using iron sulfate octahydrate ($Fe_2(SO_4)_3.8H_2O$) with 18715.5 $mg.L^{-1}$ of Fe(III) (Cromoline). Reducing agents were sodium dithionite and sodium metabisulfite (CAAS – Casa Americana). All reagents were analytical grade. A Ag/

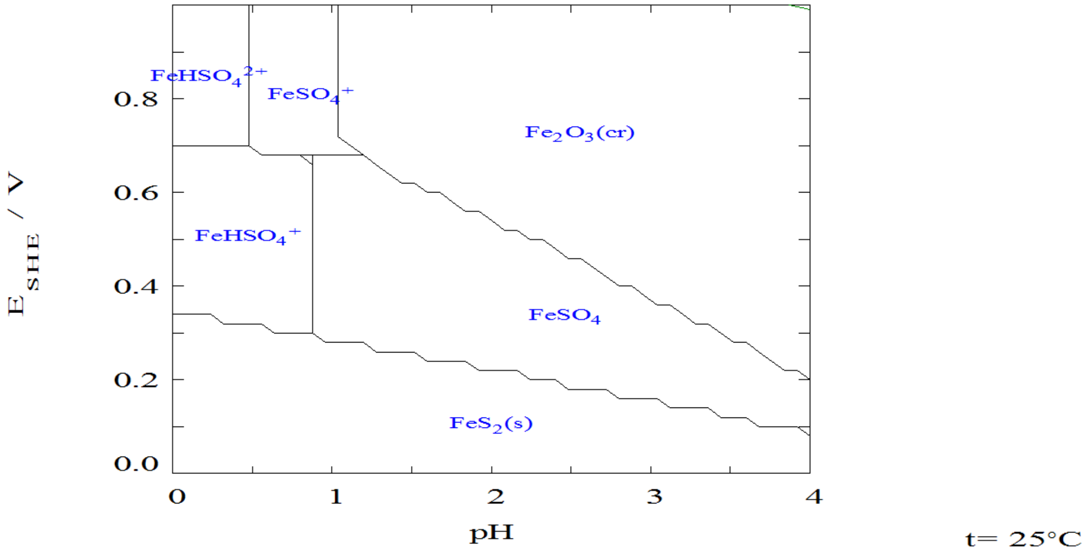

Figure 1. Pourbaix's Diagram constructed using Hydra-Medusa software at 25 ºC (potential vs pH).

AgCl (3 mol.L^{-1}) SensoGlass electrode was used to measure the potential, which was adjusted using the equation given to compare with Pourbaix's Diagram (Jardim 2014):

$$E = 240mV + E_{meas} \quad (1)$$

Study of pH Influence and Reaction Time

These experiments were performed using reducing agents at a concentration of 0.5 mol.L^{-1} and 25°C. First, the influence of the reduction process between pH 0.5 to 2 in a range of 0 and 420 min was studied. The potentials studied were 840, 740, 690 and 640 mV to quantify the minimum of reducing agent needed to reduce Fe(III) to Fe(II). These experiments were conducted without stirring.

Stirring Speed

These tests were studied at 90, 150 and 200 rpm, pH 0.5 and 640 mV. In the experiments of kaolin leaching using sodium dithionite, the agitation rate used was 90 rpm to minimize the oxygen influence on the reduction process (Cameselle et al., 1995; Luz and Lins, 2008; Luz et al., 2010; Da Silva et al., 2011). These experiments were executed in and orbital shaker at 25°C.

Reducing Agent Concentration

The reducing agent concentrations studied were 0.1 and 1 mol.L^{-1} to verify the effect on iron conversion in 2 hours and determine the consumption of reducing agents for various concentrations. The DS solution was prepared before the reducing process, because DS decomposes to sulfur elementary and sulfur dioxide at acidic pH (below 3) (Cermak and Smutek, 1975; Geoffroy and Demopoulos, 2009). The reducing agent behavior of DS is caused by decomposition to HSO_3^-, where occurs at pH 5-7, as exhibited in Equation 2 (Irwin, 2011). Bisulfite anion will reduce Fe(III) to Fe(II). The reaction between sodium dithionite and Fe(III) is presented in Equation 3 (Cermak and Smutek, 1975; Irwin, 2011; Chou et al., 2015; Luz and Lins, 2008).

$$\mathrm{Na_2S_2O_4 + 3H_2O \rightarrow NaHSO_4 + NaHSO_3 + 4H^+} \quad (2)$$

$$\mathrm{S_2O_4^{-2} + 2Fe^{+3} \rightarrow 2SO_2 + 2Fe^{+2}} \quad (3)$$

Table 1. Metal concentrations in nickel synthetic liquor.

Concentration (mg.L^{-1})	Al	Co	Cr	Cu	Fe	Mg	Mn	Ni	Zn
	4101.5	78.1	195.2	146.9	18713.5	7774.5	397.2	2434.2	36.7

The study of the reduction process in 96 hours was performed using 1 mol.L^{-1} reducing agent solution, as well as in all following experiments. In this experiment, it was possible to verify how reducing agents were influenced by oxygen for periods of times.

Obtaining Total Fe(III) Reduction

Using 1 mol.L^{-1} of reducing agent, it was possible to verify which potential was necessary to obtain total iron reduction at pH 0.5 and 2.5. It was important to discover the minimum potential necessary to reduce all Fe(III), due to iron precipitation at potentials below 350mV, as presented in Fig. 2, as well as other metals present in liquor.

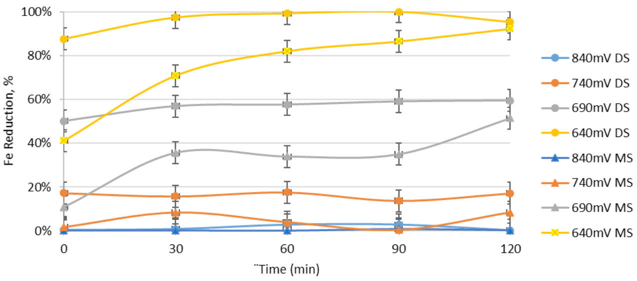

Figure 2. Fe(III) reduction percentage at pH 0.5 using DS and MS.

Temperature

The effect of temperature was studied between 25-60ºC. Sodium dithionite may degrade at high temperature, and there is greater dissolution of oxygen in the aqueous medium (Rinker et al., 1966; Cermak and Smutek, 1975). The experiments were realized at the potential verified before and pH 0.5.

Fe(III) Reduction in Synthetic Leachate from Nickel Mining Waste

Table 1 presents the concentrations of metals in liquor of leachate from nickel mining waste. In order to study the chemical reduction of Fe(III), a synthetic solution was prepared with these metal concentrations to simulate the real waste. The best conditions determined in mono-element solution were applied in the multi-element liquor, which was prepared using sulfate salts of each metal. All reagents were analytical grade.

Analyses

The experiments were performed to investigate the effect of reaction time on the reduction process, pH and potential. The analyses of Fe^{+3} and Fe_{total} were conducted using UV/vis spectrophotometry (Spectroquant Pharo 300), withdrawing an aliquot and diluting it 1:4 with H_2O at pH 1.0. A sample of 0.1 mL was removed and 3 mL of 5-sulfosalicylic acid 10% w/v (SSA) and 97 mL deionized water added to quantify the Fe(III) concentration at 500 nm; and 3 mL of 25% w/w ammonia added to quantify Fe_{total} (Karamanev et al., 2002; Paipa et al., 2005).

The following experiments were analyzed using ion chromatography with a Fe(II)/Fe(III) 882 Compact IC plus speciation column (Metrohm). In order to quantify the iron that was reduced in the liquor, a Voltametry Analyzer (797 VA Computace - Metrohn) was used.

RESULTS

Study of pH Influence and Reaction Time

Results of chemical reduction using sodium dithionite as reducing agent have been published (Botelho Junior et al., 2017). The following results are a comparison between sodium dithionite and sodium metabisulfite.

Fig. 3 presents chemical reduction of iron at pH 0.5 from 840mV to 640mV using DS and MS as reducing agent. The first experiments were executed for 420 min; however it was observed that in 120 min the reaction was stabilized. As can be observed, using a potential of 640 mV provided almost 95% of reduction. While it was possible to reach the maximum reduction percentage after 30 min for any potential with DS, 120 min were necessary using MS to reach the maximum value.

At 690mV, conversion of Fe(III) reached 59.55% using DS and 51.43% using MS. At 740mV, this conversion was 17.15% and 8.27% using DS and MS, respectively. At 840mV there was no conversion of Fe(III) to Fe(II).

These values were similar at pH 1.0 and pH 1.5 using both reducing agents. At pH 2.0, with 690 mV the Fe(III) was converted 39.60% and almost 0% at 740mV and 840mV, respectively, using MS; however, it was possible to obtain 90.84% of Fe(III) conversion at 640mV at the same pH.

Using DS, the value is retained at pH 1 and pH 1.5 as presented in Fig. 2. At pH 2, with 690mV Fe(III) was converted 40% and 20% with 740mV. At 640mV, the conversion stayed at 95% (Botelho Junior et al., 2017).

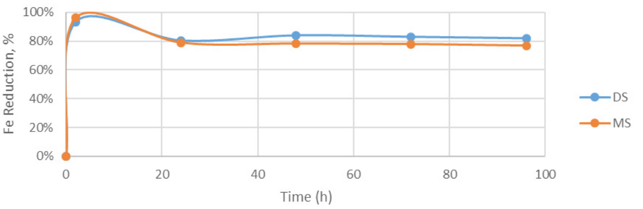

Figure 3. Percentage of Fe(III) reduction with time.

At pH 2.5 and 640mV using DS there was only 36.62% of Fe(III) reduction, and other potentials were below 10%. Observing the Pourbaix's Diagram (Fig. 2), it can be possible to see that at 640 mV and pH 2.5 iron is present as Fe_2O_3, and the 36.62% of iron reduction probably was possible due to the reducing agent action, but maybe Fe(II) could be oxidized to Fe(III) later. So, to have stable Fe(II) at pH 2.5 it is necessary to decrease the potential below 640mV.

The following experiments were executed at pH 0.5 and 640mV. Results of the reduction process at pH between 0.5 to 2 shows no difference at 640 mV, either using DS or MS. In addition, nickel leach waste also has this pH value, therefore the option to study at pH 0.5.

Stirring Speed

In order to examine the effect of stirring speed on the reduction process, the experiments were performed at 90, 150 and 200rpm using an orbital shaker. Despite the references of the kaolin reducing process (Da Silva et al., 2011; Martínez-Luévanos et al., 2011; Tuncuk et al., 2013), the stirring speed had no influence on the reduction process in this study and there was no difference in percentage of chemical reduction.

In addition, Cameselle et al. (1995) used a biological process for reducing iron from kaolin. It was verified that agitation had the least effect between 100–300 rpm, and the stirring speed was found to be enough to maintain kaolin in suspension avoiding mass transfer problems. In this work, with no presence of solids and mass transfer is not a problem, this allowed more choise of agitation rate. Ion exchange processes in batch experiments were performed at 200 rpm to increase contact between resin and metals in solution. So, the agitation rate was maintained at 200 rpm in the following experiments.

Reducing Agent Concentration

Reducing agent solution was prepared to be used to decrease the potential of the iron solution. Using reducing agent concentrations of 0.1 $mol.L^{-1}$ and 1 $mol.L^{-1}$ no difference was verified in the reduction process. The conversion was the same at all reducing agent concentrations studied over 2 hours, when the potential used as reference was 640 mV and the only difference observed was the amount of reducing agent solution spent. Using 0.1 $mol.L^{-1}$, the proportion of DS solution:Fe solution was 2:1, while MS solution:Fe solution was 5:1. Using 1 $mol.L^{-1}$, 7% of the final solution was DS solution, while using MS it was 46%.

Nickel laterite waste has valuable metals in low concentration, which is the case of cobalt with 78.1 mg.L^{-1} while iron has 18713.5 mg.L^{-1}. Using 0.1 mol.L^{-1} of DS or MS would dilute these metals to low concentrations, which would make the ion exchange process difficult and expensive. Thereby, the following experiments were carried out using the reducing agent concentration of 1 mol.L^{-1}.

Using a concentration of 1mol.L^{-1}, an experiment was performed at 640 mV in order to study the influence of days (96 hours) on the reduction process (Fig. 3). Whereas 420min still gave the maximum iron reduction, after 24hours the percentage of reduction drops from 96% to 80%, with either DS or MS, and then this percentage stabilizes over 96 hours.

The potential (Fig. 4) decreased from 640 mV to 620 mV in the first 2 hours due to the reduction process. After 24 hours, the potential increased to 660 mV and remained there for 96 hours. The oxygen might have had an influence as oxidizing agent only for the first 24 hours, but after that no effect was noticed on the process

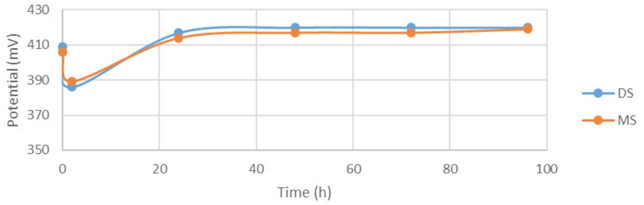

Figure 4. Potential (mV) over the 96 hours.

Obtaining Total Fe(III) Reduction

Using 1 mol.L^{-1} of DS and MS an experiment was made in order to quantify the potential where the total reduction of Fe(III) would occur. At pH 0.5, it was verified that 590 mV was the minimum potential to fully reduce Fe(III), using both reducing agents. At 590 mV, observed in Fig. 1, iron is present as Fe(II). At pH 2.5 a potential of 240 mV was necessary using DS, however it was not possible using MS, where a limiting factor of 240 mV was found.

Another factor to be considered was the control of pH in the reduction process at pH 2.5, that was vital to the process. At pH below 2, this control was not necessary.

Temperature

The effect of temperature was studied. Using the total iron reduction result obtained, temperatures of 35, 45, and 60 were tested comparing with 25ºC results. Fig. 5 demonstrates the results in percentage of iron reduction and temperatures, respectively. A decrease was observed of 5% between 25ºC (100%) and 35ºC (94.8% and 94.9% to DS and MS, respectively), which it maintains at 45ºC and 60ºC. So, it may be deduced that temperature has an influence on the reduction process, decreasing Fe(III) conversion, and 25ºC was found to provide the best results. It is plausible to attribute this to decomposition of DS and MS at temperatures higher than 25ºC. The decrease of Fe(III) conversion might also be caused by an increase in oxygen dissolution while the temperature increased (Cermak and Smutek, 1975).

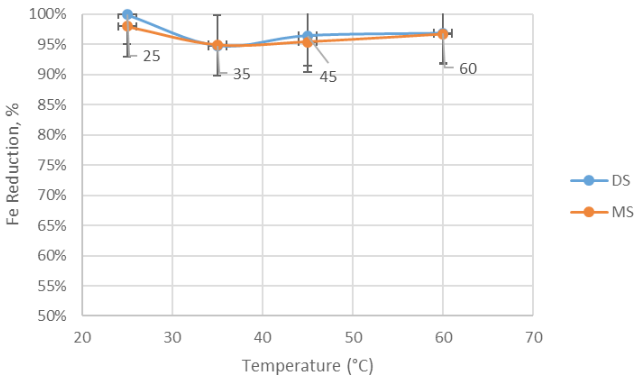

Figure 5. Percentage of Fe(III) reduction according to temperature.

Fe(III) Reduction in Synthetic Leachate from Nickel Mining Waste

The optimum parameters determined before are: 590mV, 2 hours, 25°C and 200 rpm, using DS. Using voltametry to determine Fe(II) and Fe$_{total}$, it is possible to quantify Fe(III) ions in multi-element solution. With these parameters, 70% iron conversion was possible. The decrease in chemical reduction in the multi-element compared to the mono-element solution may be caused by the presence of other metals in the solution, which could compete with iron in the reduction process. In order to increase Fe(III) conversion, the potential was decreased to 490 mV, where it was possible to verify 77% of reduction and precipitate formation.

An experiment was performed at 240 mV, that gave 78.5% of iron conversion, but all copper in solution precipitated. Using SEM (scanning electron microscope) and EDS (energy-dispersive X-ray spectroscopy) it was possible to verify which elements were present in the precipitate. Fig. 6 and Fig. 7 present the SEM image and spectrum of the precipitate formed. It is possible to verify copper and sulfur in the solid.

The SEM image (Fig. 6) shows that copper sulfide is obtained by decreasing the potential of solution to 240 mV. Fig. 7 makes it clear that only copper among all metals present in the synthetic solution was precipitated with sulfur. Fig. 8 presents Pourbaix's Diagram of copper, and at 240 mV and pH 0.5 it is possible to verify that copper and sulfur precipitate

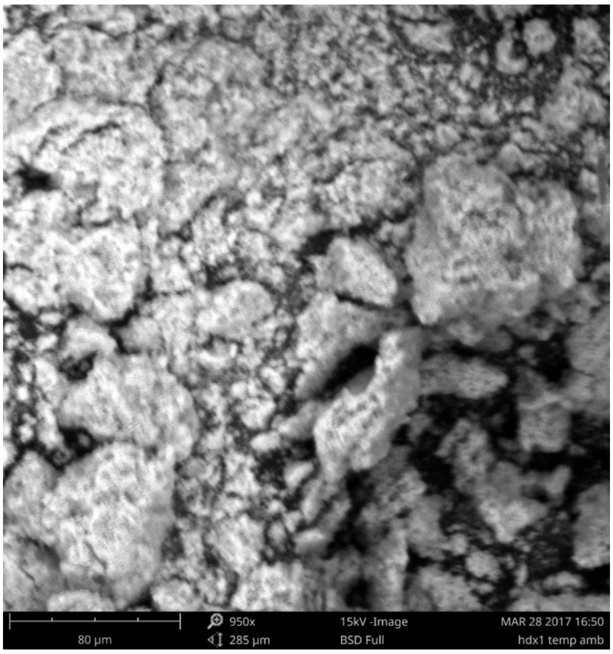

Figure 6. SEM image of precipitate formed in 240 mV experiment.

in these conditions. So, 590mV is the limit that it is possible to reduce the potential for nickel laterite leach. Besides in Fig. 1, the presence of iron was not verified in the precipitate.

DISCUSSION

Based on the results obtained in this study, the parameters to reduce Fe(III) to Fe(II) were established; the reduction process using DS had same results at the potentials studied at pH 0.5-2, where it was to possible convert all Fe(III) at 590 mV. At pH 2.5, all conversion was possible at 240 mV. The reaction reached equilibrium in 120 min. Stirring speed had no influence up to 200 rpm, but the conversion was decreased after 24 hours. This may have been caused by oxygen present in air. Oxygen is an oxidant that reacted with the reduction agent in solution, decreasing the reducing process. However, between 24 and 96 hours there was no decrease of iron conversion. The potential of the solution increased, indicating oxidant action.

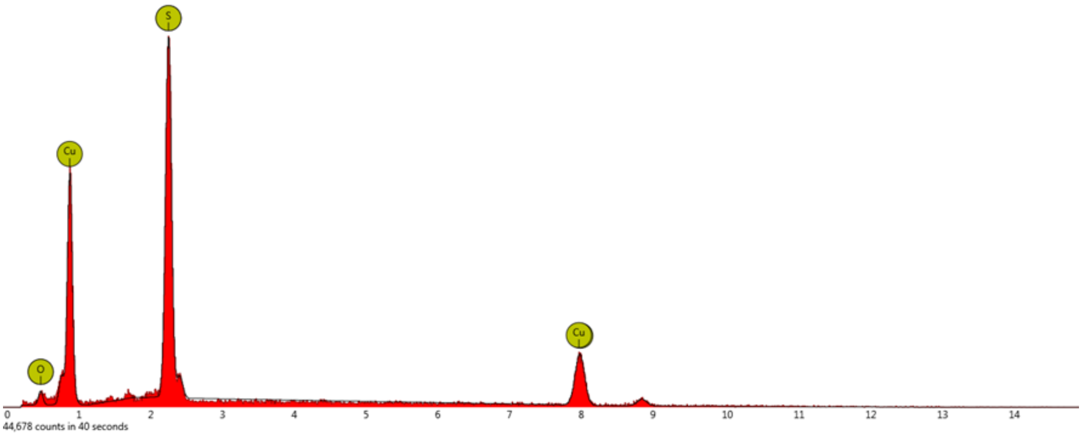

Figure 7. Spectrum of the precipitate formed in the 240mV experiment.

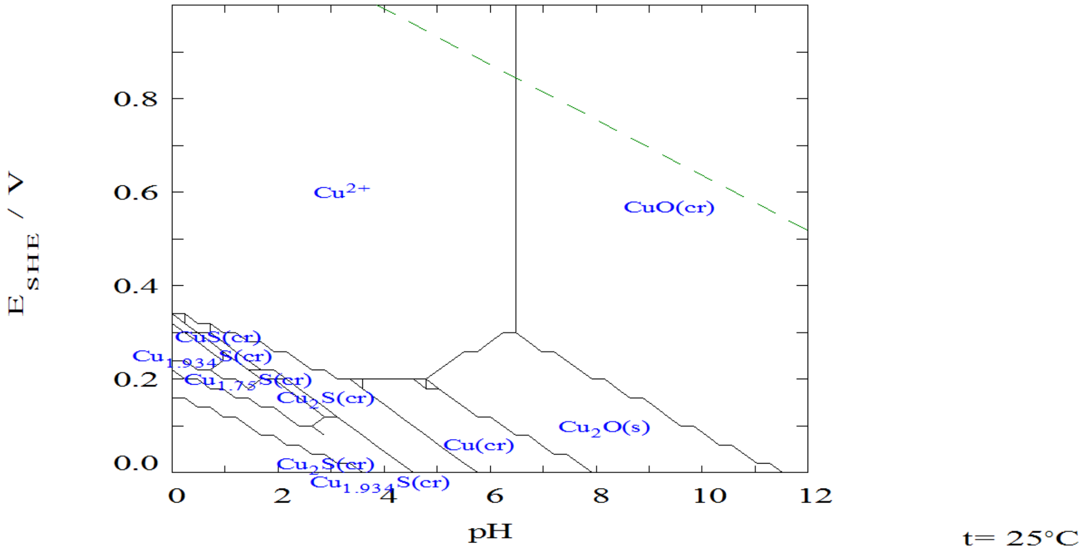

Figure 8. Pourbaix's Diagram of copper constructed using Hydra-Medusa software at 25ºC (potential vs pH).

Experiments carried out in order to study the influence of temperature showed that the reduction process efficiency decreased at temperatures above 25°C. This could be due to degradation of DS and MS at the temperatures studied. Another factor that should be considered is oxygen adsorption in the solution when temperature increase.

Studies of a synthetic solution of nickel laterite leach waste showed that the potential limit was 590 mV; if the potential decreased more, copper would precipitate.

CONCLUSION

The experimental work described demonstrated how to reduce iron in liquor of nickel laterite, but this value was limited by a potential of 590 mV. At potentials below 590 mV, it was possible to form precipitate, and at 240 mV all copper precipitated. Sodium dithionite was a stronger reducing agent than sodium metabisulfite. In liquor, it was not possible to use MS as reducing agent, because the consumption of MS was higher to arrive at 590 mV (380 mL of MS 1 mol.L^{-1} for each 100 mL of liquor) compared to DS (27 mL of DS 1 mol.L^{-1} for each 100 mL of liquor). The importance of this study was that reducing iron could improve the recovery of metals by an ion exchange process, because Fe(III) precipitates at pH above 2 and occupies more active sites of the resin than Fe(II). Thus, it was feasible using this technique to recover more metals from liquor with Fe(II) than as Fe(III).

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