Reactivity of Manganese Sulphate From Sumbawa Manganese Ore With Precipitating Agent: Theoretical and Experimental Evaluation

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Abstract. Manganese oxide (Mn₃O₄) was successfully synthesized from manganese sulphate using co-precipitation method. The manganese sulphate recovered from Sumbawa manganese ore. In order to predict the manganese oxide product, the Gibbs free energy calculation was performed for the possible reaction between MnSO₄ and NaOH. The experimental results showed that the manganese oxide product was Mn₃O₄, which is consistent as the calculated Gibbs free energy is the lowest among other products. No secondary phase such as MnO, MnO₂ or Mn₂O₃ were found in the X-ray diffraction analysis. However, Mn₃O₄ had coarse particle size, i.e., 1669 ± 431 nm, which is not the type of co-precipitation’s results. Therefore, further study is needed to obtain fine particle size of Mn₃O₄.

1. Introduction
Manganese is widely used in many industries. In recent years, demand of manganese has come from soaring steel production. Steelmaking is the highest consumption of manganese which makes 85% to 90% from total demand [1]. Manganese oxides, such as MnO, MnO₂, and Mn₃O₄ have been used in wastewater treatment, catalyst, sensor, supercapacitors, and alkaline rechargeable battery [2]. Manganese salts are important in human life, it has function to take care of neuron, immune systems and regulate the blood sugar stability. In agriculture sector, manganese sulphate uses as fertilizer. The other manganese derivative is required by many industries such as dyes, pharmaceuticals and textiles.

Naturally, manganese is mostly found along with the other elements in the mineral form such as pyrolusite (MnO₂), psilomelane (BaMn₉O₁₆(OH)₄), manganite (Mn₂O₃·H₂O), bementite (Mn₅Si₆O₁₅(OH)₁₀), cryptomelane (KMn₅O₁₆) and wad (hydrus mixture of oxides). Pyrolusite, psilomelane, manganite and wad are widely used to extract manganese (Mn) since it is economically valuable [3]. Manganese ore can be categorized based on Mn contents in the minerals; (1) high grade for Mn contents more than 44%, (2) medium grade for Mn contents at range 40-44%, (3) low grade for Mn contents at range (35-40%) and (4) steel mill grade for Mn contents at 28-35% [4]. Manganese ore
from West of Nusa Tenggara was categorized as high-grade due to high content of Mn. However, the utilization of manganese ore is limited. In general, the manganese ore are sold directly without further processing. Hence, the value of manganese ore can be increased with processing to obtain derivative products, which has higher market value compared to untreated manganese ore.

Hydrometallurgy is one of the ways to obtain Mn product from manganese ore. Hydrometallurgy process includes the removal of metals from different types of ore, concentrates and waste products by aqueous solutions containing different chemical reagents. Some procedure in hydrometallurgy generally consist of roasting, leaching by acid, base or water, removal of impurities elements, separation and recovery and the last is refining to obtain the pure metals [3]. In our previous study, we successfully obtain manganese sulphate from the manganese ore using hydrometallurgy process [5]. However, the phase of manganese oxide product was not examined with theoretical calculation. Noviyanto and Yoon was successful to determine the product of reaction SiC and oxides sintering additive with theoretical calculation and experiment [6].

The objective of this study is to synthesize manganese oxide form manganese sulphate obtained from manganese ore. In the present study, we used co-precipitation method to regenerate manganese oxide. Prior to the experiment, we calculate the Gibbs free energy of the possible reaction to predict the manganese oxide product.

2. Experimental Methods
Manganese ore was obtained from Sumbawa, West of Nusa Tenggara. The procedure to synthesise manganese sulphate from manganese ore were published previously [5]. Manganese sulphate from manganese ore was precipitated by sodium hydroxide at 60°C for 30 minutes. The amount of sodium hydroxide was added carefully to maintain the stoichiometry following Equation (3) to (7) below. The solution which has brown colour aged for 72 hours. Then, the manganese oxide was obtained by separating the residue from the solution.

The phase that was formed after the reaction was analyzed by X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to observe the microstructure of the powder after reaction with sodium hydroxide. Moreover, elemental analysis of the powder was examined by energy dispersive spectroscopy (EDS) equipped in SEM. Gibbs free energy of the reaction was calculated using the Equation (1) below. Spontaneous reaction occurs if the value of Gibbs free energy is negative

\[
\Delta G_f = \Delta H_f - T \Delta S_f
\]

\[
= \left( \Delta H_{f,298} + \int_{298}^{T} \Delta C_p dT \right) - T \left( \Delta S_{f,298} + \int_{298}^{T} \frac{\Delta C_p}{T} dT \right)
\]

3. Results and Discussion
Figure 1 shows the XRD pattern of manganese ore from Sumbawa, which showed pyrolusite mineral (MnO₂ PDF # 01-081-2261). However, the XRD cannot resolve any impurity in the ore. Our previous study showed that the major impurity was Fe (17.77%) with the amount of Mn was 78.80% in weight [5].

Manganese sulphate was obtained by the reaction of manganese ore with sulphate acid and hydrogen peroxide, following reaction Equation (2). This reaction was spontaneous because the Gibbs free energy of the reaction equation (2) was negative at room temperature (25°C). Therefore, the reaction goes to right and MnSO₄ was formed along with water and oxygen.

\[
\text{MnO}_2(s) + \text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}_2(l) \rightarrow \text{MnSO}_4(aq) + 2\text{H}_2\text{O}(l) + \text{O}_2(g)
\]

The formation of manganese oxides from manganese sulphate may be varied depend on the reaction. Reaction equation (3) – (7) showed the possible reaction between MnSO₄ with NaOH.
According to those equations, the product of manganese oxide may be Mn(OH)$_2$, MnO, MnO$_2$, Mn$_3$O$_4$ or Mn$_2$O$_3$. Based on the Gibbs free energy calculation, the reaction equation that had the lowest Gibbs free energy was reaction equation (7), as shown in figure 2. Hence, the reaction between MnSO$_4$ and NaOH would form Mn$_3$O$_4$ instead of Mn(OH)$_2$, MnO, MnO$_2$ or Mn$_2$O$_3$.

\[
\begin{align*}
\text{MnSO}_4(aq) + 2\text{NaOH}(aq) &\rightarrow \text{Mn(OH)}_2(s) + \text{Na}_2\text{SO}_4(aq) \quad (3) \\
\text{MnSO}_4(aq) + 2\text{NaOH}(aq) &\rightarrow \text{MnO}(s) + \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \quad (4) \\
\text{MnSO}_4(aq) + 2\text{NaOH}(aq) &\rightarrow \text{MnO}_2(s) + \text{Na}_2\text{SO}_4(aq) + \text{H}_2(g) \quad (5) \\
\text{MnSO}_4(aq) + 2\text{NaOH}(aq) &\rightarrow \frac{1}{2}\text{Mn}_3\text{O}_4(s) + \text{Na}_2\text{SO}_4(aq) + \frac{1}{2}\text{H}_2\text{O}(l) + \frac{1}{2}\text{H}_2(g) \quad (6) \\
\text{MnSO}_4(aq) + 2\text{NaOH}(aq) &\rightarrow \frac{1}{3}\text{Mn}_3\text{O}_4(s) + \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \quad (7)
\end{align*}
\]

![Figure 1. XRD pattern of Sumbawa manganese ore.](image1)

![Figure 2. The Gibbs free energy of equation (3) – (6) as a function of temperature.](image2)
Figure 3. XRD pattern of manganese oxide product.

Figure 4. SEM images of manganese oxide product with different magnification.

Figure 5. EDS analysis of Mn$_3$O$_4$.

Table 1. EDS analysis of Mn$_3$O$_4$

| Element | at.% | 1  | 2  | 3  | 4  | 5  |
|---------|-----|----|----|----|----|----|
| Mn      |     | 28.28 | 39.04 | 47.69 | 59.84 | 49.41 |
| O       |     | 71.29 | 60.76 | 51.87 | 39.75 | 50.21 |
| Fe      |     | 0.43  | 0.20  | 0.44  | 0.41  | 0.37  |
Figure 3 shows the XRD pattern of manganese oxide product. The manganese oxide was Mn$_3$O$_4$ (PDF # 01-075-1560), which was coincident match with our calculation using Gibbs free energy, as shown in figure 2. No other phases were observed in XRD analysis. Therefore, we can conclude the reaction between manganese sulphate and sodium hydroxide would form manganese oxide in the form of Mn$_3$O$_4$.

Figure 4 shows the SEM images of Mn$_3$O$_4$. As shown in figure 4, the Mn$_3$O$_4$ consist particle that experience agglomeration. Although the co-precipitation was used to synthesize Mn$_3$O$_4$, the particle size of the resultant powder was coarse. The average particle size of MnSO$_4$ was 1669 ± 431 nm. Therefore, further study is needed to obtain Mn$_3$O$_4$ with fine particle size. The EDS analysis of Mn$_3$O$_4$ is shown in figure 5 and table 1. This EDS result is in agreement with XRD analysis in figure 3, which showed major elements were Mn and O. One notable finding in this study is the amount of Fe was <1% of Fe, which decreased significantly from 17.77% in the manganese ore.

4. Conclusions

Mn$_3$O$_4$ was successfully synthesized by reaction MnSO$_4$ with NaOH. Although there are several possibilities of the reaction of MnSO$_4$ and NaOH, such as MnO, MnO$_2$ and Mn$_2$O$_3$, Mn$_3$O$_4$ was formed because this reaction has the lowest Gibbs free energy. Our calculation is consistent with the experimental result. XRD analysis showed single phase Mn$_3$O$_4$ without any trace of secondary phase. In addition, the impurity of this Mn$_3$O$_4$ was less than 1%. However, the particle size of the result powder had relatively coarse size. Further study is needed to obtain fine particle size of Mn$_3$O$_4$.

Acknowledgments

The funding for this research was provided by National Intensive Research System Innovation Program 2018 (INSINAS), Ministry of Research and Technology of Indonesia, based on contract number 06/INSINAS/PPK/E4/2018.

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