

PRECIPITATION OF METALS FROM LIQUOR OBTAINED IN NICKEL MINING

Mónica M. Jiménez Correa¹, Paula Aliprandini¹, Jorge A. Soares Tenório¹, Denise Crocce Romano Espinosa¹

¹Chemical Engineering Dep., Polytechnic School, University of São Paulo; 158 Av. Prof. Luciano Gualberto, Trav. 3; Caixa postal 61548, São Paulo, SP 05424-970, Brazil.

Keywords: Nickel, selective precipitation, lateritic ore, ferric ion, ferrous ion

Abstract

In recent years, alternative treatment processes of nickel low-grade ores have been studied for nickel mining. The present work intends to study the precipitation of metals such as nickel, aluminum, cobalt, iron, zinc and copper from liquor obtained in the atmospheric leaching of a limonite nickel waste. Initially, synthetic solutions were prepared to simulate the sulfuric leach liquor. The iron in the first solution was found in the form of ferrous ions (Fe^{+2}), while in the second solution was found as ferric ions (Fe^{+3}). Precipitation tests were carried at 25°C and pH was varied with KOH additions. Metal concentration in aqueous and solid samples were analyzed by energy-dispersive X-ray (EDX) and a scanning by electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively. Around 100% of iron, 60% of cobalt and 10% of copper were precipitated at pH 3,0 from the solution with ferric ions, while in the solution with ferrous ions, the highest metal precipitation were achieved at pH 5,5.

Introduction

Sulphide and lateritic nickel ores are the main sources of nickel metal. Lateritic ores contain about 60% world's know nickel resources, whereas 40% of world's nickel are found in sulphide ores. Limonite, $(\text{Fe},\text{Ni})\text{O}(\text{OH})\cdot n\text{H}_2\text{O}$, is a part of nickel laterite and can be processed through pyrometallurgical, hydrometallurgical or a combination of both techniques (Mudd, 2010; USGS, 2014).

In general, the first hydrometallurgical stage is the leaching process, which can be performed using sulfuric acid, ammonia or chloride acid at atmospheric or high pressure. The resulting leach liquor containing mainly iron is treated with separation techniques such as precipitation, solvent extraction and electrowining (McDonald and Whittington, 2008; Moskalyk and Alfantazi, 2002).

Precipitation is used to remove impurities from liquor and can be divided in chemical or physical. In the hydrometallurgical field selective precipitation is used to purify solutions by addition of reagents to form an insoluble metallic compound (Heck, 2010; Lewis, 2010). Iron precipitation is the most widely used method to obtain a solution without high iron concentration level. The solid precipitated can form jarosite, goethite and hematite (Chang et al., 2010).

The present work aims to investigate the precipitation of metals such as nickel, aluminum, cobalt, iron, zinc and copper from liquor obtained in the atmospheric leaching of a limonite nickel waste. Particular interest was devoted to iron precipitation that affects the metals loss during its precipitation process.

Materials and methods

The solutions used in this study were based on the leaching from nickel limonite ore. Two solutions were prepared to reproduce the limonite solution. Reagents used were of analytical grade of the metals as sulfates. The composition used containing 4.5g/L Al [as $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$], 0.07g/L Co [as $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$], 0.13g/L Cu [as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$], 8.09g/L Mg [as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$], 0.37g/L Mn [as $\text{MnSO}_4 \cdot \text{H}_2\text{O}$], 2.52g/L Ni [as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$] and 0.04g/L Zn [as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$]. In the first solution was added 21.40g/L ferrous ions (Fe^{2+}) as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, while in the second solution was added 21.40g/L ferric ions (Fe^{3+}) as $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$. In both solutions, the liquor was prepared with deionized water. The pH was adjusted to 1.5 at room temperature (25°C).

The experiments were carried out in batch scale by stirring of the synthetic solutions for 5 minutes after a constant pH was obtained by a drop-wise addition of 1 molar potassium hydroxide (KOH) as precipitant. To study the influence of pH on the precipitation of metals, both solutions ranged pH at: 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 5.5. The choice of pH values was determined considering the metals concentration and pH at which precipitation occurs at 25°C when a hydroxide is used as the precipitant. The relationship of these two factors is shown in Figure 1.

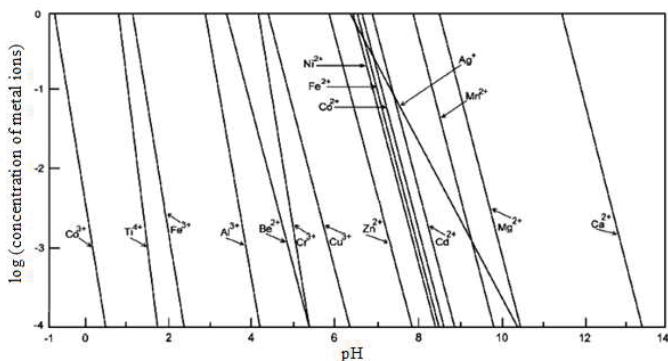


Figure 1: Relationship between concentration of metal ions and pH to precipitation at 25°C using hydroxide as the precipitant (Gupta, 2003).

After the reaction, the solid residues were filtered, washed and dried in oven at 50°C for 24 hours. The precipitated were subsequently analyzed by scanning electron microscope and energy dispersive X-ray spectroscopy (SEM-EDS) to determine the morphology and composition of the precipitate formed. The final liquor concentration was determined by energy-dispersive X-ray (EDX).

Results

Metals precipitation

Metals precipitation from liquors after leaching steps has been studied by several authors in order to separate metals and to purify solutions (Dorella and Mansur, 2007; Lewis, 2010; Provazi et al., 2011).

Iron precipitation is an interest topic in metallurgy and mining fields, since iron removal is an important stage to recover other metals. Then, precipitation of metals from liquor obtained in the atmospheric leaching of a limonite nickel waste was studied in the present work. Figure 2 shows precipitation percent of metals obtained by EDX chemical analysis of both liquors (solution with ferrous ions and solution with ferric ions) after experiments.

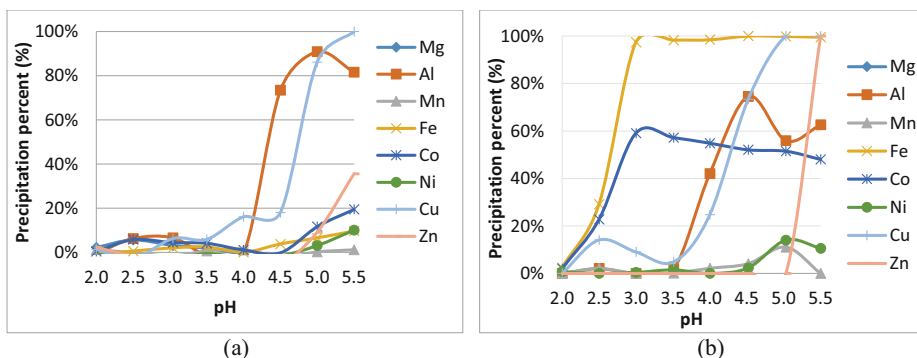


Figure 2. Metals precipitation percent after experiments using solution with (a) ferrous ion and (b) ferric ion.

Metals precipitation was promoted by pH increment using KOH. Reaction 1. defines metals precipitation using hydroxide reagents.



Where, M^{+z} is metallic cation.

For the solution with ferrous ion, aluminum and copper significant precipitation occurred since pH 4.5, whereas a lower iron precipitation (10%) was obtained at pH 5.5. The best aluminum precipitation was achieved at pH 5.0, in which around 90% aluminum was deposited. Already, copper was effectively precipitated at pH 5.5, in which 100% copper was attained. The solid morphology obtained after the tests that used pH 5.5 was examined by SEM and EDS. Figure 3 shows elements presents in the sample. Analysis by EDS showed peaks corresponding to the main elements of solid like iron and aluminum, which ones were expected to be present in solid sample.

For the solution with ferric ion, precipitation of iron, cobalt and copper started at pH 2.5. Iron achieved 100% of precipitation at pH 3, at the same pH 60% cobalt was precipitated that value corresponds to the best cobalt precipitation. Still, aluminum and copper precipitation in the ferric solution was similar than precipitation in the ferrous solution. Nevertheless the best aluminum precipitation was at pH 4.5, where precipitation percent was 78%, while 100% copper was precipitated at pH 5.0.

Precipitation of iron and cobalt had a similar behavior in the solution with ferric ion. According to Gupta (2006) cobalt precipitation for low metal concentration only take place on pH around

8.5(Gupta, 2003). However, in precipitation cobalt was started at pH 3.0 This effect could be induced for the high iron concentration and chemical affinity. Ions that are more concentrated can drag and co-precipitate other metals in selective precipitation (Farley et al., 1985; Silva and Afonso, 2008). Also the atomic ratio for both ions are close to each other, then metal co-precipitation occurs(Jackson, 1986).

After precipitation experiments at pH 3.0, the solid morphology obtained was examined by SEM and EDS. Elements presents in the solid sample can be observed in Figure 4. The main elements of solid like iron and aluminum were found by EDS, which one showed peaks corresponding.

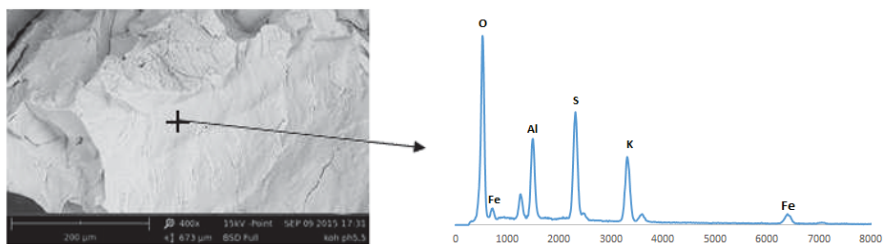


Figure 3. Scanning electron micrographs and EDS of solid precipitate for a solution with ferrous ion.

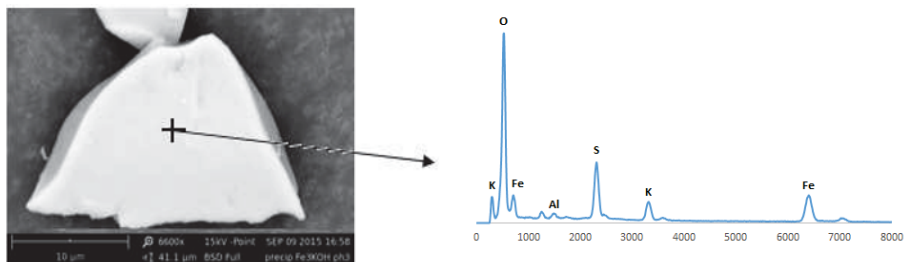


Figure 4. Scanning electron micrographs and EDS of solid precipitate for a solution with ferric ion

Comparison between ferrous ion and ferric ion precipitation

According to Gupta (2003), ferrous ion precipitation ion occurs at pH 8.0, while ferric ion the pH of precipitation is 3.5. The difference between iron ions behavior is due especially to: i) the size of the atomic radius, ii) the number of valence electrons and iii) the chemical activity.

The ferrous ion is greater than the ferric ion since ferrous ion has one electron more than the other one. When valence electrons are removed, remaining electrons are attracted strongly by the nucleus. Smaller ions have more available space than bigger ions, then its interaction with other chemical species is also higher. The opposite happens on ions that have huge nuclei atomic. Figure 5 shows the comparative between ionic radius and electron configuration for zero-valence iron and its ions (Feltre 1996; Santana, 2015).

Considering valence electrons, ferrous ion (Fe^{+2}) is more stable than Ferric ion (Fe^{+3}). As it can be observed in ferric electron configuration (Figure 5-c), one orbital in the 3d sublevel is not

complete with electrons, while in ferrous configuration three orbitals in the 3d sublevel are filled. Therefore, bond formation between OH^- and Fe^{+3} ion is preferred (Feltre, 1996).

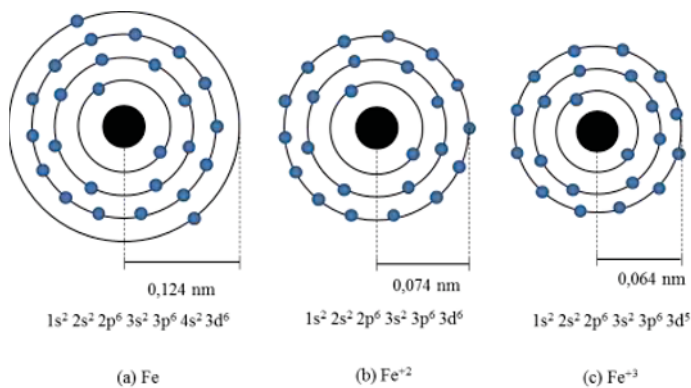


Figure 5. Ionic radius and electron configuration for (a) Fe; (b) Fe^{+2} and (c) Fe^{+3} (Adapted from Feltre, 1996)

For a given ionic strength, when ion charge increases the difference between activity coefficient and the unit also increases. For ferric ion the activity is farther from ideality (activity = 1) than for ferrous ion. On acid pH ferric activity achieves a value where precipitation occurs, however for ferrous ion attains the same activity value, the pH have to be raised at 8 (Jackson, 1986; Santana, 2015).

Conclusions

Precipitation experiments with constant agitation, at 25°C using KOH were performed. After analysis of results obtained can be concluded that:

- For the solution with ferrous ion, aluminum and copper significant precipitation occurred since pH 4.5, whereas a lower iron precipitation (10%) was obtained at pH 5.5. The best aluminum precipitation was achieved at pH 5.0, in which around 90% aluminum was deposited. Already, copper was effectively precipitated at pH 5.5, in which 100% copper was attained.
- For the solution with ferric ion, precipitation of iron, cobalt and copper started at pH 2.5. Iron achieved 100% of precipitation at pH 3, at the same pH 60% cobalt was precipitated that value corresponds to the best cobalt precipitation. Still, aluminum and copper precipitation in the ferric solution was similar than precipitation in the ferrous solution. Nevertheless the best aluminum precipitation was at pH 4.5, where precipitation percent was 78%, while 100% copper was precipitated at pH 5.0.
- Ferric ion has a different precipitation behavior when compared with ferrous ion, because their chemical characteristics are particular of each one. Ion in ferric form began its precipitation at pH 3.0, while iron in ferrous form had its precipitation at pH 5.5.

Acknowledgements

To the Counsel of Technological and Scientific Development (CNPq) for the financial support through doctorate grant.

To the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the financial support through master grant.

To the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support through the research project 2012/51871-9 ,

References

Chang, Yongfeng, Xiujing Zhai, Binchuan Li and Yan Fu 2010. Removal of iron from acidic leach liquor of lateritic nickel ore by goethite precipitate. *Hydrometallurgy* 101: 84-87.

Dorella, Germano and Marcelo Borges Mansur 2007. A study of the separation of cobalt from spent Li-ion battery residues. *Journal of Power Sources* 170: 210-215. doi: <http://dx.doi.org/10.1016/j.jpowsour.2007.04.025>

Farley, Kevin J, David A Dzombak and François MM Morel 1985. A surface precipitation model for the sorption of cations on metal oxides. *Journal of Colloid and Interface Science* 106: 226-242.

Feltre, Ricardo 1996. *Fundamentos da Química* . São Paulo, Ed Moderna :p67.

Gupta, Chiranjib Kumar 2003. *Chemical Metallurgy: Principles and Practice*. India.

Heck, Nestor Cezar 2010. *Precipitação In Precipitação Rio Grande do Sul*.

Jackson, E. 1986. *Hydrometallurgical extraction and reclamation*. New York: Ellis Horwood Limited.

Lewis, Alison Emslie 2010. Review of metal sulphide precipitation. *Hydrometallurgy* 104: 222-234. doi: <http://dx.doi.org/10.1016/j.hydromet.2010.06.010>

McDonald, R. G. and B. I. Whittington 2008. Atmospheric acid leaching of nickel laterites review: Part I. Sulphuric acid technologies. *Hydrometallurgy* 91: 35-55. doi: <http://dx.doi.org/10.1016/j.hydromet.2007.11.009>

Moskalyk, RR and AM Alfantazi 2002. Nickel laterite processing and electrowinning practice. *Minerals Engineering* 15: 593-605.

Mudd, Gavin M. 2010. Global trends and environmental issues in nickel mining: Sulfides versus laterites. *Ore Geology Reviews* 38: 9-26. doi: <http://dx.doi.org/10.1016/j.oregeorev.2010.05.003>

Provazi, Kellie, Beatriz Amaral Campos, Denise Croce Romano Espinosa and Jorge Alberto Soares Tenório 2011. Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques. *Waste Management* 31: 59-64. doi: <http://dx.doi.org/10.1016/j.wasman.2010.08.021>

Santana, Genilson Pereira 2015. *Equilíbrio químico*. Brazil.

Silva, Cristiano Nunes da and Júlio Carlos Afonso 2008. Processamento de pilhas do tipo botão. *Química Nova* 31: 1567-1572.

USGS, United States Geological Survey 2014. *Mineral Commodity Summaries-Nickel 2014*. In *Mineral Commodity Summaries-Nickel 2014*.