Preliminary Research of Synthesizing Battery Grade Nickel Sulphate from Dissolution of Nickel Matte in Dilute Sulphuric Acid

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Abstract. Nickel matte is a smelter product of Indonesia mining, and it was produced from laterit ores by pyrometallurgy. The nickel matte composition is about 77% Ni, 1% Co and 0.3% Fe. This study is involving with synthesizing nickel sulphate by dissolution of nickel matte in sulphuric acid. The dissolution condition was varied by sulphuric acid grade, temperature and time of process. The dissolution process will be more effective in higher temperature and longer process time, with additional mangan oxide as catalyst. The efficiency process was observed from the filtrate, residue and nickel sulphate. The filtrate was evaluated by using Atomic Absorption Spectrometer, and residue/nickel sulphate were analysed by XRD. The more efficient process of nickel dissolution was observed at 95 °C for 3 hours, with the conversion rate about 55% - 60%. There was no difference result between sulphuric acid technical grade and pure analytic grade. After dissolution process, the synthesizing was using co-precipitation method in varied pH and alcohol/oxalic acid. The characterization of nickel sulphate has been carried out by X-ray Diffraction. The most effective of synthesizing of nickel sulphate is adjusting the pH above 5. The product of nickel sulphate will be used a precursor material for lithium battery cathode materials.

1. Introduction
Indonesia is third nickel producer in the world, with the production about 97 Metric tonnages and 69 Metric tonnages as reserved [1]. The nickel can be found in Kalimantan, Sulawesi, Halmahera and Papua Island. The nickel sources in Indonesia is nickel laterite, about 0.8% - 2% of nickel content. The nickel laterite is processed by pyrometallurgy process for resulting either ferro nickel [2] or nickel matte [3]. There are different composition between nickel matte and ferronickel. The nickel matte composition is 77% Nickel, 1% Cobalt, 0.3% Ferrous and 22% Sulfur. And the ferronickel is 17% - 24% Nickel, 1.2% Cobalt and about 70% of Ferrous. They are used as raw materials from certain industries, such as coating, electronic, battery, and etc.

Nowadays, nickel takes an important role for electrical vehicle. Nickel will be used as raw material of lithium battery, as cathode active material. In electric vehicle, lithium battery is functioning as energy storage, with the cost more than half of vehicle’s price [4,5]. The lithium battery’s main components are cathode, anode, electrolyte and separator. And among of its components, the cathode is the most expensive, and takes about 53% of the total cost [6]. For cathode, there are active materials such as lithium mangan oxide (LMO), lithium ferrophosphate (LFP), lithium Nickel Cobalt Alumunium oxide (Li-NCA), Lithium Nickel Manganese Cobalt oxide (Li-NMC), and etc. Every active material has its own characteristic and costs [7]. Based on the characteristic and
cost, many developments have been made to improve its properties. And for Li-NMC, the developments have been made in ratio/composition as well as other feature. The initial combination of Li-NMC was ratio nickel manganese and cobalt 1:1:1. Nowadays, there is a trend in increasing the nickel content and lowering the cathode content for cathode active material [8,9]. The other ratio is nickel manganese cobalt 5:3:2, and called NMC 532. There others development of ratio of Nickel manganese cobalt, such as 6:2:2 (NMC 622) and 8:1:1 (NMC 811). Their aims are for improving the specific energy, energy density, cycle life and thermal stability and also cost reduction [10].

Based on the requirement of NMC as the cathode active material, nickel matte could be used as an alternative route for synthesizing cathode active material of Li-NMC [11]. Based on nickel matte composition, it will be more efficient that ferro nickel for synthesising cathode active material. The lower content of ferrous was considered.

There many route for synthesizing of cathode active material. One of the routes is nickel sulphate. The nickel sulphate, combined with cobalt sulphate and manganese sulphate, could be processed to become Li-NMC by using co-precipitation process. This preliminary research was dealing with synthesizing nickel sulphate from nickel matte, as precursor of cathode active material. The nickel matte was dissolved in dilute sulphuric acid in specific condition resulting mixture solution of nickel, cobalt and mangan sulfate [12]. The impurities such as copper and ferrous were eliminated. Copper was eliminated from solution by adding more nickel matte. It was cemented by nickel matte. And ferrous was eliminated by adjusting the pH, and it will precipitate from solution [13]. And synthesizing of nickel sulphate was using co-precipitation method in ethanol and oxalic acid condition [12]. Then, it will be processed with other precursor material such as Cobalt sulphate and mangan sulphate for synthesizing the NMC by co-precipitation method. The co-precipitation method is one of method for producing NMC cathode active material [14, 15].

2. Experimental process
The nickel matte was characterized using electrogravimetry and ICP method. It was prepared by grinding into 200 mesh. The dissolution process was involving dilute sulphuric acid. The residue of solution was separated, and the filtrate was adjusted the pH using ammonium hydroxide. There were variations of time and temperature process. Every variation was evaluated from the mineral content of filtrate and the residue. Also, the effectivity of dilution process was evaluated using XRD Bruker D8 Advance.

The nickel sulphate was synthesized by co-precipitation method in varied of pH and chemical addition. The nickel sulphate as a product was characterized using XRD.

3. Results and discussion
The nickel matte is a smelter product that contains about 70-75% of nickel. The composition of nickel summarized in Table 1. The composition was analyzed using eletrogravimetry and ICP. The data was obtained from process technology analytical laboratory PT. Vale Indonesia Tbk.

| Composition (% w/w) | NiCoCu | NiCo | Ni | Fe | Co | Cu | S | P |
|---------------------|--------|------|----|----|----|----|---|---|
| Nickel matte        | 78.022 | 77.879 | 76.898 | 0.301 | 0.98 | 0.144 | 21.67 | < 0.0001 |

The nickel matte was dissolved using manganese oxide as catalyst. The result of dissolution process was the mixture of Nickel Mangan Cobalt Sulphate in specific concentration/composition. Based on other research data, the dissolution process of nickel matte was affected by air flow rate, stirring speed, ratio between nickel matte and sulphuric acid, sulphuric acid concentration, process temperature, concentration of oxidator (ferrous sulphate) and particle size [12]. And this research, the process was analyzed from variation of sulphuric acid concentration, temperature and time of process,
and also oxidator mangan oxide. The ferrous sulphate could not be used in this result, due to its content should be eliminated. The effectivity of the process was evaluated using AAS and XRD of filtrate and residue. The filtrate was analyzed using AAS that shown in Table 2. Based on Table 2, the more efficient process was involving mangan oxide at temperature process of 95 °C for 3 hours. By increasing temperature of process and manganese oxide addition, there was 5% increasing of Ni dissolution efficiency.

Table 2. The efficiency of dissolution process

| Process | Composition (% w/w of nickel matte) | Remarks     |
|---------|-------------------------------------|-------------|
|         | Ni  | Mn | Co  | Fe  | Cu |               |
| 1       | 40.26 | 0 | 0.21 | 0.16 | 0 | Without catalyst |
| 2       | 45.66 | 0 | 0.19 | 0.12 | 0.07 | Without catalyst |
| 3       | 55.05 | 13.74 | 0.24 | 4.33 | 0.05 |
| 4       | 57.50 | 0.02 | 0.24 | 0.16 | 0.03 | T process 95 °C |
| 5       | 53.27 | 2.88 | 0.39 | 1.75 | 0.01 |

Other than from the filtrate, the efficiency of dissolution process was evaluated from the residue. The residue was analyzing by XRD (shown by Figure 1 and Figure 2). Based on Figure 1 and Figure 2, the dissolution process was not effective. It was observed that there is some nickel matte in the residue. The analysis in both of qualitative and quantitative. The Figure 3 and Figure 4 showed the quantitative analysis. The nickel matte was evaluated as a reference. In this research, the dissolution process will be more effective in addition of mangan oxide as oxidator, and temperature at 95 °C. Eventhough, the process was ineffective by observing the residue analysis. Based on XRD analysis that shown by Figure 3 – 4 and summarized in Table 3, the nickel matte was dissolved about 53%. Based on the literature [12], the dissolution process should be longer to get more nickel in solution. So, the next research will be done longer, within 36 hours.

From the data of Tabel 3, the residue contains higher nickel than nickel matte. Thus, the dissolution process could reduce nickel matte (Ni (+2)) become nickel (Ni (0)). So, The nickel could be more processed become nickel sulphate by adding more sulphuric acid. And for the next research project, the sulphuric acid will be added more in quantity or higher concentration.

Besides nickel, there is nickel sulphate in the residue, about 33.86%. This is caused by improper separation process. The next process, the filtration process should be improved and developed.

Figure 1. The XRD diffraction of nickel matte
Figure 2. The XRD diffraction of residue

Figure 3. The quantitative analysis of nickel matte

Figure 4. The quantitative analysis of residue

Table 3. The quantitative analysis of dissolution process

| No. | Mineral                        | composition (%) |
|-----|--------------------------------|-----------------|
|     |                                | Nickel matte    | Residue         |
| 1   | Heazlewoodite (Ni$_3$S$_2$)    | 88.46%          | 41.27%          |
| 2   | Nickel                         | 10              | 24.87%          |
| 3   | Retgersite (NiSO$_4$·6H$_2$O) | -               | 33.86%          |

After dissolution, the process was followed by co-precipitation to produce nickel sulphate. The co-precipitation process was varied from pH and alcohol/oxalic acid. The variations of co-precipitation are pH 1 and pH 5, and addition of alcohol and oxalic acid. The aim of increased pH was eliminating ferrous and solidifying. The effectivity of each process was evaluated of nickel sulphate using XRD. The diffractions were shown by Figure 5-Figure 8.

Figure 5 and 6 showed the nickel sulphate was impured by ammonia. The ammonia was added to increase the pH 1 - 5. Thus, the next research project should be developed the washing process.
Figure 5. The XRD diffraction of nickel sulphate at pH 1 process

Figure 6. The XRD diffraction of nickel sulphate at pH 5 process

The pH increasing was aiming for co-precipitated the nickel sulphate, also for eliminating of ferrous (Fe). The increasing of pH did not eliminated Fe effectively. There was 21% higher of Ferrous removal in higher pH. So, The process should be developed for better eliminating Fe process.

Besides adjusting the pH, the co-precipitation process for synthesizing of nickel sulphate was achieved by alcohol and oxalic acid addition. The effectivity of co-precipitation was evaluated by XRD, as shown by Figure 7 and Figure 8.

Based on Figure 7, the co-precipitation using oxalic acid did not result nickel sulphate, but nickel oxalic. So, this process will not be further developed. Eventough, the co-precipitation by alcohol resulted nickel sulphate, with impurities of potassium. It should be analysed more detail.

By observing the diffraction of nickel sulphate, the most co-precipitation effective method was adjusting the pH above of 5. But the process should be developed for resulting nickel sulphate as precursor material of active material for cathode (battery grade).
Figure 7. The result of co-precipitation by oxalic acid

Figure 8. The result of co-precipitation by alcohol

4. Conclusion
The preliminary study of synthesizing of battery grade nickel sulphate could be evaluated by analyzing of residue and filtrate of dissolution process of nickel matte, and the quality of nickel sulphate. The following conclusion had been achieved:

1. The nickel sulphate could be synthesized from nickel matte by dissolution process in dilute sulphuric acid and continued by co-precipitation method by adjusting the pH above of 5. The purity of nickel sulphate should be improved to eliminate the ammonia.

2. The nickel sulphate could be used as a route for synthesizing cathode active material of lithium battery.

3. The research should be developed about dissolution process time, additional oxidator and catalyst, co-precipitation process and washing and separation process, etc. Also, there should be comparative study between nickel sulphate and battery grade nickel sulphate commercial.

5. Reference
[1] www.psdg.geologi.esdm.go.id
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