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## SEPARATION OF NICKEL AND IRON FROM LATERITIC ORE USING A DIGESTION – ROASTING – LEACHING – PRECIPITATION PROCESS

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**Abstract:** This paper investigates extraction of nickel and iron from a lateritic nickel ore from the Caldag region of Manisa in Turkey. The ore sample contains 1.2% Ni, 24.77% Fe and 0.062% Co. The process applied includes digestion with 40 wt-% sulfuric acid at 200 °C for 60 min, roasting at 700 °C for 15 min, leaching with water for 30 min at 1:5 solid/liquid ratio (by weight) and precipitation of the remaining iron at pH 3 and 60 °C. In order to improve nickel and cobalt extractions using the digestion-roasting-leaching-precipitation process (DRLP), Na<sub>2</sub>SO<sub>4</sub> addition in the roasting stage was examined. Under the optimum conditions and in the presence of Na<sub>2</sub>SO<sub>4</sub>, 86.2% Ni and 94.2% Co extractions were obtained with almost zero iron content. As a result, 2.07 g dm<sup>-3</sup> Ni, 0.12 g dm<sup>-3</sup> Co and 0.05 g dm<sup>-3</sup> Fe could be achieved in the pregnant leach solution within nearly 2.5 hours.

**Key words:** *laterite, digestion, roasting, salt addition, leaching, precipitation*

### Introduction

Increasing stainless steel demand in the world markets, especially in China, has made the situation difficult to be met with sulfide nickel deposits, based on the declining reserves (Dalvi et al., 2004). Therefore, lateritic nickel deposits have increased their importance and new economically feasible technologies for lateritic ores are being developed (McDonald and Whittington, 2008). However, nickel laterite ores cannot be easily concentrated owing to their low nickel content and isomorphous goethite or serpentine crystalline structure (Mudd, 2010; Eckelman, 2010). Depending on their complex mineralogical structure, laterites do not respond to physical beneficiation methods (Norgate and Jahanshahi, 2011). Thus, hydro- and pyrometallurgical methods are used. Pyrometallurgical techniques are appropriate for treating saprolite type of laterites, which has high garnierite and low iron content. But the main disadvantage of this process is a substantial energy input (Norgate and Jahanshahi, 2010).

Currently, various hydrometallurgical processes are applied for extraction of nickel and cobalt from lateritic ores. Lateritic ores are rich in iron and after leaching process high contents of nickel and cobalt as well as iron exist in the solution. In atmospheric leaching (AL) operations, which are not commercially proven yet for laterites, high content of iron exists in pregnant leach solutions (Chander, 1982; Neudorff, 2007; McDonald and Whittington, 2008). High pressure acid leaching (HPAL) is preferred as the main industrial process, since iron content can be decreased with high pressure and temperature. However, autoclave and maintenance costs are the most important disadvantages for HPAL. Also, there is another industrial process known as Caron process, in which nickel is reduced at temperatures between 500-800 °C and leached with ammoniacal solution (Dalvi et al., 2004). Nevertheless, these extraction methods require significant capital costs including infrastructure and equipment. In addition, nickel laterite deposits are generally located in areas where access to power and transportation may be difficult. Therefore, interest to alternative nickel extraction methods has been increased (Harris et al., 2011). In order to overcome the problems of these processes, sulfating roasting process has become important in extraction of metallic values from laterite ores (Kar and Swamy, 2000; Swamy et al., 2003). In this process nickel and cobalt are converted to sulfate form, which are highly soluble in water, but iron remains in insoluble oxide form. This process is applied by adding concentrated sulfuric acid, roasting and water leaching (Xu et al., 2005). Keeping in view this process, pug-roast-leach (PRL) process has also been developed, which includes selective sulfation of nickel and cobalt under appropriate conditions resulting in reduced acid consumption as compared to other processes (Swamy et al., 2003). It was reported that pugging of the lateritic ore with sulfuric acid and roasting in two stages improved the metal extraction over single stage roasting of the material at 700 °C (Kar and Swamy, 2000). Also it was reported that use of alkali and alkaline salts (sulfates and chlorides) played a significant role in catalyzing the sulfation process (Fu, 1993; Chakraborty and Srikanth, 2000; Kar and Swamy, 2000; Guo et al., 2009; Guo et al., 2012). In this study, an alternative approach for nickel and iron separation from a laterite nickel ore was investigated applying digestion – roasting – leaching – precipitation (DRLP) process in the presence of a basic additive.

## **Materials and method**

The lateritic ore sample taken from Caldag-Manisa in Turkey was used in the tests. Chemical analyses of the lateritic ore sample and other details were presented elsewhere (Basturkcü and Acarkan, 2016). It was presented there that nickel was present in goethite [(Fe,Ni)O(OH)], while chromite and hematite were the gangue minerals. The lateritic ore sample consisted of mainly quartz and goethite. Serpentine minerals were also present.

Differential thermal and thermogravimetric (DTA-TG) analyses were conducted using Seiko SII Exstar 6300 on the raw ore sample from 20 to 800 °C with a linear

heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  using air. The DTA-TG curves of the sample (Fig. 1) show a peak at about  $300\text{ }^{\circ}\text{C}$  with a weight loss due to the dehydroxylation of goethite to hematite ( $\text{Fe}_2\text{O}_3$ ).

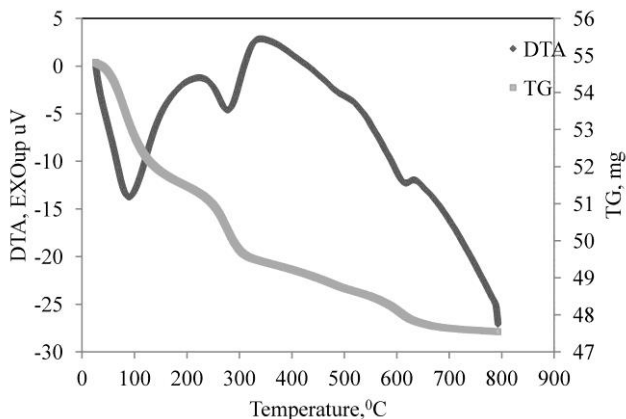


Fig. 1. DTA-TG curves of the raw sample

The lateritic ore sample used in the tests was ground below  $74\text{ }\mu\text{m}$  particle size and dried in an oven at  $105\text{ }^{\circ}\text{C}$ . The digestion tests were carried out at laboratory scale with  $10\text{ g}$  of solid in Pyrex glasses. For sulfuric acid addition tests a solid-liquid mixture was prepared using  $60\text{ wt-}\%$  acid. Also, Guo et al. (2009) and Swamy et al. (2003) indicated that addition of water was necessary for good mixing and helped sulfation reaction.

The digestion process was performed with different dosages of sulfuric acid in a muffle electric furnace at different temperatures for various durations under atmospheric conditions. The sulfation of the metal oxides resulted in agglomeration of the particles. Therefore, the digested sample was cooled to room temperature and ground below  $74\text{ }\mu\text{m}$  again for the roasting stage at higher temperatures. Roasting tests were conducted with the digested sample in porcelain crucibles under atmospheric conditions. At the end of roasting, the calcined mineral was leached with distilled water for  $30\text{ min}$  at room temperature,  $1:5$  solid/liquid ratio (by weight), and  $400\text{ rpm}$  using a magnetic stirrer. The pulp was filtered by Buchner funnel. In order to reduce the iron content in pregnant solution, the remaining iron was precipitated after leaching at  $\text{pH } 3$  and  $60\text{ }^{\circ}\text{C}$ . All the tests were repeated to provide reproducibility. Ni, Co and Fe contents in the pregnant solution were analyzed by atomic adsorption spectrophotometer AAS (Varian AA240 Flame model). The flow sheet of DRLP process is given in Figure 2.

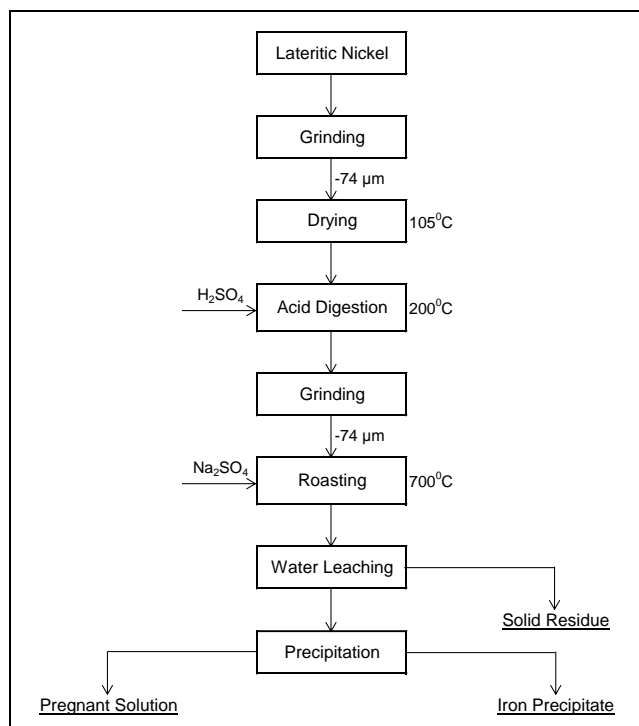


Fig. 2. Flow sheet of DRLP process

## Results and discussion

### Sulfuric acid digestion. Effect of duration

A series of digestion tests were carried out by changing digestion durations of 1, 1.5, 2, and 3 hours. Digestion process was conducted with 40 wt-% H<sub>2</sub>SO<sub>4</sub> addition at 250 °C temperature. As shown in Figure 3, nearly 60% Ni, 40% Fe and 78% Co extractions were obtained in different durations. Although there were some minor changes in metal extractions, they were found to be insignificant. Since the economic aspects were considered, the optimum digesting duration was determined as 60 min.

During digestion process, nickel, iron and cobalt are partially converted to sulfate forms with sulfuric acid. Sub-stoichiometric amount of H<sub>2</sub>SO<sub>4</sub> is added at room temperature and the mixture is heated to desired temperature. The transformation of metal oxides to metal sulfates was observed through XRD analyses demonstrated in Figure 4. It can be observed that the iron oxide minerals are transformed to synthetic iron sulfate. Since the constituent mineral of the nickel sample is quartz, it can be expected to observe quartz peaks.

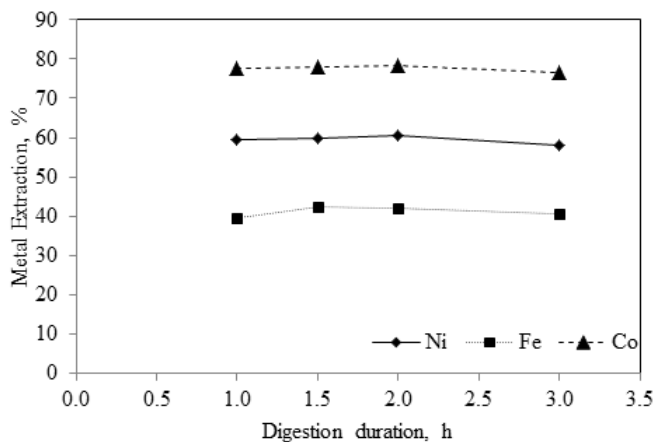


Fig. 3. Effect of acid digestion for various durations (40% H<sub>2</sub>SO<sub>4</sub> addition, 250 °C temperature, water leaching at 1:5 solid/liquid ratio for 30 min)

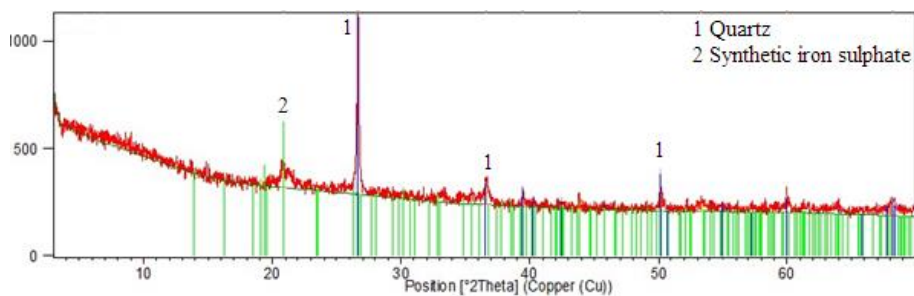


Fig. 4. XRD patterns of the digested sample

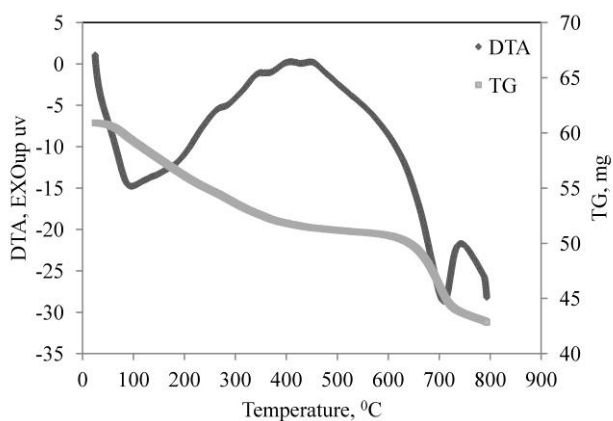


Fig. 5. DTA-TG curves of the digested sample

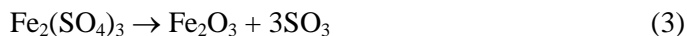
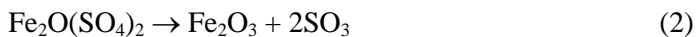
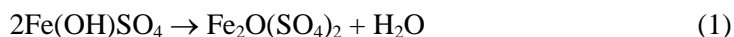
As result, significant amounts of nickel, cobalt and iron were transformed to metal sulfate forms, which can be leached in water easily. However, it is known that the iron content of the final nickel product must be as low as possible. In order to remove the iron from the material, further thermal treatment was necessary. Therefore, DTA-TG analyses were performed on the digested sample to determine the decomposition temperatures of the metal sulfates (Fig. 5). According to the experimental results, weight losses are observed at temperatures above 650 °C, which shows the decomposition of metal sulfates. It is thought that mainly iron sulfate structure is decomposed at 700 °C and above this temperature the other metals are decomposed. Ultimately, the digested product was decided to be roasted at 700 °C for the decomposition of iron sulfates to iron oxides.

### Sulfuric acid digestion – effect of temperature and H<sub>2</sub>SO<sub>4</sub> addition

In the literature, a two stage roasting process was tested, which included a digestion stage and a roasting stage. Generally, the first process is performed at 450-500 °C (Kar and Swamy, 2000; Kar et al., 2000; Swamy et al., 2003). In this pugging–roasting–leaching called method, after pugging, roasting at 700 °C was performed to separate nickel and iron selectively. When pugging process was performed before roasting at 700 °C, Kar and Swamy (2000) found that 16% Ni and 3% Fe improvement could be provided. This was attributed to pre-heating at 450 °C, in which partial transformation of soluble iron sulfate to insoluble basic iron sulfate takes place. Also this process liberated SO<sub>3</sub> gas, which reacts with nickel oxide to form nickel sulfates.

In this study, the possibility of a successful sulfation at temperatures lower than 450 °C was observed. In order to investigate the effect of temperature and H<sub>2</sub>SO<sub>4</sub> addition on sulfation, 200, 225, 250 and 275 °C temperatures were tested with each of the H<sub>2</sub>SO<sub>4</sub> dosages of 10, 20, 30, 40 and 50 wt-%. After digesting the samples under these conditions for 60 min, the ground sample was roasted at 700 °C for 15 min. Then, the roasted product was leached with water at 1:5 solid/liquid ratios for 30 min at room temperature.

In the roasting stage at 700 °C, iron and aluminum sulfates decompose, while nickel sulfate remain in sulfate form till 760 °C (Swamy et al. 2003). During roasting the following reactions occur:



According to Figures 6-8, it can be understood that an increase in H<sub>2</sub>SO<sub>4</sub> dosage resulted in higher metal extractions, since sulfuric acid addition helps sulfating of metal

oxides. However, the sulfating effect of 40% and 50%  $\text{H}_2\text{SO}_4$  additions were nearly the same. In terms of digestion temperature, while no significant enhancements in nickel extraction could be obtained with the changes in temperature, increasing the temperature had a positive effect on cobalt and iron extractions.

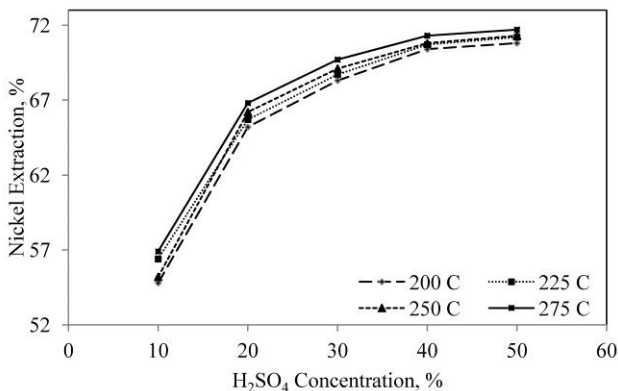


Fig. 6. Effect of digestion temperature on nickel extraction during leaching (60 min digestion, water leaching at 1:5 solid/liquids for 30 min)

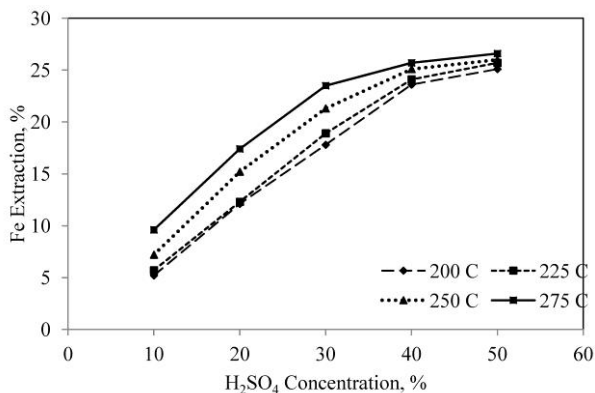


Fig. 7. Effect of digestion temperature on iron extraction during leaching (60 min digestion, water leaching at 1:5 solid/liquids for 30 min)

When 200 °C digestion temperature was applied and 40 wt-%  $\text{H}_2\text{SO}_4$  was used, nearly 70% Ni, 24% Fe and 84% Co extractions were achieved. These digestion conditions could be accepted as the optimum digestion conditions before 700 °C roasting for 15 min.

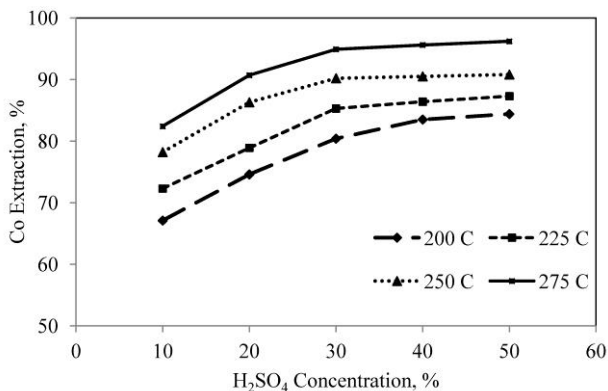


Fig. 8. Effect digestion temperature on cobalt extraction during leaching (60 min digestion, water leaching at 1:5 solid/liquids for 30 min)

The transformation of the digested product to the roasted product can be observed from the XRD patterns demonstrated in Fig. 9. Iron sulfate peaks observed in the digested sample were disappeared and the formation of hematite from decomposition of iron sulfates can be seen. Since the processes applied did not affect quartz, quartz peaks still can be seen.

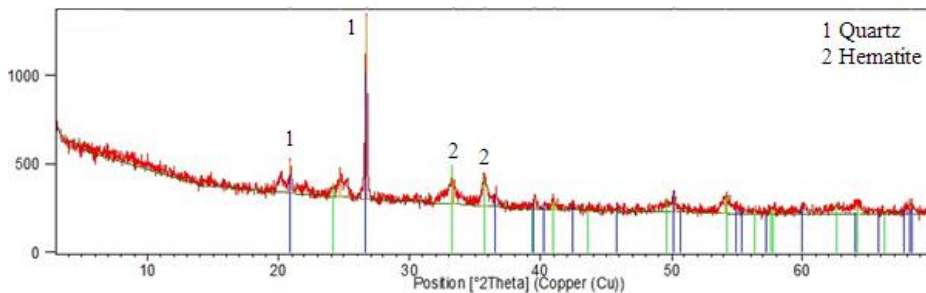


Fig. 9. XRD patterns of roasted sample

### Effect of Na<sub>2</sub>SO<sub>4</sub> addition

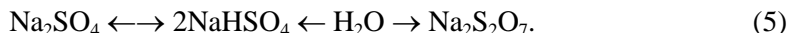
In this part of the study, possibility of improving nickel extraction was investigated. In the literature, it was reported that an impermeable layer of metal sulfate is formed on the surface of the metal oxides during sulfation. This formation prevents diffusion of SO<sub>3</sub> gas into the oxide surface. However, additions of alkali substances provide a catalytic effect to the sulfation process (Kar and Swamy, 2000; Guo et al., 2009).

Improving the reduction kinetics and the catalytic reaction activity of sodium sulfate depends on its dosage and reduction temperature. While higher temperature enhances catalytic activity, increasing the dosage of sodium sulfate accelerates the surface



reaction rate and facilitates the formation of a Fe-S solid solution. This solid solution improves mass transfer and diffusion (Lu et al., 2013).

Kar and Swamy (2000) found that alkali sulfate is decomposed at high temperature and transformed to pyrosulfate, which makes the reactant surface porous. This porous surface enhances the diffusion of  $\text{SO}_3$  gas. The related chemical reaction was indicated in Eq. 5:



In the light of these data, 10, 20, 30, 40, and 50 wt-% of  $\text{Na}_2\text{SO}_4$  were added to the roasting stage. Table 2 shows the results of these experiments, and  $\text{Na}_2\text{SO}_4$  addition had a positive effect on metal extractions, especially on nickel. The nickel extraction without  $\text{Na}_2\text{SO}_4$  addition was found as 70.4% in previous section increased up to 86.2% by adding  $\text{Na}_2\text{SO}_4$ . However, iron extraction also increased from 23.6% to 28.3%, even the aim was to reduce it.

Table 2. Effect of  $\text{Na}_2\text{SO}_4$  addition

$\text{Na}_2\text{SO}_4$ , wt. %	Metal Extractions, %		
	Ni	Fe	Co
0	70.4	23.6	83.5
5	76.2	24.1	87.2
10	81.7	24.5	89.0
20	83.6	25.8	91.7
30	84.9	27.2	92.5
40	85.5	27.9	93.4
50	86.2	28.3	94.2

When iron precipitation was applied, the iron content decreased dramatically to 0.001% Fe without any nickel and cobalt loss (Fig. 10). The precipitation process was carried out after leaching at pH 3 for 30 min using  $\text{Ca}(\text{OH})_2$  at 60 °C. Since the initial pH of the leaching solution was around 2.5,  $\text{Ca}(\text{OH})_2$  additions remained in small quantities.

The sulfating and porosity improving effects of  $\text{Na}_2\text{SO}_4$  has been observed as indicated in literature. As concentration of alkali salt addition increased, nickel, cobalt and iron extractions increased as well. With reference to these results, the pregnant leach solution contained 2.07 g  $\text{dm}^{-3}$  Ni, 0.12 g  $\text{dm}^{-3}$  Co and 0.05 g  $\text{dm}^{-3}$  Fe. The raw lateritic ore sample had a Fe/Ni ratio of 20.64, which improved to 0.02 showing the high selectivity of nickel extraction over iron.

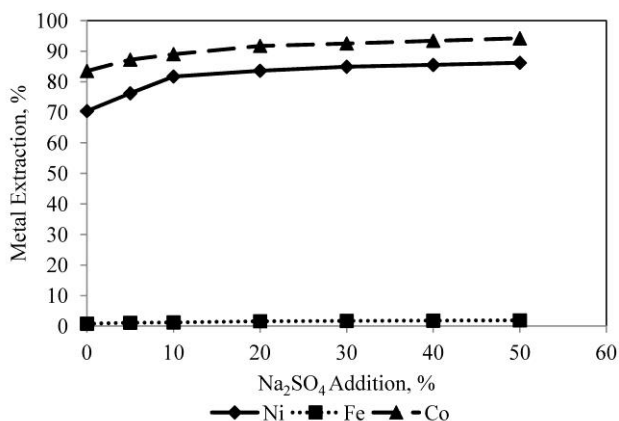


Fig. 10. Effect of Na<sub>2</sub>SO<sub>4</sub> additions on metal extractions after precipitation (200 °C digestion, 700 °C roasting with Na<sub>2</sub>SO<sub>4</sub>, water leaching at 1:5 solid/liquids for 30 min, precipitation at 50 °C)

## Conclusion

Digestion with sulfuric acid, roasting, leaching with water and precipitation of iron (DRLP) process in the presence of Na<sub>2</sub>SO<sub>4</sub> was applied on a lateritic nickel ore sample, which contains 1.2% Ni, 24.77 Fe and 0.062% Co. This process provided 86.2% Ni and 94.2 % Co extractions with 0% Fe after its precipitation using Ca(OH)<sub>2</sub> in the presence of Na<sub>2</sub>SO<sub>4</sub>.

While the digestion and roasting processes were completed in 75 min, duration of leaching and precipitation processes were 60 min. Although the energy costs of sulfation and roasting, the total process time (nearly 2.5 hours) created advantage to the process with 0.02 Fe/Ni ratio. However, agitation leaching process takes about 12-15 hours considering the leaching, thickening and precipitation processes. When the total duration and acid consumption are evaluated, DRLP process has the edge over agitation leaching process examples in these issues.

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