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The Study of Mixed Hydroxide Precipitate (MHP) from Local Mineral Resources in Indonesia

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Abstract. Indonesia has the largest nickel source in the world. It is estimated, there are about 21 million metric tons of nickel reserves in Indonesia. Laterite nickel ore is the most abundant nickel source especially in tropical regions. Mixed hydroxide precipitate (MHP) is intermediate product of this process. In this research, the MHP product from PT. Smelter Nickel Indonesia (PT.SNI) was investigated. The MHP quality content is important for further process of nickel refinery to become Nickel and Cobalt sulphate for battery industry. The MHP was characterized by an X-ray diffraction (XRD), a Scanning Electron Microscope (SEM), a Differential Thermal Analysis. The XRD shows that the untreated MHP was an amorphous-like material that corresponded to Jamborite type mineral, consisting of Ni-O-H. The microstructure consists some unregular shapes with various particle sizes of 1 to 20 μm, whereas some was agglomerated. The thermal data shows there are two endothermic peaks related to the dehydration of moisture and hydrated crystal, while the second was the dehydration of OH group. After the heat treatment of MHP at 850°C, the X-ray diffraction pattern consisted of several phases identified as 82.6% Bunsenite (NiO), 12.4% Cobalt Dicobalt(III) Oxide (Co_3O_4) and 5% Aluminum Oxide -Alpha (Al_2O_3) according to Rietveld refinement analysis. The NiO was expected to be the highest content of MHP, followed by Co_3O_4. **Keywords:** *Mixed Hydroxide Precipitate (MHP), Nickel Laterite, NiOH, NiO, Co_3O_4, Hydrometallurgy, Jamborite.*

INTRODUCTION

Indonesia has the largest nickel source in the world. It is estimated, there are about 21 million metric tons of nickel reserves in Indonesia. Nickel is one of the most important metals in industry [1,2]. Laterite nickel ore is the most abundant nickel source especially in tropical regions. Laterite nickel with low nickel content ore is mainly found as deposits below the ground surface. Sources of nickel can be classified into two groups: sulfide and laterite ores [3]. Due to the application of battery industry, laterite ore is becoming more potential [4-12]. Based on preliminary Study of Smelting of Indonesian Nickel Laterite Ore by Y.I. Supriyatna *et al.,* it was found that the highest nickel content from laterite ore using PKSC as reductant shows that the best Ni extraction is 89.35% [13]. Hydrometallurgical process is a popular method to recover nickel trough pressure/high pressure acid leaching by utilized sulphuric acid as leaching agent.

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 [14]. Nickel and cobalt are two elements that have very similar aqueous chemical properties due to their adjacent position in transition metal series in the periodic table. When these

elements are both present in aqueous solution, they cannot be easily separated by a simple separation method such as chemical precipitation by pH adjustment.

Nickel and cobalt are mostly recovered in the forms of intermediate products such as mixed hydroxide precipitate (MHP) and mixed sulfide precipitate (MSP). Recent trend in extraction of nickel and cobalt from laterite ore through hydrometallurgical route is by using leaching agents that can be effectively regenerated, such as hydrochloric and nitric acid. Z.Mubarok and I.L. Hanif, has reported the separations of cobalt and nickel in nitrate solution and in pregnant leach solution of nickel laterite ore from Indonesia. Separation was processed in Nitric Acid Solution by Solvent Extraction Using Cyanex 272 and Versatic 10 [15]. Processing mixed nickel cobalt hydroxide precipitate by sulfuric acid leaching followed by selective oxidative precipitation of cobalt and manganese has also been conducted by this research group [16].

Recently the lithium-ion battery based on the nickel-manganese-cobalt (NMC) has become significantly important in the application of electric vehicle worldwide [7,11,12, 19-21]. The precursor NMC were produced by the co-precipitation method of NMC sulfate mixed with chelating agent. Due to this reason, research on nickel-cobalt separation from the MHP has been increasing, potential for battery industry. MHP has been produced from the nickel laterite of the local mineral resources, such as in Sulawesi Island [1-3]. There is also MHP that produced by a company name PT. Smelter Nickel Indonesia (SNI), whereas the nickel laterite ore was mined from Sulawesi. Despite so many papers discussed on the nickel-cobalt separation, but none explore the insight of MHP. Therefore, this paper will study the characteristic of MHP from PT. SNI, in order to observe the crystal structure, microstructure and thermal properties that examined by an X-ray diffraction, a Scanning electron microscope and a Thermogravimetric analysis (TGA), respectively.

METHODOLOGY

Mixed Hydroxide Precipitate (MHP)

The Mixed Hydroxide Precipitate (MHP) raw material was obtained from the PT. Smelter Nickel Indonesia (SNI), located in Balaraja, Banten Province, Indonesia. The MHP forms were looked like green unregular granules and was rather wet, since taken directly from the plant. The MHP is shown in Figure 1.

FIGURE 1. MHP produced by PT. Smelter Nickel Indonesia at Balaraja, Banten Province.

MHP Characterization

The MHP sample was first measured by an XRD and SEM after drying process. Then it was measured by TGA to observe the phases changed at higher temperature. Afterwards, the sample was heated at temperature above 800ºC, then the dried MHP sample was measured by an XRD.

RESULTS AND DISCUSSION

Figure 2 shows the result of X-ray diffraction of the untreated MHP material. The untreated MHP material was shown only amorphous-like peaks, that looked like humps and broad located at 2Theta of 11º, 23º, and 35º.
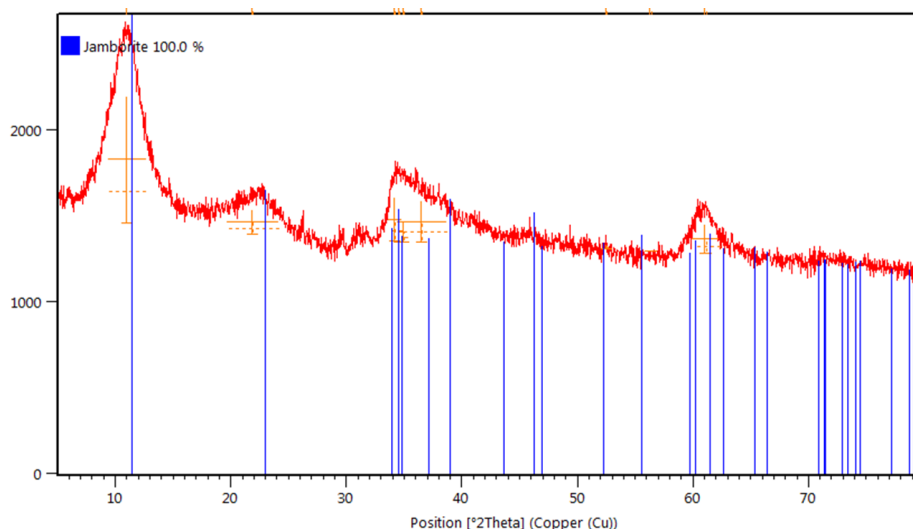
FIGURE 2. The result of X-ray diffraction of the untreated MHP material.

A search and match analysis using High Score Plus program has identified that the spectra of dried MHP belongs to mineral group named Jamborite (JCPDS No. 27-340). Based on the reference standard, its spectra correspond to 100% Jamborite, with the chemical formula $H_{1.857119}$ $Ni_{1.000119}$ $O_{2.000238}$ ($\approx$Ni (OH)$_2$) as shown in Table 1. Similar diffraction pattern also observed when Ni, Co, and Mn (with ratio 6:2:2, respectively) was co-precipitated by NaOH [17, 18]. The peaks of coprecipitated Ni-rich Ni-Co-Mn were identified as α-Ni (OH)$_2$·0.75H$_2$O (JCPDS card no. 38-0715) for 2θ 11, 22.5, 33, 34.5 and 60°. This is in accordance with our observations that the XRD pattern was corresponds to Ni (OH)$_2$ when Ni-rich solution was precipitated by hydroxide. The expected Co (OH)$_2$ in both MHP and precipitated Ni-Co-Mn is not observed may be due to its small concentration or Co was entered the lattice of Ni (OH)$_2$.

TABLE 1. Reference standard of MHP from the XRD analysis

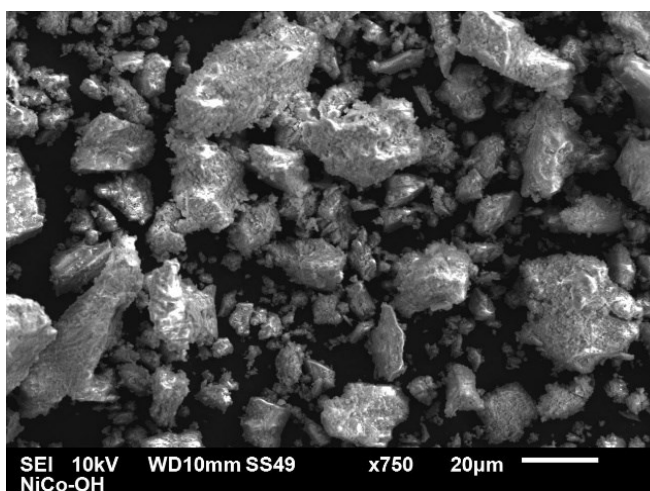| Reference Code	98-007-6650
Mineral Name	Jamborite
Compound Name	Jamborite
Common Name	Jamborite
Chemical Formula	$H_{1.857119}$ $Ni_{1.000119}O_{2.000238}$

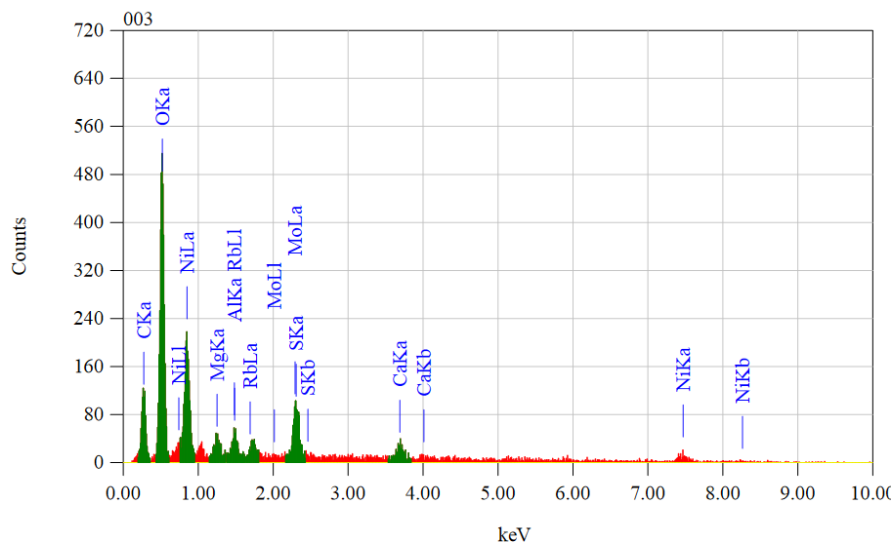

FIGURE 3. The SEM image of untreated MHP material from PT.SNI

FIGURE 4. EDX result of dried MHP from PT.SNI

TABLE 2. EDX result of dried MHP from PT.SNI

Element	(keV)	Mass%	Error%	Atom%
C K	0.277	11.49	0.15	24.83
O K	0.525	29.87	0.29	48.45
Mg K	1.253	1.22	0.33	1.30
Al K	1.486	1.76	0.35	1.69
S K	2.307	2.55	0.67	2.07
Ca K	3.690	3.47	1.00	2.24
Ni L	0.851	34.36	1.22	15.19
Rb L	1.694	2.98	1.01	0.90
Mo L	2.293	12.30	2.27	3.33
Total		100.00		100.00

Figure 3 shows the SEM image of the untreated MHP. This microstructure identified some unregular shapes with various particle sizes of 1 to 20 μm. The shiny colors are coming from the agglomerated MHP, those may be due to the wet sample. To observe in more detail of MHP characteristic, further examined to the sample was conducted. The sample then was heated and observed by using the Thermal Gravimetric Analysis from temperature 49.5°C up to above 750°C. From the EDX results (Figure 4 and Table 2), the nickel and oxygen are 34 and 29 mass%, respectively. Some impurities are Ca, Al and Mg, with 3.47, 1.27 and 1.22mass%, respectively. The Co was not detected in this first investigation of untreated MHP.

Figure 5 shows the TGA analysis of the untreated MHP. In general, there are two processes of mass reduction based on the shape of TG curve: RT-420°C, and 420-750°C. It can be explained that the first region was the dehydration of moisture and hydrated crystal, whereas the second was the dehydration of OH group. In region of 221-227°C, there was a weight gain accompanied by the release of energy. This may be due to metal oxidation, which is a metal with minor concentration considering the relatively small weight gain (2.22%). From the heat flow, there is an endothermic peak maximum at around 334°C. This could be related with the phase transition, at lower phase was releasing the hydrates and at higher temperature the phase transition from Jamborite type into a new crystal structure. The thermal data confirmed us to investigate more about the higher temperature phase of MHP. The sample was then heated up at above 800°C in the furnace before measured by X-ray diffraction.
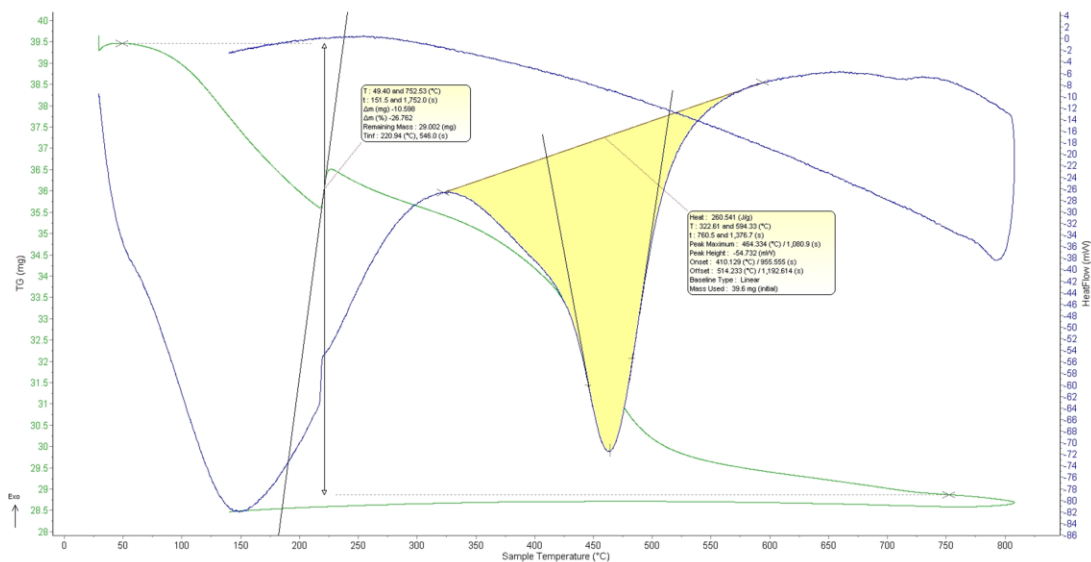
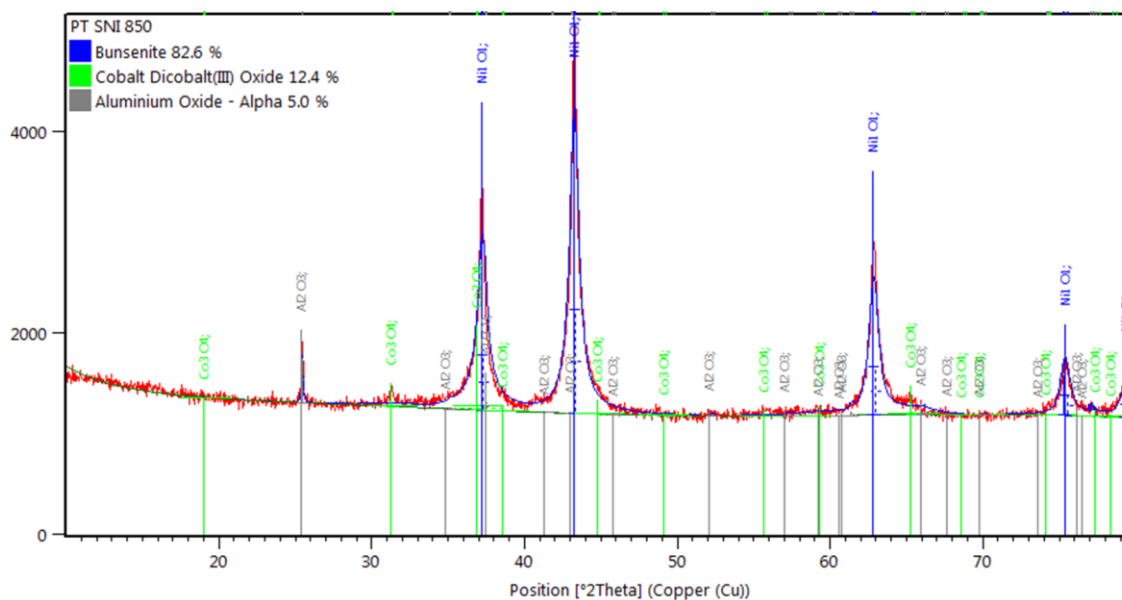**FIGURE 5.** Thermal measurement of untreated MHP by using TGA.

FIGURE 6. X-ray diffraction data of the MHP heated at 850°C.

Figure 6 shows the X-ray diffraction pattern of MHP after heated at 850°C. The spectrum was quite different with the X-ray spectrum of the untreated MHP. Previously, MHP was an amorphous-like material that corresponded to Jamborite type mineral, consisting of Ni-O-H [3]. After the heat treatment of MHP at 850, the X-ray diffraction pattern consisted of several phases identified as 82.6% Bunsenite (NiO), 12.4% Cobalt Dicobalt(III) Oxide (Co_3O_4) and 5% Aluminum Oxide -Alpha (Al_2O_3) according to Rietveld refinement analysis. The NiO was expected to be the highest content of MHP, followed by Co_3O_4 [13-15,17, 18]. The oxidation number of Co^{3+} in Co_3O_4 explained that the small weight gain in region of 221-227° of TGA analysis was the exothermic oxidation of Co^{2+} by reaction with oxygen in the air.

CONCLUSION

The study of MHP from PT SNI has been successfully conducted. The untreated MHP was the amorphous-like, corresponds to Jamborite type of crystal structure. The nickel has been detected but none of cobalt was observed for the untreated MHP. However, new crystal structure was occurred after the heat treatment of MHP at 850°C. The Rietveld refinement analysis showed that the treated MHP consisted of 82.6% Bunsenite (NiO), 12.4% Cobalt Dicobalt(III) Oxide (Co_3O_4) and 5% Aluminum Oxide-Alpha (Al_2O_3). The NiO was expected to be the highest content of MHP, followed by Co_3O_4. The Al was at minor concentration, and it is a common impurity in MHP that processed from laterite ore.

ACKNOWLEDGMENTS

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