

STUDY OF INFLUENCE TIME IN THE IMPROVEMENT OF NICKEL CONTENTS ON LIMONITE PROCESSING USING NaOH

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ABSTRACT

Logam nikel didominasi oleh bijih sulfida, namun 70% sumber nikel dunia adalah bijih laterit, yang hanya menyumbang 40% dari output nikel dunia. Menanggapi kenaikan permintaan dan penurunan deposit nikel sulfida, pemurnian nikel bijih laterit dan teknik produksi hidrometalurgi untuk bijih laterit semakin intensif. Silikon dapat diekstraksi dari bijih nikel laterit dengan NaOH. Berbagai penelitian menunjukkan bahwa metode ini dapat meningkatkan kandungan nikel dari residu pelindian, memungkinkan limbah sisa untuk digunakan kembali dan mengurangi dampak lingkungannya. Penelitian ini bertujuan untuk mengetahui apakah mekanisme pengendapan dapat secara efektif memisahkan nikel dan kobalt dari pengotor lainnya. Limonit dilindi menggunakan larutan NaOH dengan konsentrasi 60 g/L. Durasi pelindian bervariasi antara 30, 60, 90, dan 120 menit. Pengaruh NaOH sebagai larutan pelindian diselidiki dengan pengujian XRD dan AAS. Hasil dari analisis XRD menunjukkan proses pelindian menggunakan NaOH membentuk fasa nikel dan kobalt oksida dan hidroksida dari goetit dan NaOH, dengan fasa lain pada residu pelindian terbentuk seiring dengan bertambahnya waktu pelindian. Pengujian AAS menunjukkan nilai perolehan nikel negatif yang dapat dihasilkan oleh kontaminan pada sampel awal, pelarutan ion nikel, dan kopresipitasi, dimana ion nikel diserap ke dalam fase besi hidroksida. Selain itu, uji AAS juga menunjukkan nilai perolehan kembali kobalt pada waktu pelindian 30 menit adalah 1,41%, yang berarti bahwa waktu tersebut adalah waktu optimum untuk pelindian kobalt. Sedangkan waktu yang melebihi 30 menit dapat menurunkan kadar kobalt karena pengenceran ulang dan pengendapan bersama.

Keywords: Nikel, Kobalt, Limonit, NaOH, Silikon

INTRODUCTION

The source of nickel metal has been dominated by sulphide ore for a long time, but 70% of the world's nickel source is found in laterite ore which accounts for only 40% of the world's total nickel production. With the increasing demand and nickel consumption of the world, supported by the decline of nickel sulphide reserves, the nickel purification of laterite ore and the development of hydrometallurgical production methods for laterite ores are increasingly intensified [1]. Approximately 65% of nickel production is used in the stainless-steel industry, and another 20% is used in superalloys and nonferrous alloys [2], [3]. Indonesia is one of the countries with the most deposits of laterite in the world. The amount of Indonesian nickel reserves in laterite ore reaches 15% of the world's reserves and nickel production of Indonesia contributes 14% of world nickel production [3].

The formation of laterite layers is derived from ultramafic rocks with ferro-magnesian minerals (olivine, pyroxene, and amphibole) in parts of the earth exposed to climate or tropical weather [4], [5]. This tropical climate leads to a natural leaching process by

water which removes soluble elements such as Mg, Ca, Si and precipitates insoluble elements such as Fe, Ni, Mn, Co, Cr, Al, Ti, and Cu. The humidity level of a zone climate affects the amount of laterite ore and minerals in it [1], [2].

In general, hydrometallurgy [6]–[8], pyrometallurgy [9], or a combination of pyro- and hydrometallurgy are used to convert nickel lateritic ore in metallurgical extraction processes [10]. High-pressure acid leaching (HPAL) and atmospheric pressure acid leaching (AL) have been the essential hydrometallurgical techniques for nickel processing on a commercial basis. High-Pressure Acid Leaching (HPAL) has successfully dissolved lateritic nickel ore with a high nickel and cobalt recovery. The HPAL technique relies heavily on the ore's purity because it requires a titanium autoclave, which is expensive to run and generates waste that is somewhat harmful to the environment [11], [12].

Several studies have been conducted to increase nickel levels from lateritic ore, ranging from thermodynamic calculations for the reduction [13], the characterisation of the microstructure and

phase changes during the process of reduction and leaching [14], the preparation parameters by mixing limonite ore, coal, bentonite, and Na_2SO_4 additives of the pelletising method before the reduction process [15]–[17], the mechanism of its reduction with coal as a reducing agent [9], and the effect of sodium chloride [18] or sodium sulfate [19].

An alternate method for extracting silicon from laterite nickel ore uses NaOH as a leaching reagent. Multiple studies have demonstrated that this process not only maximises the utilisation of silicon-containing minerals but also raises the nickel content of leaching residues, allowing residual waste to be utilised and reducing its environmental impact [20].

Based on the preceding discussion, this study intends to evaluate if a precipitation mechanism can efficiently separate nickel and cobalt from other contaminants.

RESEARCH METHODOLOGY

Materials

The limonite sample used in this study is examined with X-Ray Diffraction (XRD) and Atomic Absorption Spectroscopy (AAS) to determine contained compounds along with nickel and cobalt contents. The results are shown in Figure 1 and Table 1 and initial quantities of nickel and cobalt in the sample shown in Table 2.

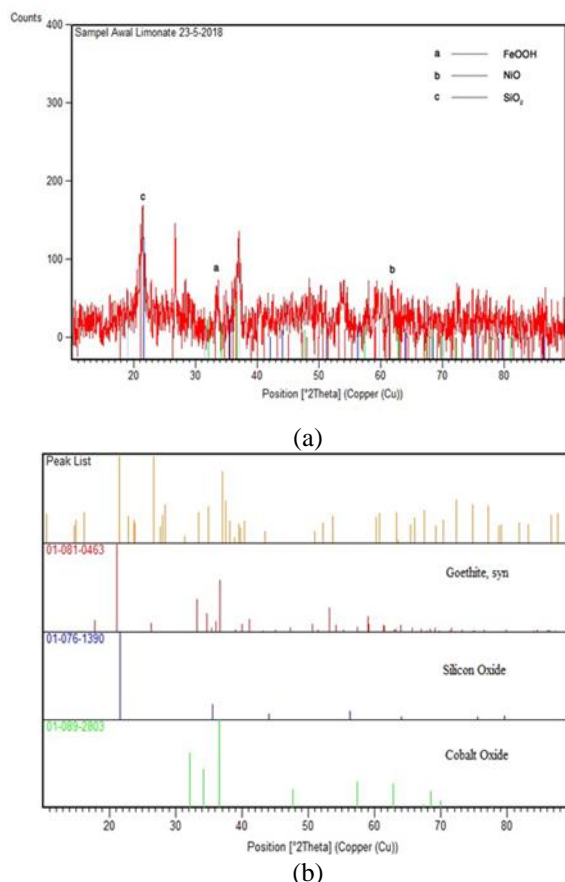


Figure 1. (a) XRD result and (b) XRD patterns of iron sand initial samples

Table 1. Semi-quantitative analysis of initial samples

Compounds	Chemical Formula	Semi-quant (%)
Goethite	FeO(OH)	61
Silicon oxide	SiO ₂	23
Cobalt oxide	CoO	16

Table 2. Initial levels of nickel and cobalt

	Initial Weight (ppm)
Nickel	175,263.87
Cobalt	35,516.56

Experimental of Method

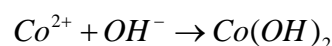
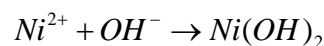
The ore used was taken from Sulawesi, Indonesia. The feed varies; ore generally has a diameter of more than 1 cm. The first process is crushing to reduce the ore size to reach the size of approximately 100 mesh. Samples that have been done crushing then performed ball milling process for 2 hours at room temperature. The powder is then separated by its grain size (mesh) using a sieve machine for 1 hour. The particle size used for the leaching process is a particle with a size of +200 mesh.

The sieved powder is then leached using NaOH. The sample ratio with the NaOH solution used in this process is 1: 5. The concentration used was 60 g / L with a leaching time variation of 30, 60, 90, and 120 minutes. The leaching process is performed on a magnetic stirrer with speed is set constants for all concentrations, ie 300 rpm. Meanwhile, the temperature used is room temperature. Next, the leaching results are filtered and dried. The drying results and initial samples were characterised using XRD and AAS.

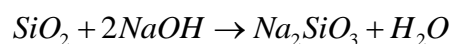
RESULTS AND DISCUSSION

XRD Characterisation

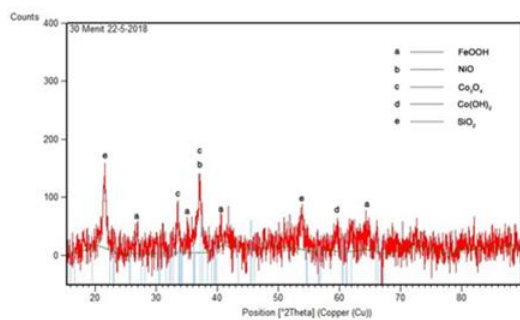
Based on the XRD test graph after leaching with NaOH, found several other compounds on some XRD chart peaks. The presence of these other compounds is due to the Goethite compound reacting with NaOH and damaging its crystal structure. The damaged goethite crystal structure releases Ni^{2+} and Co^{2+} ions into the NaOH solution, which then react to form cobalt oxide, nickel oxide, nickel hydroxide, and cobalt hydroxide, per the following equation [21], [22]:



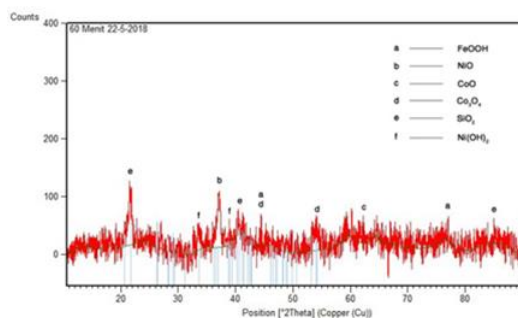
In addition to nickel and cobalt ions, impurities such as silicon also react with NaOH solution based on the following reactions [20]:



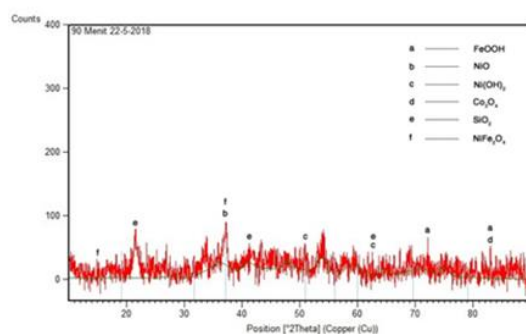
Nickel and cobalt tend to bind to O^{2-} and OH^- than to the goethite phase; therefore, the leaching NaOH solution will cause nickel to separate from the goethite phase and form oxide and hydroxide compounds. In contrast to compounds of iron oxide that have a low solubility in alkaline solutions [23]. At 90 minutes and 120 minutes leaching times, nickel reacts with iron oxide on the co-precipitation mechanism forming $NiFe_2O_4$ compounds seen in Figures 2c and 2d [23]. The XRD results in Figure 2 still show the presence of SiO_2 impurities that should have dissolved in the form of sodium silicate. The presence of silicon oxide can be caused by the number of other impurities that react with NaOH, thus blocking the reaction between silicon and the solution.



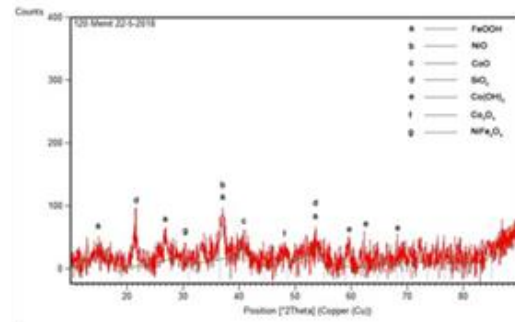
(a)



(b)



(c)



(d)

Figure 2. XRD results of NaOH leaching with time variations (a) 30 min, (b) 60 min, (c) 90 min, and (d) 120 min

AAS Characterisation

The initial weight sample of nickel and cobalt has a concentration of 175,263.87 mg/kg and 35,516.56 mg/kg, respectively. Based on Table 3 and figure 3, at a leaching time of 30 minutes, the recovery rate of nickel has decreased.

Table 3. Final weights of nickel and cobalt after NaOH leaching

Leaching Time (min)	Weight of Nickel (mg/Kg)	Weight of Cobalt (mg/Kg)
30	141.325,82	36.017,21
60	145.585,60	32.917,96
90	132.580,03	29.475,50
120	142.956,47	34.408,88

This can be caused by impurities still in the laterite nickel ore having a higher reactivity to NaOH than nickel so that the dissolved nickel cannot react with the OH^- ions and precipitates to form oxide or hydroxide compounds. At 60 minutes, the hydroxide and oxide deposits of nickel begin to form can be seen in the graph where the recovery rate of nickel increased compared to the leaching time of 30 minutes but was not able to reach the initial nickel weight. At a more extended time, that is, 90 minutes, recovery has decreased again. This is because some nickel compounds have been precipitated to become dissolved at longer leaching time into NaOH solution; other than that, the adsorption of nickel ions can also cause this event into the iron oxide structure due to the almost equal size of an atom, besides the co-precipitation contributes to reduced nickel deposits [23]. At a longer time of 120 minutes, the recovery percentage increased again due to the increasing number of goethite compounds reacting with NaOH and forming the precipitate [24]. In a separate study, longer leaching times and higher acid concentrations reduced nickel and cobalt levels. This is possible because the ferronickel slag contains nickel, cobalt, and numerous impurity minerals [25]. Another study revealed the same thing: the longer the leaching, the higher the chance that the sample will come into

contact with acid, especially if there is a magnetic stirrer causing deeper diffusion into the ferronickel slag grain [26], [27].

The percentage recovery of cobalt increases during a leaching time of 30 minutes. This is because cobalt hydroxide will form in the precipitate form at high pH. At high pH, also can occur re-dissolution of cobalt hydroxide. The longer the leaching process, the more dissolution of precipitates into NaOH solutions. This can be seen in Figure 3, where the cobalt recovery graph decreases after leaching over 30 minutes.

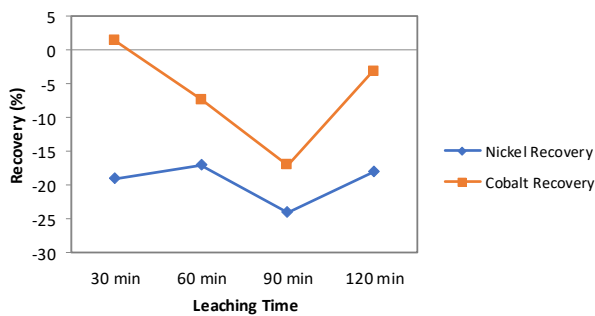


Figure 3. Recovery percentage graph

In addition to the re-dissolution of the adsorption, the event will also affect the final conditions of cobalt hydroxide in which the divalent cobalt ion will be adsorbed on iron hydroxide (FeOOH) and iron oxide (Fe₂O₃) [23]. In addition to adsorption, there is a co-precipitation event in which metal ions form a solid solution with iron hydroxide and oxide (Co-FeOH). Co-precipitation can sometimes remove more precipitated metals than adsorption [28], [29].

CONCLUSION

Based upon the conducted research associated with the effect of variation of limonite leaching time, the attained results are as following:

1. Based on the results of XRD analysis, the phase formed from the leaching process using NaOH is the oxide and hydroxide phases of nickel and cobalt from the reaction of goethite and NaOH, with the increasing leaching time being formed in other phases present in the leaching residue.
2. Based on the AAS test showing the presentation of negative nickel recovery values which can be caused by the number of impurities contained in the initial sample, the occurrence of nickel ion dissolution, and the co-precipitation phenomenon in which the nickel ions are adsorbed into the hydroxide iron phase.
3. AAS test showed a positive result on cobalt recovery value at a leaching time of 30 minutes i.e. 1.41%, showed the optimum time for cobalt leaching was 30 minutes. Leaching time exceeding 30 minutes leads to decreased cobalt levels due to re-dilution and co-precipitation events.

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