

POTENCY OF MAKING THE CHEMICAL MANGANESE DIOXIDE (CMD) FROM EAST NUSA TENGGARA PYROLUSITE

POTENSI PEMBUATAN MANGAN DIOKSIDA DARI PIROLUSIT NUSA TENGGARA TIMUR

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ABSTRACT

Chemical manganese dioxide has not yet commercially developed in Indonesia. It is supplied by import sector. The fact that Indonesia has manganese resources as many as 60,893,820 tons is inconsistent with above condition. Research on CMD making employed pyrolusite as the raw material with size of -100+150 mesh. The material was then reacted with sulfuric acid 6% and various concentration of molasses as reductant from 10, 20, 30, 50 and 100 %. The manganese sulfate leachate was then purified using sodium hydroxide and then filtered to have a nonferrous manganese sulfate. The Mn was precipitated from manganese sulfate using sodium bicarbonate. The precipitated manganese carbonate was then calcined at 600°C by injecting the air at various flow rates (100, 200, 300, 400 cc/minute) and different calcination time (2, 3, 4 hours) to get manganese dioxide. The best extracted Mn reached 97.58% using 50% of molasses as a reductant. The precipitation of manganese carbonate had produced sodium carbonate as an impurity. The calcination had not yet changed the manganese carbonate into manganese dioxide due to extremely high calcination temperature.

Keywords: pyrolusite, molasses, precipitation, calcination

ABSTRAK

Mangan dioksida belum diusahakan di Indonesia dan kebutuhannya dipenuhi dari impor. Hal itu bertentangan dengan fakta bahwa Indonesia memiliki sumber daya bijih mangan sebanyak 60.893.820 ton. Penelitian pembuatan mangan oksida menggunakan bijih pirolusit berukuran -100+150 mesh dan direaksikan dengan asam sulfat 6% serta molases sebagai reduktor dengan variasi konsentrasi 10, 20, 30, 50, 100 % telah dilakukan. Larutan mangan sulfat hasil pelindian dimurnikan dengan natrium hidroksida untuk memisahkan besi terlarut dan kemudian disaring untuk mendapatkan larutan mangan sulfat bebas besi. Mangan diendapkan menggunakan sodium bikarbonat. Presipitat mangan karbonat dikalsinasi pada 600°C dengan mengalirkan udara menggunakan laju alir dan waktu yang bervariasi masing-masing secara berurutan adalah 100, 200, 300, 400 cc/menit dan 2, 3, 4 jam untuk menghasilkan mangan dioksida. Ekstraksi mangan terbaik yang diperoleh sebesar 97,58% menggunakan molase 50% sebagai reduktor. Pada presipitasi mangan karbonat dihasilkan natrium karbonat sebagai pengotor. Kalsinasi mangan karbonat belum mengubah material tersebut menjadi mangan dioksida karena temperatur kalsinasi yang dilakukan terlalu tinggi.

Kata kunci: pirolusit, molases, presipitasi, kalsinasi

INTRODUCTION

Manganese is the twelfth most common element in earth's crust and fourth ranked

after iron, aluminum and copper as widely used metal. More than 90% manganese is used as metallurgical product in steel manufacturing. The second largest is used as

a dry cell battery (Webb, 2008). Those added values of manganese have not yet applied in Indonesia as reported by Ministry of Energy and Mineral Resources (Anon, 2014).

Indonesia has manganese resources as many as 60,893,820 tons (Anon, 2015). The manganese had previously been exported without any processing until the Ministry of Energy and Mineral Resources Regulation No. 8, 2015 issued a regulation regarding the minimum limit of major element percentage for metal commodities. Therefore some processing efforts have to be accomplished to fulfill the regulation.

Methods for processing the ore usually depend on the ore grade. High grade manganese ores are generally treated to produce ferromanganese (FeMn) and silicon manganese (SiMn) through pyrometallurgy technique while the low grade ores are processed through hydrometallurgy method into chemical manganese dioxide (CMD) or electrolytic manganese dioxide (EMD) to replace the roasting step by reductive leaching (Sumardi, 2013).

Reductive leaching is a leaching process in reductive condition. The condition has to be applied in order to transform Mn(IV) from manganese ore into Mn(II) as seen in Figure 1. It is shown that the manganese ore leaching has to be managed in reductive

condition within acid circumstances or low pH. The kinetics of manganese reductive leaching is controlled by diffusion through insoluble layer of the associated minerals (Su et al., 2010).

Leach liquors resulted from leaching usually dissolve undesirable elements. Some treatments are needed to increase the liquor concentration through purification to eliminate or separate undesirable metals. Several options of purification process include precipitation, cementation, solvent extraction, ion exchange etc. Carbonate precipitation of manganese solution using ammonium carbonate is suitable to separate nickel and cobalt as well as manganese in ammine complexes solution to solid carbonates (Baba et al., 2014).

Some researches regarding reductive leaching of manganese ore especially pyrolusite have been conducted using sulfuric acid with different reducing agent or additive. Sponge iron is proved to be a good additive by Bafghi et al. (2008). The efficiency of Mn dissolution after 10-minute-reaction was 98% at room temperature using the particle size of $-250+150\ \mu\text{m}$ and the H_2SO_4 to MnO_2 molar ratio of 0.8 as well as sulfuric acid to MnO_2 molar ratio of 3.0. The result has a better performance than that of previous researchers that used ferrous iron as the additive.

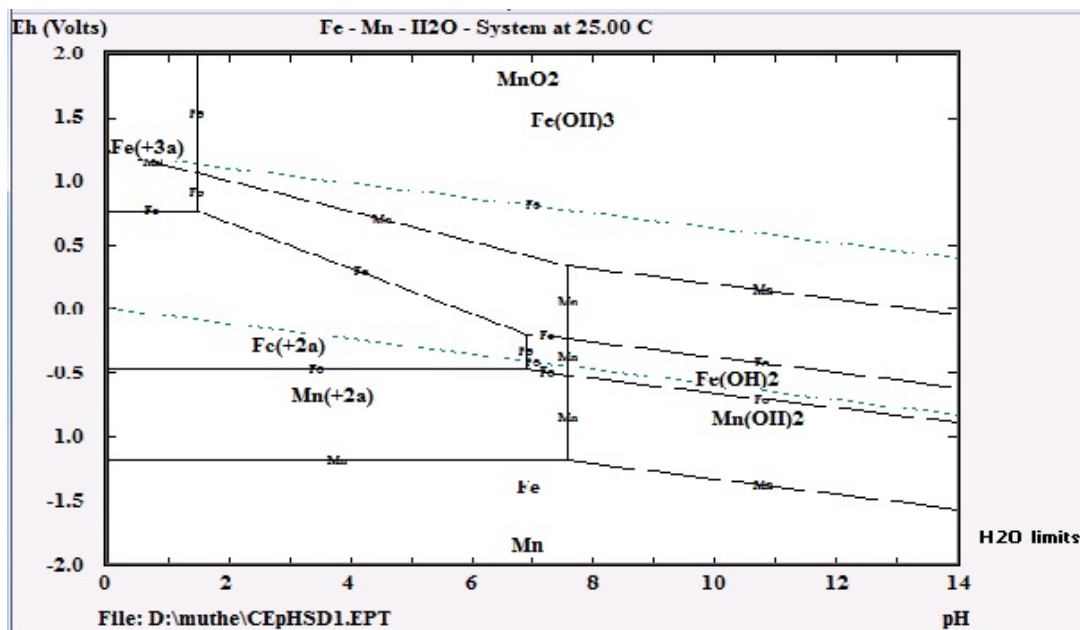
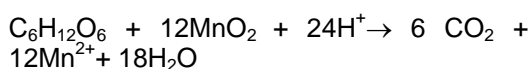


Figure 1. Eh- pH system of Mn-Fe-H₂O at 25°C (Sumardi, 2013)

Another research on manganese reductive leaching from pyrolusite using sulfuric acid as solvent had also been conducted by Nayl et al. (2011). The leaching was performed optimum condition using H_2O_2 as a reductant. The optimum condition of the leaching was achieved at 40°C for 90 minutes using 4.0 M H_2SO_4 and 0.8 M H_2O_2 on particle size of 44–37 μm pyrolusite. The manganese leaching efficiency was 92%.

Various reductants have been applied but the organic reductant has approved to be simple and efficient to leach pyrolusite (Su et al., 2009). The organic one is also environmental friendly. Some of them that can be used as reducing agent are molasses, hay, corn cob and sawdust (Sumardi, 2013). The use of corncob as reductant in reductive pyrolusite leaching had been conducted by Aliet al. (2106). The siliceous manganese ore were diluted in 1.9 mol/dm^3 sulfuric acid solution. Best manganese extraction was 92.8% and accomplished in 60 minutes at 90°C and 4 grams of corncob.

Su et al. (2009) had conducted reductive pyrolusite leaching using sulfuric acid as a solvent and molasses of alcohol wastewater as the reductant. The optimum condition for such a leaching was performed by 1.9 mol/L H_2SO_4 and 2.0 mL/g of alcohol-wastewater molasses based on Mn content in pyrolusite. The reductive leaching conducted at 90°C for 120 minutes and resulted Mn efficiency more than 93%. While, the recoveries of Fe and Al about 37 and 25% respectively. Another research dealing with pyrolusite reductive leaching was conducted using molasses from sugar production waste. The highest percentage of manganese dissolution reached up to 95.33% using condition 70°C -temperature, 6%-sulfuric acid (H_2SO_4), 10%-percent solid, 100 g/L -molasses, 200-rpm and 6-hour leaching time. Chemical reaction of the leaching was as follows (Sumardi, 2013):



Previous research (Su et al., 2009; Sumardi, 2013) proved that molasses is a good reductant. However some improvements are required to get a higher extraction percentage. This research tried to seek a

better molasses composition to have higher manganese dissolution efficiency than previous ones using molasses as a reductant. Nevertheless, the manganese sulfate production using molasses as a reductant has not yet available to be applied for making the chemical manganese dioxide. The potency of chemical manganese dioxide production using molasses as a reductant through hydrometallurgy method needs to be proved.

METHODOLOGY

The experiments used manganese ore from East Nusa Tenggara. The ore was dried by oven at 110°C for 24 hours then was prepared through sampling and milling to get representative samples size of -100+150 mesh. The sample was then reacted within 2-mole/L sulfuric acid and various molasses concentration (10; 20; 30; 50; 100 %) as reductant at 90°C in 6 hours. Equipments for process was shown in Figure 2. The leachate from filtered leaching solution heated at 70°C along with 10-% NaOH until pH 5-6 as seen in Figure 3 to precipitate the ferrous hydroxide. Then the solution was filtered to separate ferrous hydroxide. Remained solution was heated to 50°C and added with sodium carbonate to pH 9 to get precipitated manganese carbonate. The manganese carbonate was then calcined in tube furnace at 600°C with various air rate (200; 300; 400) cc/minute for 2 hours. The best air rate was used for next experiments using various calcination temperatures. Figure 4 showed the flowchart of the process.



Figure 2. Leaching process of pyrolusite



Figure 3. Ferrous precipitation from leaching solution

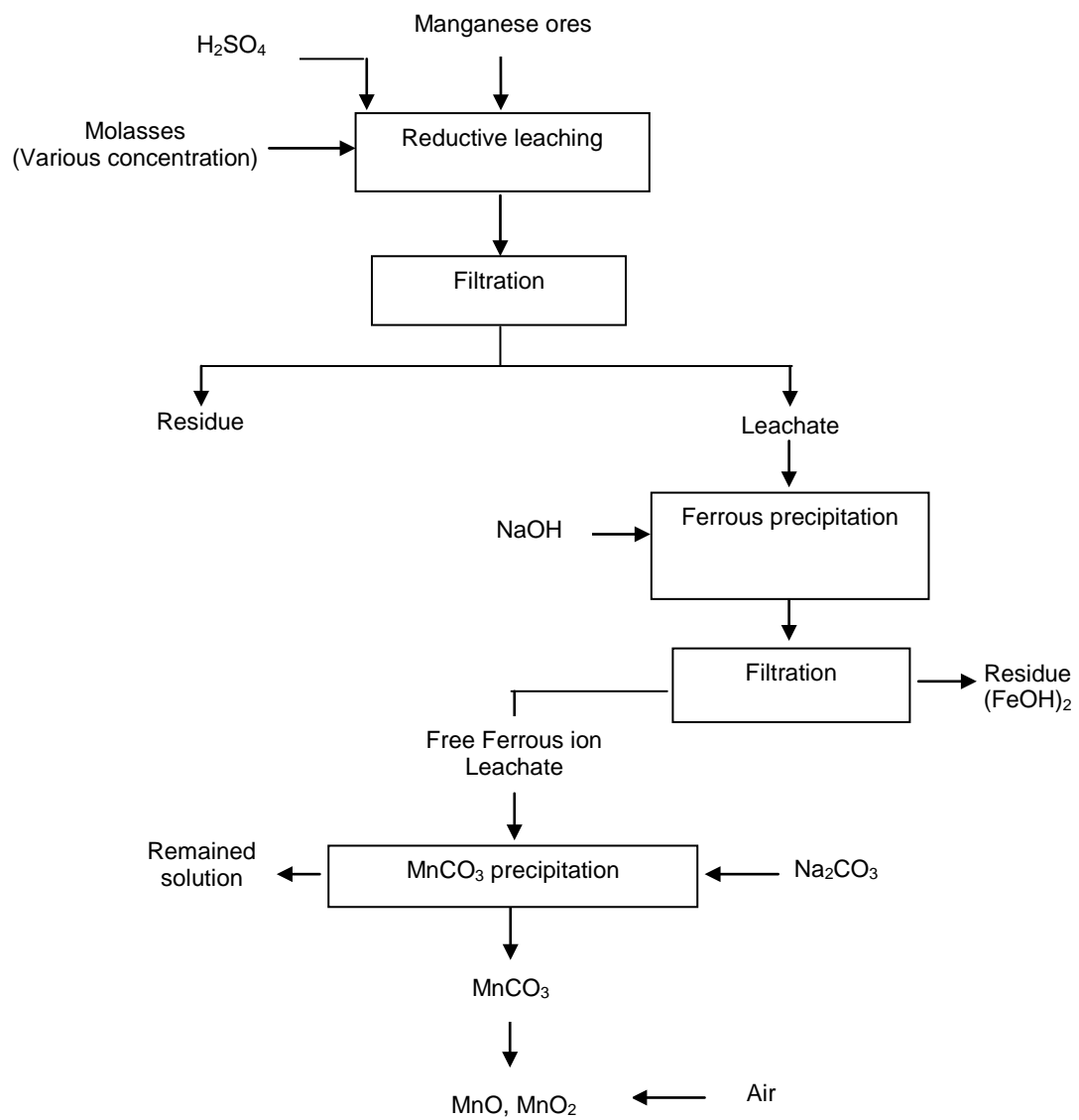


Figure 4. The flowchart regarding the process to get manganese dioxide

RESULTS AND DISCUSSION

XRD analyses of manganese ore showed (Figure 5) pyrolusite (MnO_2) and manganite ($\text{Mn}(\text{OH})_3$) along with quartz (SiO_2). However the presence of potassium was also detected by X-ray mapping (SEM-EDS method) test result as shown in Figure 6. Through SEM photo-micrograph test, it is known that manganese mineral is associated with silicate mineral.

Mineral composition is supported by chemical composition as presented in Table 1. It is showed that the manganese as the primary component followed by SiO_2 as the major impurity. The amount of Al, Mg, and Ca present the silicate content in the ore. Manganese contents in the ore used as a basic calculation for sulfuric consumption. Result of the manganese ore leaching is presented in Table 2 and illustrated in Figure 7.

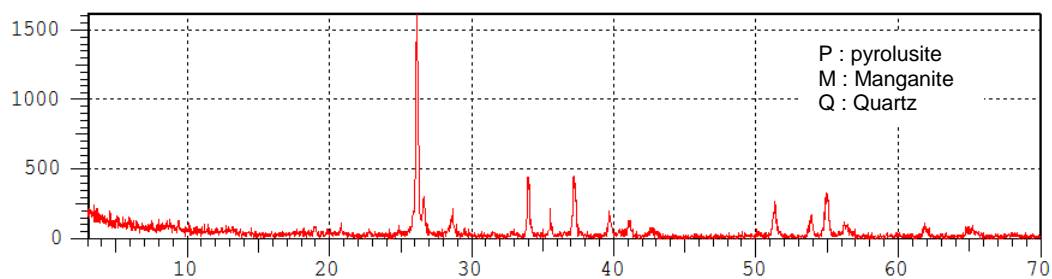
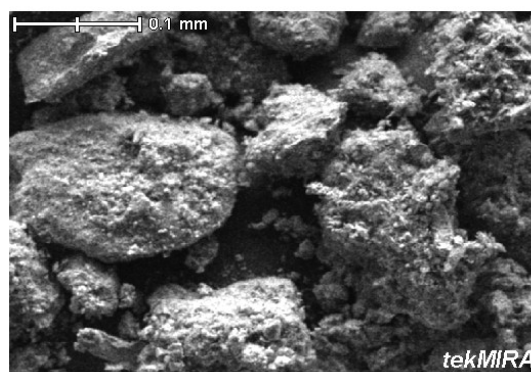
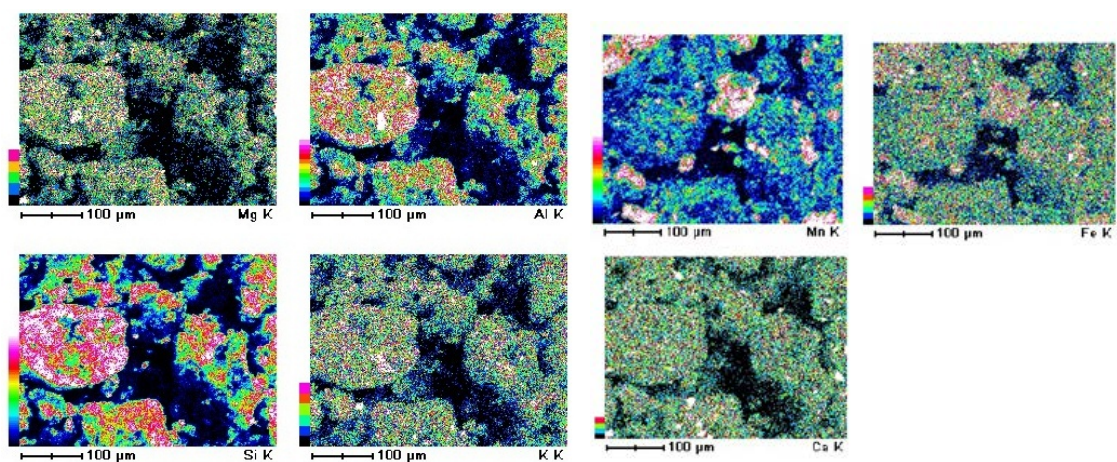


Figure 5. XRD pattern of manganese ore



(a)



(b)

Figure 6. (a) SEM photo-micrograph of manganese ore and (b) X-Ray mapping analysis of the ore

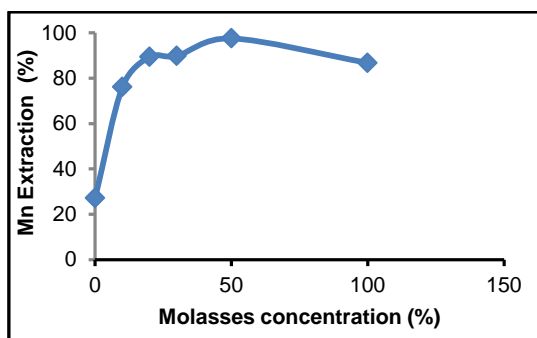


Figure 7. Mn extraction behavior versus molasses concentration

Table 1. Chemical composition of manganese ore

Element/oxide	Amount (%)
Mn total	43.8
MnO ₂	40.6
MnO	23.4
SiO ₂	14.61
Al ₂ O ₃	2.74
Fe	1.43
K ₂ O	1.42
BaO	1.69
MgO	0.23
CaO	0.50
Cu	0.029

Table 2. Result of manganese ore leaching using various molasses concentrations in 2.0 moles/Liter H₂SO₄

Molasses Concentration (%)	Mn Extraction (%)
0	27.09
10	76.10
20	89.42
30	89.85
50	97.58
100	86.79

The results proved that leaching condition was supposed to be reductive as shown in Eh- pH system of Mn-Fe-H₂O at 25°C (Figure 1). It is confirmed that without molasses the extraction percentage was poor compares to others concentration. The

result also proved that molasses is a good reductant for manganese ore reductive leaching. Mn extraction improved as the molasses concentration increased to 50% (97.58%) and decreased when 100% concentration of molasses were added. The excessive amount of molasses will trigger others element besides Mn reduction; the elements consumed more sulfuric acid. Constant amount of sulfuric acid would reduce Mn dissolution rate than that of previous molasses concentration.

The best Mn extraction which is used 50% of molasses concentration was purified from ferrous ion with sodium hydroxide (NaOH) addition to precipitate the ferrous. Remained solution was added with sodium carbonate (Na₂CO₃) to precipitate the manganese carbonate as visualized in Figure 8. Confirmation of the precipitated mineral composition was conducted through XRD analysis as shown at Figure 9 that affirmed the precipitate was manganese carbonate.



Figure 8. Precipitated manganese carbonate

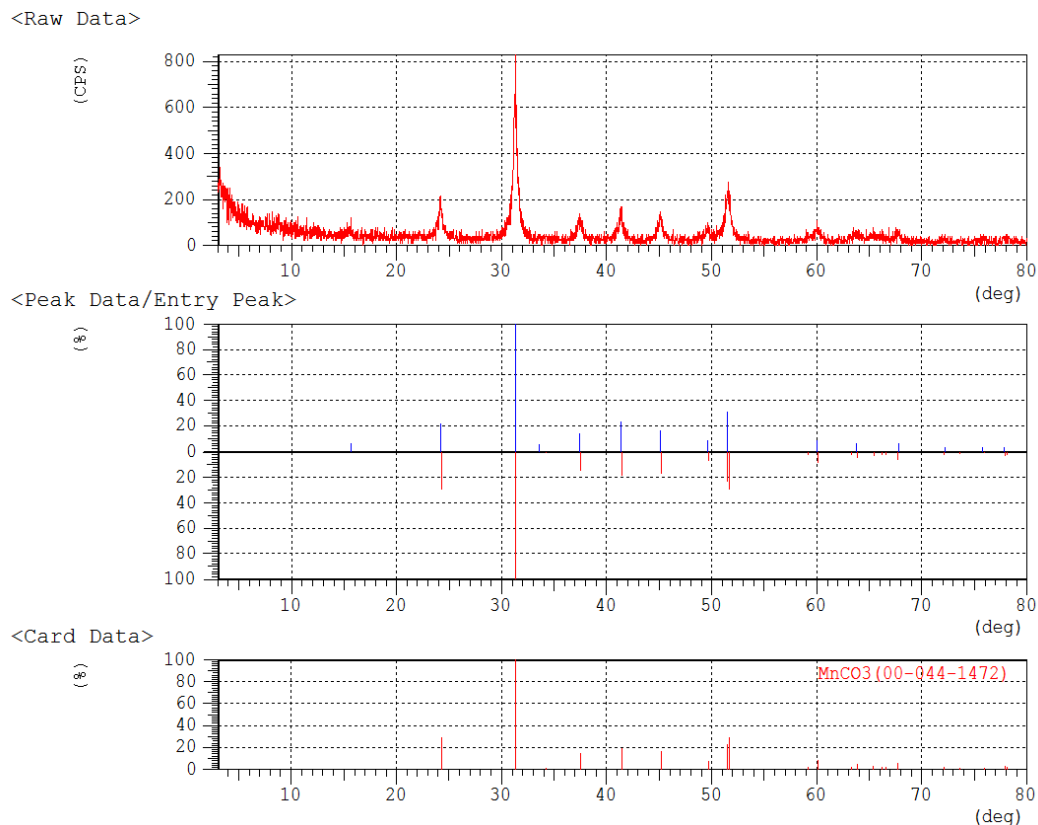
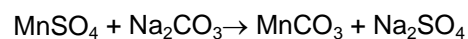


Figure 8. XRD analysis of precipitated manganese carbonate

In terms of making CMD, the manganese carbonate was calcined in a tube furnace equipped with a compressor to supply the air. The product was shown in Figure 10. Calcination was performed firstly at 600°C with various air flow rates. As seen in Table 3, the MnO_2 content under condition of 300 cc/minute air injection is bigger therefore it continued to perform at various temperatures as seen in Table 4. Different temperatures of calcination would produce different MnOx crystal form along with MnO and MnO_2 . The possible MnOx phase that can be produced were Mn_3O_4 , Mn_5O_8 even Mn_2O_3 (Ren et al., 2014).

According to TGA test for MnO_2 and MnCO_3 under air and argon atmosphere, the MnCO_3 would transform to MnO at 450°C while MnO_2 to Mn_2O_3 at 550°C and further transformation into Mn_3O_4 at 950°C (Saputra et al., 2013). The XRD test of manganese carbonate calcination at 600°C resulted transformation into manganese oxide-haussmanite (Mn_3O_4) containing sodium sulfate (Na_2SO_4) as an impurity (Figure 10). The presence of sodium sulfate was

considered to occur during precipitation of manganese carbonate. The precipitation of such a material was illustrated as follows:



while illustration for calcination process was shown below:

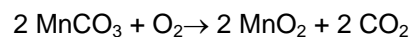


Figure 9. Calcined manganese carbonate

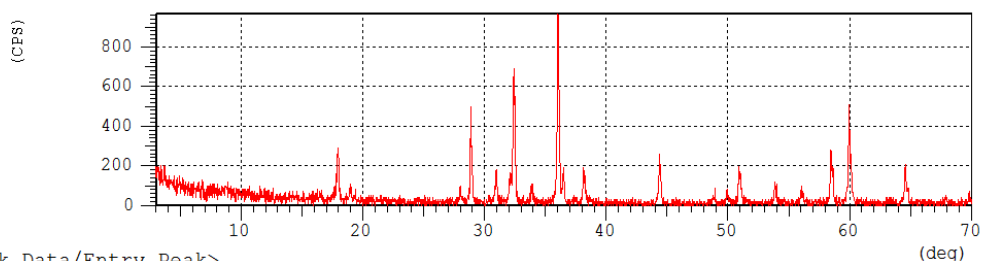
Table 3. Mn content in calcined manganese carbonate at 600°C for 2-hour reaction with various air flow rate (200, 300, 400 cc/minute)

Compounds	Content (%)		
	200 cc/minute	300 cc/ minute	400 cc/ minute
Mn Total	55.2	56.7	56.68
MnO	43.16	40.44	44.8
MnO ₂	34.78	40.17	34.78

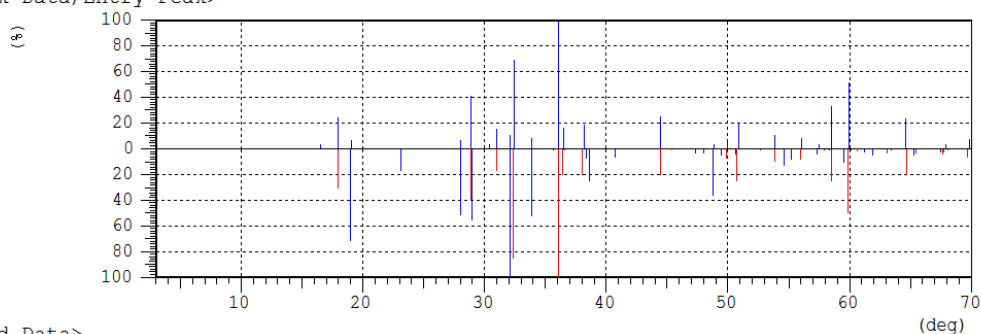
Table 4. Mn content in calcined manganese carbonate for 2-hour leaching using 300 cc/minute of air with various temperature (600, 700, 800°C)

Compounds	Content (%)		
	600°C	700°C	800°C
Mn Total	56.7	54.47	55.82
MnO	40.44	44.57	46.19
MnO ₂	40.17	31.73	31.73

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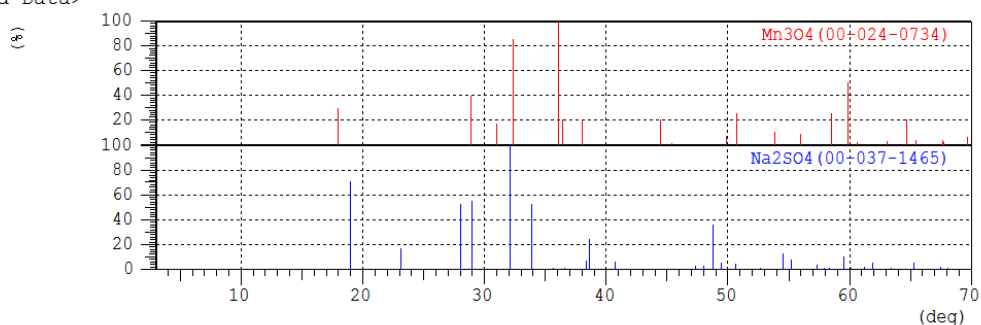


Figure10. XRD test on calcined manganese carbonate at 600°C for 2-hour leaching using 300 cc/minute air as the oxidant.

CONCLUSIONS

Molasses has a good ability as a reductant. Optimum amount of 50% concentration of molasses can extract 97.58% of Mn from pyrolusite. Precipitation of Mn from manganese sulfate leachate can be conducted using sodium bicarbonate but yielded sodium sulfate as an impurity. Therefore, it is suggested to use ammonium carbonate to precipitate the manganese in terms of avoiding the formation of sodium carbonate. The change of manganese carbonate into manganese dioxide has not yet succeeded but it turns into hausmannite because the calcination temperature that applied was too high. It is suggested to apply calcination temperatures below 600°C.

ACKNOWLEDGEMENT

The authors would like to acknowledge the Ministry of Energy and Mineral Resources for the research funding. It is also granted to Mr. Slamet Sumardi, a researcher at Indonesian Institute of Sciences, for providing the molasses.

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