Abstract

Mixed Hydroxide Precipitate (MHP) is one of intermediate products of nickel laterite ore processing through hydrometallurgical route. This type of product can be further treated in Caron Process and/or atmospheric acid leaching to produce separate pure nickel and cobalt. In the present work, precipitation behaviour of nickel hydroxide from artificial and pregnant leach solution of Indonesian nickel laterite ore is discussed. The effects of pH, temperature, seed addition, types of neutralizing agents (i.e. NaOH, NH$_3$ and MgO) on the nickel precipitation percentage, activation energy and the constant rate of nickel precipitation were investigated. The kinetics study was done in artificial solution which contains adjusted nickel, cobalt and iron concentration. Product characterization was performed by chemical composition, particle size distribution, SEM-EDX, and XRD analysis. The highest nickel precipitation percentage of 99.9% was obtained from the precipitation under pH of 9 at 50°C. The addition of seed material promotes nickel precipitation at lower supersaturation through heterogeneous nucleation. The type of neutralizing agent for pH adjustment has some influence on the percentage of nickel precipitation. The use of MgO as neutralization agent exhibited a better percentage of nickel precipitation and precipitation kinetics than NH$_3$ and NaOH. It is suggested that MgO slurry as neutralizing agent gives a seeding effect on nickel hydroxide precipitation that is not fulfilled by the other two types of neutralizing agent. SEM analysis result indicated that by aggregation of small particles occurs during the formation of nickel hydroxide precipitate.

Keywords: nickel laterite; leaching; solution; precipitation; hydroxide

1. Introduction

Nickel laterite ore is one of the main primary sources of nickel which contributes to about 70% of world land-based nickel resources [Dalvi, D.A. et. al. 2004]. In term of processing route, the production of nickel from lateritic ore has been done either through pyrometallurgical or hydrometallurgical routes as well as through a combination of these processing routes. Pyrometallurgical processes usually treat high grade saprolite ore to produce ferronickel and nickel matte. In China, Greece and Balkan countries low grade limonite ore is also being used as the raw material for production of ferronickel and nickel pig iron (NPI) through pyrometallurgical processes. The proven technology
for hydrometallurgical treatment of low-grade laterite ore is through pressure/high pressure acid leaching (PAL/HPAL) using sulphuric acid as leaching agent. Due to high investment cost and some operational problems of PAL/HPAL plants, there has been a growing trend to shift the route to atmospheric leaching in tank and heap leaching [Mubarok, M.Z. and Purwandaria, S. 2009].

There are several options of the final product types of hydrometallurgical plant. These include pure nickel metal and cobalt as well as in the form of intermediate products such as mixed hydroxide precipitate (MHP), mixed sulphide precipitate (MSP), nickel carbonate and mixed nickel oxide [Sist, S. and Demopoulos, G.P., 2003, Oustadakis, P., et. all. 2006]. Assessment of technical, economical (i.e. capital and operating expenditures) and market aspects determines the type of final product which is regarded as the most suitable one for certain hydrometallurgical plant.

When pure nickel and cobalt metals are selected as the final product, the higher added-value will be obtained which leads to the higher revenue from the product sale. On the other hand, to produce pure metals, higher capital and operating costs must be provided. The additional costs when the pure metals selected as the final product are generally as follows:

- Facilities for solution purification and cobalt separation. The concentration-purification method which is widely used is solvent extraction.
- Facilities for electrowinning, including power generation and/or electricity cost.

When the final product is the intermediate products, the above mentioned facilities are not required. The most prominent intermediate products are MHP and MSP. The MHP has nickel content of approximately 40%, about 1.5% of cobalt and the rest are water and impurities. The followings are the advantages of MHP in comparison to MSP:

- MHP production requires lower capital cost; no H2S plant is required.
- Simpler process with easier materials handling. The MSP precipitation is more complex involving the flammable hydrogen gas handling with the risk of explosion.
- Less problem of maintenance due to corrosion.

Further treatment of MHP can be done by atmospheric pressure leaching. In contrast, the subsequent processing of MSP must be performed by pressure oxidative leaching.

On the other hand, MSP has advantages in terms of higher nickel content (±55%) and lower contents of impurities. The moisture content of MSP is also lower than that in MHP which leads to the lower transportation cost.

Nickel hydroxide precipitation is in correlation with supersaturation of nickel ions at which nickel exceeds its solubility in solution. Supersaturation is one of the most important parameters which determine the behaviour of solid crystal formation from its ion in aqueous solution. For the following reaction of solid formation:

\[ M_{a}A_{b}(s) = aM^{z+}_{aq} + bA^{x-}_{aq} \]  

(1)

The formation of solid \( M_{a}A_{b} \) can occur when \( \log Q > \log K_{sp} \), in which \( Q = [M^{z+}]^{a}[A^{x-}]^{b} \), \( K_{sp} \) is solubility product constant and \( Q = K_{sp} \) at saturated condition.

To satisfy the condition where \( \log Q > \log K_{sp} \), two different approaches can be made [Lapin, G.L, 2012]:

(a) For a given \( \log Q \), decrease \( \log K_{sp} \) and
(b) For a given \( \log K_{sp} \), increase \( \log Q \).

The first approach typically refers to a term of “crystallization” in which \( \log K_{sp} \) is decreased by temperature alteration (i.e. by heating and cooling), while “precipitation” term is usually associated with the condition where \( \log Q > \log K \) (i.e. second approach). The second approach is fulfilled by the addition of chemical reagent (precipitant) which changes \([M^{z+}]\) or \([A^{x-}]\).

Precipitation and crystallization involve three main stages, initiated by the formation of supersaturation condition, followed by nucleation and crystal growth. To attain supersaturation, four main methods are generally taken which include temperature alteration, solvent vaporization, chemical precipitant (neutralizing agent) addition and the alteration of solution composition [Allan, et. al, 2012]. In this paper, the influences of some variables on the precipitation behaviour of nickel hydroxide from atmospheric-leach solution of nickel laterite ore are discussed.
2. Experimental

Series of batch agitation leaching tests were carried out at temperature of 95°C for 8 hours using 1 molar sulphuric acid. The nickel laterite ore samples were received from Gag Island in Indonesia. After solid-liquid separation, iron precipitation was performed by pH adjustment and solution aeration for 24 hour. After separations of the iron precipitate, the filtrates are collected for further nickel hydroxide precipitation tests. The precipitation tests were conducted by stirring of the solution for 1 hour after a constant pH was attained by a drop-wise addition of sodium hydroxide solution. The influences of pH, temperature and seed addition on the percentage of nickel precipitation were studied. The pH and temperature were varied at 7, 8 and 9, 25°C, 50°C and 75°C, respectively. The seed used was nickel hydroxide precipitate obtained from the previous precipitation test. After filtration and washing of the precipitate, the solution filtrate was analysed by Atomic Absorption Spectrophotometer (AAS) to determine the residual concentration of nickel in solution. The kinetics of nickel hydroxide precipitation were investigated by using artificial solution containing certain concentration of dissolved Ni, Fe and Co and various types of neutralizing agents (i.e. NaOH, NH₃ and MgO). The artificial solution was prepared by dissolving Ni, Fe, and Co from the powders of NiSO₄.6H₂O, FeSO₄.7H₂O and CoSO₄.7H₂O of analytical grade in NH₃ solution. The nickel hydroxide precipitate obtained from the condition which resulted in the highest nickel recovery was characterized by AAS, XRD, SEM-EDX and particle distribution analyses.

3. Results and Discussion

Experimental results show that increasing pH and temperature and the addition of Ni(OH)₂ seed enhance the precipitation of nickel hydroxide. The highest nickel precipitation percentage of 99.9 was obtained from the precipitation under pH of 9 at 50°C. Higher solution pH at higher concentration of hydroxyl ion dissociated from NaOH, leads to the increase of supersaturation (S) and lowering activation energy for nucleation according to the following equation:

\[
\Delta G_r = -RT \ln \left( \frac{[Ni^{2+}][OH^-]}{[Ni^{2+}]_{\text{eq}}[OH^-]_{\text{eq}}} \right) = -RT \ln S
\]

(2)

The effect of temperature on the precipitation of nickel hydroxide in the presence and absence of Ni(OH)₂ seed at a constant pH of 7 for 1 hour can be seen in figure 1. The addition of Ni(OH)₂ seed increases the precipitation rates where 99.8% of nickel precipitation was obtained at temperature of 50°C after 1 hour of stirring.

![Figure 1. Profile of nickel precipitation percentage as a function of temperature at a constant pH of 7 after 1 hour of stirring](image)

The presence of seed gives catalytic effect for nickel hydroxide nucleation which promotes heterogeneous nucleation to perform at lower supersaturation level. At higher temperature, Ni(OH)₂ tends to be converted to NiO indicated by the change of precipitate colour. Thermodynamically, NiO is more stable at higher temperature
indicated by a higher equilibrium constant of \( \text{Ni(OH)}_2 = \text{NiO} + \text{H}_2\text{O} \) reaction.

Typical of SEM micrograph of the nickel hydroxide precipitate is illustrated in figure 2. The SEM micrograph indicates that the formation of nickel hydroxide particles occur through aggregation of small particles. Aggregation mechanism of the nickel hydroxide crystal growth was also previously stated by Cheng et al [Cheng, J. 2008]. EDX analysis on several spots on the precipitate shows the presences of sodium, sulphur and iron as the main impurities in the precipitate. The presences of sodium and sulphur in the form of sodium sulphate generated by the reaction of sodium hydroxide as pH adjustor and sulphuric acid is also detected by XRD analysis of the precipitate as can be seen in figure 3.

![Figure 2. SEM micrograph of nickel hydroxide precipitate](image)

Figure 2. SEM micrograph of nickel hydroxide precipitate

![Figure 3. XRD analysis of the precipitate showing the peak for nickel hydroxide and sodium sulphate](image)

Figure 3. XRD analysis of the precipitate showing the peak for nickel hydroxide and sodium sulphate

Chemical composition of precipitate was determined by AAS analysis. After washing, filtration and drying, the precipitate sample was weighed carefully and dissolved in sulphuric acid solution. Chemical composition of nickel hydroxide precipitate determined by AAS analysis is presented in Table 1. Profile of particle size distribution of the nickel hydroxide precipitated obtained by screening analysis is shown in figure 4. It was found that the particle size of nickel hydroxide precipitate is quite fine in which more than 95% of the nickel hydroxide particle has a size of finer than 110 microns with major fractions are under 74 microns (-200 mesh).
Table 1. Chemical composition of nickel hydroxide precipitate determined by AAS analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>35.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.53</td>
</tr>
<tr>
<td>Mg</td>
<td>1.37</td>
</tr>
<tr>
<td>Co</td>
<td>0.16</td>
</tr>
<tr>
<td>Cu</td>
<td>0.02</td>
</tr>
<tr>
<td>Zn</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Kinetics study of nickel precipitation was done at temperatures of 25°C, 50°C and 75°C using artificial solution which contains certain concentrations of Fe, Ni, Co and NH3. The addition of NH3 gives a buffer effect through the following mechanisms:

\[ NH_3 + H^+ = NH_4^+ \]  \hspace{1cm} (3)

\[ NH_4^+ + OH^- = NH_3 + H_2O \]  \hspace{1cm} (4)

Nickel is stable in solution in the form of Ni(NH3)6^2+ complex:

\[ Ni^{2+} + NH_3 = Ni(NH_3)_6^{2+} \]  \hspace{1cm} (5)

Nickel precipitation is done by the additions of NaOH, NH4OH and MgO and occurs through the following mechanism:

\[ (Ni(NH_3)_6)^{2+} + 2OH^- \leftrightarrow Ni(OH)_2 + 6 NH_3 \]  \hspace{1cm} (6)
Calculation of nickel hydroxide precipitation was performed by the following assumptions:

- The concentration of OH\(^{-}\) is constant due to the buffer effect of NH\(_3\)
- All nickel forms (Ni(NH\(_3\))\(_6\))\(^{2+}\) complex prior to the precipitation of Ni(OH)\(_2\); therefore the initial concentration of nickel = \((C_{Ni(NH_3)_6}^{2+})_0\)
- The reaction of Ni(OH)\(_2\) formation (Reaction 6) is regarded as first order
- The rate of Ni(OH)\(_2\) formation is equal to the decrease rate of nickel concentration in solution.

By using the above assumptions, the kinetics expression of nickel hydroxide precipitation can be written as follows:

\[
-\frac{d C_{Ni(NH_3)_6}^{2+}}{dt} = \frac{d C_{Ni(OH)_2}}{dt} = k'[OH^-][Ni(NH_3)_6^{2+}] = k[Ni(NH_3)_6^{2+}]
\]

\[
ln \left( C_{Ni(NH_3)_6}^{2+} \right) + ln \left( C_{Ni(OH)_2} \right) = -k_t t + ln \left( C_{Ni(NH_3)_6}^{2+} \right)_0
\]  

A rate constant (k) of Ni(OH)\(_2\) precipitation was then determined from the gradient of a linear plot of \(ln \left( C_{Ni(NH_3)_6}^{2+} \right)_t\) or \(ln \left[ C_{Ni^{2+}} \right]\) versus time (t). A plot of \(ln \left[ C_{Ni^{2+}} \right]\) vs. \(t\) for the experimental result at 50\(^\circ\)C is illustrated in figure 5. As can be seen in figure 5, linear correlation between \(ln \left[ C_{Ni^{2+}} \right]\) and \(t\) is exhibited. Similar behaviours are also obtained from the experimental results at temperature of 25\(^\circ\)C and 75\(^\circ\)C.

![Figure 5. Profile of ln \left[ C_{Ni^{2+}} \right]\) and t made from the experimental result at 50\(^\circ\)C using NaOH as neutralizing agent](image)

Activation energy (E\(_a\)) for Ni(OH)\(_2\) precipitation was determined by using Arrhenius Equation:

\[
ln k = ln A - \frac{E_a}{R} \left[ \frac{1}{T} \right]
\]  

in which \(A\) = frequency factor, \(R\) = ideal gas constant, and \(T\) = absolute temperature of precipitation. The plot of \(ln k\) versus \((1/T)\) for temperatures of 25\(^\circ\)C, 50\(^\circ\)C and 75\(^\circ\)C is given in figure 6. The profile of \(ln k\) versus \((1/T)\) gives a gradient of \((-E_a/R)\) from which the activation energy of nickel hydroxide precipitation of 21.5 kJ/mole was obtained. In term of chemical reaction, this level of activation energy is typically within a mixed controlled kinetics where the process rate is controlled either by chemical reaction and mass transfer.
Experimental works by using artificial solution was also carried out to study the effects of neutralizing agent type on the kinetics of nickel hydroxide precipitation at 25°C, 50°C and 75°C. The results show that the neutralizing agent type has remarkable influence on the kinetics of nickel hydroxide precipitation and the final residual nickel concentration in the solution. The addition of MgO gives the fastest precipitation rate followed by those of NaOH and NH₃ and this was consistent for all three temperatures varied in the investigation. Profile of ln [C_{Ni²⁺}] versus made from the experimental result at 50°C using three types of neutralizing agents is illustrated in figure 7.

Different to the other neutralizing agent used, MgO was added in the form of slurry, thus unreacted solid particle may give seeding effect and act as a substrate for heterogeneous nucleation of nickel hydroxide precipitate. In selecting the type of neutralizing agent, advantages and disadvantages of each agent for certain application must be considered. For example, sodium hydroxide is more expensive than lime but providing better solubility of sodium sulfate than gypsum that would be generated by lime addition which reduces the product purity. The feeding system of caustic is also easier than that if lime is used. Similarly, the use of MgO slurry may cause solid entrapment within the product, despite the better precipitation rate obtained by the use of this neutralizing agent.
4. Conclusions

Precipitation behaviours of nickel hydroxide from nickel laterite ore leaching are dependent on pH, temperature and the addition of seed. Increasing pH, temperature and the use of appropriate seed material enhance the precipitation of nickel hydroxide. SEM and particle distribution analyses of the precipitate shows that nickel hydroxide precipitate obtained from the precipitation at temperature of 50°C and pH 9 has fine particle size in which more than 95% of the particle has a size of finer than 110 microns. The precipitate has nickel content of ±35% with the main impurity elements of iron and magnesium. Precipitation of nickel hydroxide in artificial solution follows first order reaction kinetics with activation energy of 21.5 kJ/mole. Neutralizing agent type has remarkable effect on the kinetics of nickel hydroxide precipitation. The use of slurry MgO gives the fastest precipitation rate of nickel hydroxide than that of NaOH and NH₃ at all temperatures varied in the investigation.

Acknowledgements

The authors thank PT. Antam, Tbk. for providing the ore samples.

References