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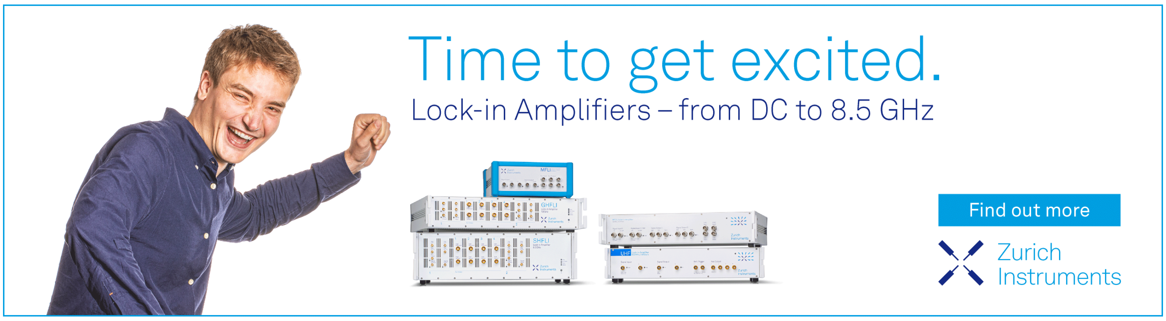

Effect of Alkali Types during Iron Precipitation on Manganese Sulfate Crystallization from Indonesian Manganese Ore

Slamet Sumardi [1, a)] Widi Astuti[1], Fika Rofiek Mufakhir[1], Yayat Iman Supriyatna[1], Muhammad Fakhrudin[2], Evvy Kartini[2, 3]

[1]*Research Center for Mining Technology, National Research and Innovation Agency (BRIN), Jl Ir Sutami km 15 Tanjung Bintang, South Lampung 35361, Indonesia*
[2]*Research Center for Advanced Material, National Research and Innovation Agency (BRIN), Kawasan PUSPIPTEK Serpong Gedung 43, Setu, Tangerang Selatan 15310, Indonesia*
[3]*National Battery Research Institute, Edu Center Building Lt 2 Unit 22260 BSD City, South Tangerang 15331, Indonesia*

[a)] *Corresponding author:* slametsumardi99@gmail.com

Abstract. NMC is a lithium-ion battery that combines three primary metals, namely Nickel, Manganese, and Cobalt. Manganese metal is used in the form of manganese sulfate ($MnSO_4$). This research has studied the effect of adding alkali in the precipitation of impurities from the solution of manganese ore leaching on the crystals of $MnSO_4$ as raw material for the manufacture of NMC. Some manganese ores are leached using oxalic acid as a reducing agent in a sulfuric acid atmosphere. Then, the impurities (mainly iron) precipitation from pregnant leached solution was carried out with pH adjustment using various alkalis. The alkalis used in this study were NaOH, NH_4OH, and $Ca(OH)_2$. The $MnSO_4$ products were characterized using XRF and XRD. The results showed that the use of $Ca(OH)_2$ in the precipitation of iron and other impurities from the pregnant leached solution could provide better $MnSO_4$ crystals than the use of NaOH and NH_4OH

INTRODUCTION

Lithium-ion batteries are the future energy for electric vehicles. This type of battery has a high energy density and has several types, namely lithium NCA (Nickel Cobalt Aluminum Oxide), lithium NMC (Nickel Manganese Cobalt Oxide) and LFP (Lithium Ferrous Phosphate) or known as lithium iron phosphate batteries [1- 4]. The electric car company, such as Tesla, currently uses NCA batteries and is currently developing the LFP type battery which is believed to be cheaper and has a longer lifespan of up to 10 years. Research on batteries for electric vehicles is being carried out [5-7]. One type of battery that is being developed is NMC [8-9]. NMC battery is a lithium type battery with the main components consisting of Nickel, Manganese, and Cobalt in the form of oxide. The source of Mn can be obtained from $MnSO_4$.

The raw material for producing $MnSO_4$ is available in Indonesia in the form manganese ores that are distributed in many areas such as Lampung, West Sumatera, Yogyakarta, East Java, and East Nusa Tenggara. Manganese ores are divided into two types, namely high grade and low-grade manganese ore. Manganese ores with high grades are usually processed by pyrometallurgical method to produce ferromanganese (FeMn) for the iron and steel industries [10-13]. Meanwhile, manganese ore with lower grades is processed through the hydrometallurgical route to become $MnSO_4$[14], MnO_2[15-17] or $KMnO_4$[18. $MnSO_4$ can be used as a raw material for NMC batteries which require high purity. To produce $MnSO_4$, several hydrometallurgical processes including reductive-leaching process, the impurities removal from pregnant leached solution, and crystallization of $MnSO_4$ product have to be conducted. The purification process is needed to remove the impurities in the leaching solution. In this study, the effect of alkali types on the iron

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and other impurities removal of pregnant leached solution will be investigated on the purity of the $MnSO_4$ product from manganese. The product of $MnSO_4$ was analyzed using XRF and XRD.

METHODOLOGY

The material used in this study was manganese ore from Way Kanan regency, Lampung Province. Chemical composition of the manganese ore was analysed using X-ray Fluorescence (XRF, PANalytical Epsilon 3 XLE, Netherland) that was shown in Table 1. The experimental processes were conducted to produce $MnSO_4$ including reductive-leaching, iron and impurities removal by precipitation using pH adjustment, and crystallization to obtain a product in the form of $MnSO_4$ crystals. In the reductive-leaching process, oxalic acid was used as a reducing agent and sulphuric acid as a leaching reagent at atmospheric condition. Leaching process was conducted in these parameters: sulphuric acid used with the concentration of 6% v/v, leaching temperature is 80ºC, leaching period is 6 hours, oxalic acid used is 30 g/l, and the ratio of ore to sulphuric acid solution is 52.63 g/l. Further, pregnant leached solution was purified to remove iron and other impurities by the precipitation method using pH adjustment. Some alkalis (NaOH, NH_4OH, $Ca(OH)_2$, and $CaCO_3$) were applied as precipitating agent to adjust the pH. Then crystallization was carried out. $MnSO_4$ product was characterized using XRF and X-Ray Diffraction (XRD, PANalytical X'pert 3 Powder, Netherland).

Table 1. Chemical composition of the manganese ore

Raw material	Composition (%)				
	Si	Mn	Fe	S	Al
Manganese Ore (Way Kanan)	4.1	36.77	6.59	0.41	0.45

RESULTS AND DISCUSSION

Crystallization of Manganese Sulphate from Filtrate after Leaching and Precipitation of Iron with NaOH

After the leaching process, the leached solution contains Mn and Fe because Fe is also dissolved in sulphuric acid. Since iron is not desired in the product, it must be separated first using precipitation with a pH adjustment. This precipitation process is carried out to reduce the amount of Fe metal contained in the leached solution. This process is carried out by adding 10% sodium hydroxide (NaOH) to the leached solution to the desired pH. The pH used were 6. After reaching the desired pH, the solution resulting from the addition of NaOH was filtered and separated from the precipitate. The filtrate obtained from the precipitation of Fe is then crystallized by heating on a hot plate at a temperature of 80ºC for approximately 5 hours to obtain white-pink crystals which are expected to be manganese sulphate crystals. The results of the XRD analysis are shown in Figure 1.

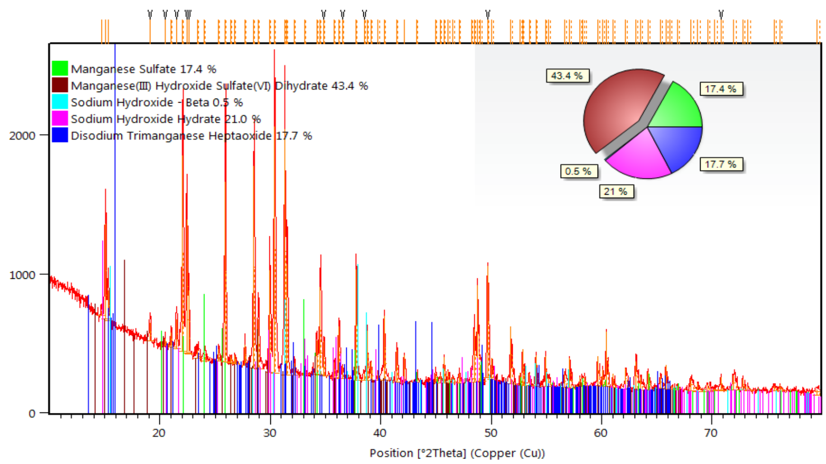

Figure 1. XRD analysis of $MnSO_4$

From the data obtained, it is concluded that the process carried out has not produced manganese sulphate powder/crystals with the expected purity because there are still impurities, one of which is sodium which may also crystallize. Sodium comes from NaOH which is used during the precipitation of Fe from the leached filtrate.

Crystallization of Manganese Sulphate from Filtrate after Leaching and Precipitation of Iron with NH_4OH

The process flow carried out in this experiment is similar to the previous one, but the NaOH used as the Fe precipitation reagent is replaced with NH_4OH. The purpose of this replacement is because based on the previous experiments, it was known that Na from NaOH also crystallized with Mn, so that the crystal product also contained a large amount of Na. The manganese sulphate product was analysed by XRD to determine the purity of the product obtained. The results of the XRD analysis are shown in Figure 2. From the XRD analysis, it is known that the manganese sulphate product still contains Ammonium Manganese Sulphate, so the resulting product is not pure.

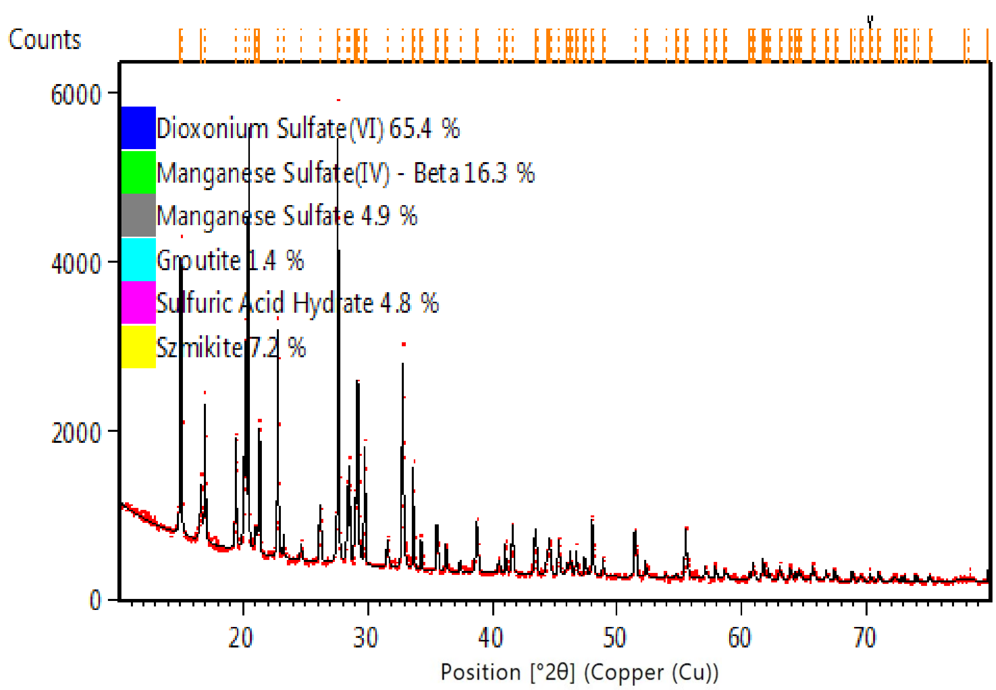

Figure 2. Data XRD $MnSO_4$

Crystallization of Manganese Sulphate from Filtrate after Leaching and Precipitation of Iron with $Ca(OH)_2$

In this experiment, $Ca(OH)_2$ was applied as the pH adjusting in the pregnant leached solution to precipitate iron and other impurities. The product of $MnSO_4$ from this experiment is the best product compare the previous experiments. The crystalline manganese sulphate product was analysed using XRF and XRD, and those compared with commercial $MnSO_4$. From Figure 3, it can be seen that the $MnSO_4$ product extracted from manganese ore produced from this process has an XRD pattern that is close similar to the XRD pattern of commercial $MnSO_4$. But there are other peaks besides $MnSO_4$ namely $CaSO_4$ (gypsum) which makes this product not pure. Further experiments are needed to obtain high-purity MnSO4 products.

The summary of all results of the XRF analysis were presented in Table 2. From Table 2, it can be seen that the use of $Ca(OH)_2$ as the precipitation agent in the removal of iron and other impurities produces the higher purity of manganese sulphate product than other precipitation agents.

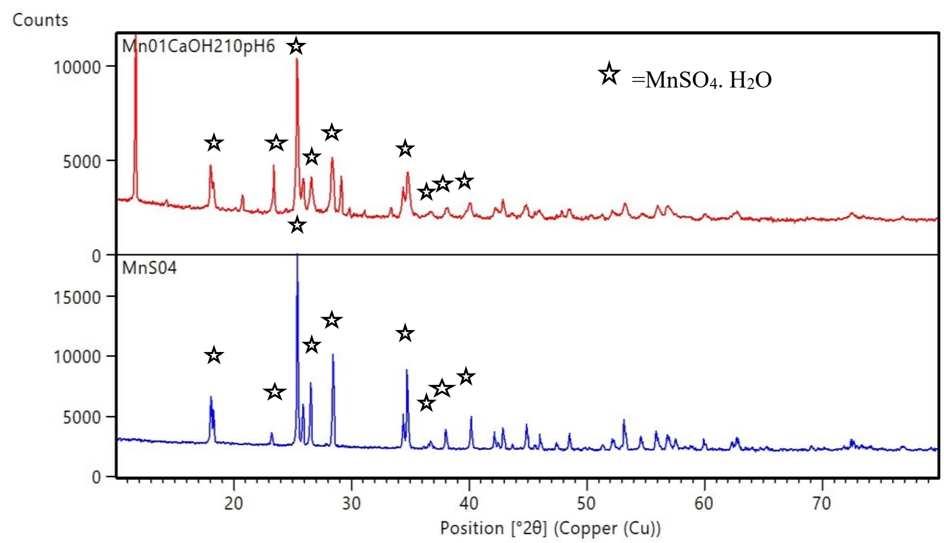

Figure 3. XRD $MnSO_4$ Synthesis Product compared to Commercial XRD MnSO4 (Merck)

TABLE 2. The summary of the results of the XRF analysis of $MnSO_4$

Product	Composition (%)				
	Mn	S	Ca	Al	K
$MnSO_4$ (commercial)	79.638	19.834	0.15	0.166	
Precipitation with NH_4OH	47.886	50.102	0.463	0.319	
Precipitation with NaOH	52.723	45.886	0.479	0.318	
Precipitation with $Ca(OH)_2$	71.863	21.937	3.160	0.167	1.128

CONCLUSION

The use of $Ca(OH)_2$ in the removal of iron and other impurities from the pregnant leached solution of manganese ore can produce $MnSO_4$ crystals with higher purity (around 93%) compared to the use of NaOH and NH_4OH. However, there is still gypsum ($CaSO_4$) in the product as the impurities. For the next study, it has to be investigated the process for calcium removal before crystallization process.

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Contributors statement: in this paper, all authors are main contributors.

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