METALURGI
Majalah Ilmu dan Teknologi
p-ISSN 0126-3188 | e-ISSN 2443-3926
ejurnalmaterialmetalurgi.lipi.go.id

RECOVERY OF MANGANESE FROM MANGANESE ORE REDUCTIVE ACID LEACHING PROCESS USING REEDS (IMPERATA CYLINDRICA) AS REDUCING AGENT

Lalu Suhaimi*, Samsul Bahtiar, Andi Sarina, Khairunnisya
Metallurgical Engineering, Sumbawa University of Technology
Jl. Raya Olat Maras, Kabupaten Sumbawa, Nusa Tenggara Barat, Indonesia 84371
*E-mail: lalu.suhaimi@uts.ac.id

Received: 09-03-2023, Revised: 04-05-2023, Accepted: 08-05-2023

Abstract

Recovery of manganese from manganese ores was investigated by reductive leaching method using reeds as a reductant in the sulfuric acid medium. Cellulose, hemicellulose, and lignin are natural reducing agents which are widely used as reducing agents to recover manganese. Effects of calcination temperature and the holding time calcination on the leaching efficiency of manganese and impurities were examined. The calcination temperature and the holding time calcination have a significant effect on the extraction of manganese. The experimental results demonstrated that the higher the calcination temperature used, the higher the percentage of manganese obtained, namely 79.58% and 87.38%, respectively. The XRD (x-ray diffraction) pattern shows that the manganese phases formed at 700 and 800 °C are Mn_3O_4 (hausmannite) and Mn_2O_3 (bixbite), respectively. The morphology in the sample with calcination temperature at 700 °C showed agglomerate- shaped particles and unevenly dispersed. Meanwhile, the sample with calcination temperature at 800 °C exhibited agglomerated particles of inhomogeneous size and were more evenly distributed. Variation of holding time in the manganese ores recovery process also affects the results of manganese recovery. The composition of the manganese recovery in the samples using holding time calcination variations of 3 and 4 hours was 83.88% and 89.24%, respectively. The results of the XRD analysis showed that the manganese phase formed using 3 hours of calcination holding time was dominated by Mn_3O_4 (hausmannite). Meanwhile, the manganese phase formed using 4 hours of holding time of calcination was dominated by Mn_2O_3 (bixbite).

Keywords: *Reeds, manganese, reductant, Mn_3O_4 (haussmannite), Mn_2O_3 (bixbite)*

1. INTRODUCTION

Global warming, as a result of increased GHGs (greenhouse gas) emission activities, has a severe impact on people's survival. One reason for the increasing of GHGs emissions is the production of ever-increasing amounts of carbon. Transportation is one of the contributing sectors to increasing carbon production. Therefore, a strategy is needed to reduce GHGs emissions in transportation.

One strategy that can be implemented to reduce GHG emissions caused by transportation is by switching to the use of electric transportation. Electric vehicles have advantages over ICE (internal combustion engine) based vehicles in reducing air pollution and GHG emissions. Electric vehicles produce far less air pollution and can be near zero compared to ICE (internal combustion engine) based vehicles [1].

Using electric transportation as a strategy to reduce GHGs emissions has encouraged researchers, especially in the fields of materials science and engineering, to continue to innovate to meet battery needs and obtain the increasing battery performance that continously. The battery in an electric car or motorcycle functions as an energy storage device in the form of DC (direct current) electricity.

Manganese is one of the materials developed by researchers to be applied as a component of battery systems [2]-[5]. In nature, manganese ore can be found in various forms. For example,

DOI : 10.55981/metalurgi.2023.705

MnO_2 (pyrolusite), $BaMn_9O_{16}(OH)_4$ (psilomelane), Mn_2O_3 (manganese), Mn_3O_4 (haussmannite), Mn_2O_3 (manganite), Mn_3O_4 (haussmannite), $MnCO_3$ (rodhochrosite), and $MnSiO_3$ (rhodonite). The investigation on the processing of manganese ores with a content of less than 40% through hydrometallurgical processes has been carried out in recent years [6]. The type of reducing agent is the important factor influencing the recovery process of manganese ore using the hydrometallurgical method. Generally, the types of reducing agents used are inorganic and organic. Inorganic reductant substances such as SO_2 (sulfur dioxide), Fe_2SO_4 (ferrous sulfate), iron powder, and other iron salts have disadvantages compared to the organic reducing agents [6]. One of the deficiencies of using inorganic reductants as reducing agents is that they are not eco-friendly. Therefore, one of the solutions is using reductants derived from agriculture or biomass.

Cellulose, hemicellulose, and lignin are natural reducing agents which are widely used as reducing agents to recover manganese. This type of reducing agent is commonly found in agriculture or biomass. Wu et.al. [7] has carried out manganese recovery from low-grade manganese ores using cellulose as the reducing agent. The results showed that the amount of manganese obtained was more than 90%. Xiong et al., [8] have studied the leaching process of low-grade pyrolusite using a lignin-reducing agent with 2M H_2SO_4 solvent. This study obtained manganese with a percentage of more than 91%. Ali et al., [9] have succeeded in the recovery of manganese with a percentage of 92,48% from a high-grade manganese ore under similar conditions by using 4% corncob as a reducing agent at 90 °C.

One of the plants that are easily found in nature that contains cellulose, hemicellulose, and lignin is reeds. Reeds (*imperata cylindrica*) contain about 40.22% cellulose, so this plant can potentially be optimized as reducing agents to recover manganese from their ores [10]. Furthermore, reeds (*imperata cylindrica*) are abundant plants in Indonesia and have yet to be utilized optimally. Based on this, this research will recover manganese ore obtained from West Sumbawa Regency, West Nusa Tenggara Indonesia, by using reeds (*imperata cylindrica*) as a reducing agent.

2. MATERIALS AND METHODS

The process of recovering manganese from its ores in this research was carried out in several stages. The first, is making reducing agent from reeds (*Imperata Cylindrica*). Second, the process of manganese recovery using the leaching method.

2.1 The Process of Making Natural Reducing Agents from Reeds (*Imperata Cylindrica*)

The fabrication of the reductor agent was strated with the reed washing process. The reeds were soaked in water for two hours. After that, the reeds were dried under the rays of the sun. The dried reeds were then cut into small pieces, mashed using a blender, and sieved. 5 grams of reed powder was macerated using 17.5% NaOH solution for 48 hours. After that, the sample was filtered using filter paper. The precipitate obtained from the maceration process is then washed using water. The sample was then dried using an oven until a dry precipitate was obtained.

2.2 The Recovery Process of Manganese Ores

The leaching process of manganese ores begins with the process of refining the manganese ores. The refined manganese ores were then dried using an oven at a temperature of 110 °C for 1 hour to remove the moisture content. The next step is the process of hydrolysis. The hydrolysis process was done by mixing 20 grams of manganese ores and 5 grams of reed powder using 100 ml of 5% H_2SO_4 acid solution. The mixture was then stirred using a magnetic stirrer with 700 rpm of speed for 2 hours at a temperature of 90 °C. The mixture obtained from this process was filtered to separate the filtrate and residue.

The filtrate obtained from hydrolysis was then precipitated by adding NaOH solution to the filtrate until a pH of 9 was obtained. The following process was to separate the deposit and the filtrate using filter paper. The precipitate obtained was then washed until it reached a neutral pH. The samples from the deposition process were then dried by using an oven at a temperature of 100 °C for one hour. The dried samples then calcined with temperature variations and in holding time calcination.

2.3 Sample Characterization

Samples that had been calcined at various temperatures of 700 and 800 °C and holding times of 3 and 4 hours were characterized. The characterization carried out on the samples included XRF (x-ray fluorescence), Brand: PANalytical, Type: Minipal 4. The characterization of the sample by using XRF aims to determine the percentage of manganese (purity) obtained. Characterization to determine the phase formed in the sample was carried out using XRD (x-ray diffraction), Brand: PANalytical, Type: Expert Pro and characterization using SEM (scanning electron microscopy), Brand: FEI, Type: Inspect-S50 used to see the microstructure manganese powder.

3. RESULT AND DISCUSSION

3.1 Various Calcination Temperatures

Table 1 shows the composition of the chemical elements contained in the precipitate from leaching after the recovery process was carried out using a calcination temperature of 700 ℃ which was analyzed using XRF (x-ray fluorescence). According to Table 1, the percentage of recovering manganese from its ores is 79.58%.

Table 1. The results of XRF analysis the sample with temperature calcination of 700 ℃

Elemen	Wt.%
Al	5.50
P	0.51
S	6.40
Ca	1.69
Mn	79.58
Cu	0.12
Zn	0.63
As	0.53
Mo	4.80
Re	0.30

Meanwhile, Table 2 shows the XRF analysis results of samples with a calcination temperature of 800 °C. The percentage of manganese recovery from manganese ores with a calcination temperature of 800 °C is 87.38%.

Table 2. The results of XRF analysis with temperature calcination of 800 ℃

Element	Wt.%
Al	1.50
P	0.10
S	3.90
Ca	0.51
Mn	87.38
Cu	0.13
Zn	0.57
As	0.88
Mo	4.80
Re	0.20

Based on the results of the XRF analysis of these samples, it was shown that a higher calcination temperature would result in a greater percentage of manganese recovery.

Figure 1 shows the results of the phase analysis of manganese samples recovered from manganese ores. Based on the XRD (x-ray diffraction) analysis, most of the manganese phase formed at a calcination temperature of 700 ℃ is dominated by bixbite (Mn_2O_3). Meanwhile, the impurities are not detected by the XRD instrument because the composition of these impurities is small. The Mn_3O_4 phase peak was detected at 2θ, ~18.022°; ~28.927°; ~32.395°; ~36.103°; ~38.105°; ~44.435°; ~50.857°; ~56.053°; ~58.533°; and ~59.938°, respectively corresponding to the crystal plane (101); (112); (103); (211); (004); (220); (105); (303); (321); and (224).

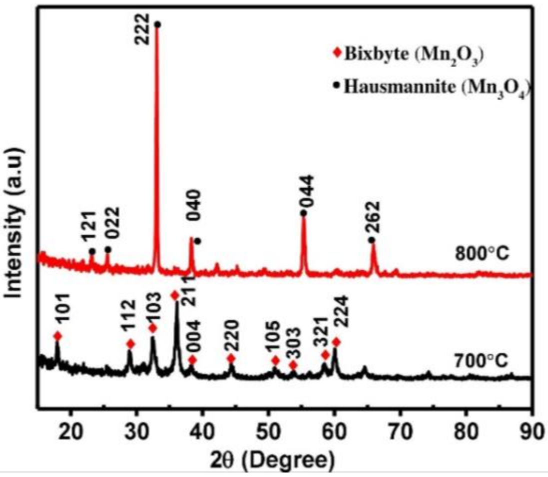
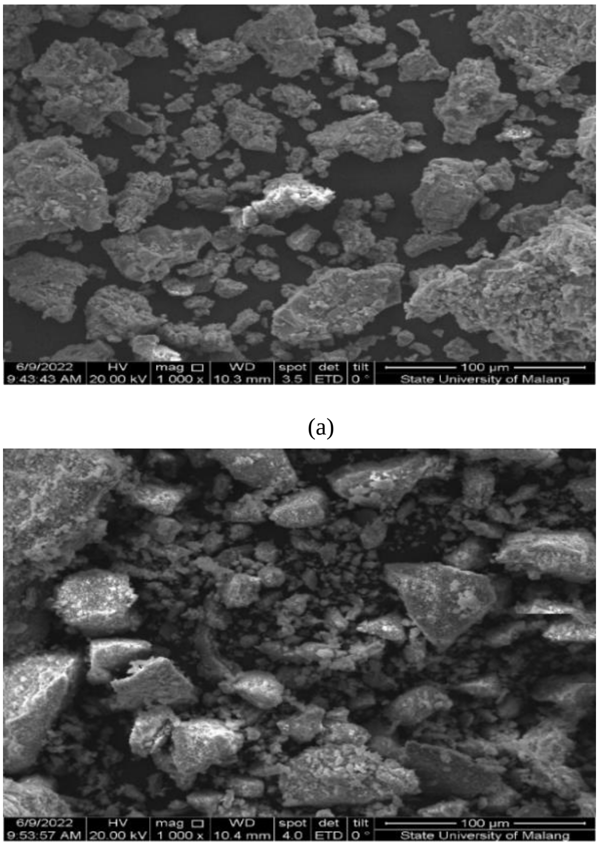


Figure 1. X-ray diffraction patterns for Mn recovered from manganese ores with calcination temperatures of 700 ℃ and 800 ℃

Meanwhile, the sample with a calcination temperature of 800 ℃ was dominated by manganese phase in the form of hausmannite (Mn_3O_4) which was detected at 2θ peaks: ~23.139°; ~26.781°; ~32.854°; ~38.235°; ~55.183°; and ~65.791° respectively correspond to the crystal planes (121), (022), (222), (040), (044), and (262). These data are also supported by the research conducted by Lan et al., [11] where calcination temperature plays an important role in the structure and the morphology of modifications. The difference in the formation of compounds resulting from calcination is because high temperatures can move the atoms to change the mineral structure into a new structure, and atomic diffusion also occurs accompanied by the release of organic compounds. Furthermore, temperature differences during the calcination process cause changes in the manganese oxide compound from the pyrochroite type to manganese oxide in various forms. The mechanism for changing the structure of pyrochroite to MnO_2 and Mn_2O_3 occurs because the pyrochroite atoms vibrate, and the arms between atoms are elongated due to heat energy in the calcination process. The process of changing the structure is caused by an increase in heat and dissolution or dissolution of atoms contained in the oxidation area, which is the ion exchange area [12].

Figure 2 shows the microstructure of the samples at the variation calcination temperatures of 700 and 800 °C (Figs. 2(a) and 2(b)) which were characterized using SEM (scanning electron microscope).



(a)

(b)

Figure 2. The SEM images of the sample calcined at (a) 700 °C, and (b) 800 °C

According to SEM analysis, the morphology of the hausmannite manganese oxide phase is in the form of agglomerated powder particles, and the powder particles are not evenly distributed (Fig. 2(a)). Meanwhile, the sample calcined at 800 °C (Fig. 2(b)) showed the morphology of the bixbite oxide phase (Mn_2O_3) in the form of agglomerated particles with inhomogeneous sizes and evenly distributed.

3.2 Various Holding Time Calcination

Table 3 shows the percentage of elemental content found in manganese ore after the recovery process was carried out using reeds as the reducing agent with a calcination time of 3 hours with a calcination temperature of 700 °C. According to Table 3, the percentage of recovering manganese from its ores is 83.88%.

Figure 3 shows the results of the analysis of the phases formed in each sample. According to the results of the XRD analysis, most of the manganese phase formed using 3 hours of holding time calcination was dominated by the hausmannite (Mn_3O_4) phase.

Table 3. The results of an XRF analysis of a sample with a holding time of 3 hours and a calcination temperature of 700 °C

Element	**Composition (%)**
Al	3.80
P	0.20
S	3.60
Ca	1.64
Mn	83.88
Cu	0.10
Zn	0.60
As	0.72
Mo	4.50
Re	0.20
Bi	0.33

Meanwhile, Table 4 shows the recovering manganese from its ores with a holding time of calcination at 4 hours with a calcination temperature of 700 °C. The composition percentage of recovering manganese with the holding time calcination of 4 hours is more significant than the holding time calcination of 3 hours, which is 89.24%. Characterizing the sample using XRF, shows that the longer the holding time calcination, the higher the recovery of the manganese obtained.

Table 4. The results of an XRF analysis of a sample with a holding time of 4 hours and a calcination temperature of 700 °C

Element	**Composition (%)**
Al	1.30
P	0.10
Si	0.60
S	2.30
Ca	0.52
Mn	89.24
Cu	0.10
Zn	0.63
As	0.70
Mo	4.00
Re	0.20

Meanwhile, the dopants are not detected by the XRD instrument because the composition of these dopants is small. The peak of the hausmannite phase was detected at 2θ, ~18.014°;

~30.990°; ~32.383°; ~36.084°; ~58,500°; and ~59,910° respectively corresponding to the crystal plane (101); (112); (103); (200); (103); (211); (321); and (224). The peak of the most dominant Mn_2O_3 phase is detected at the peak of 2θ: ~32.954°, corresponding to the crystal's plane (222).

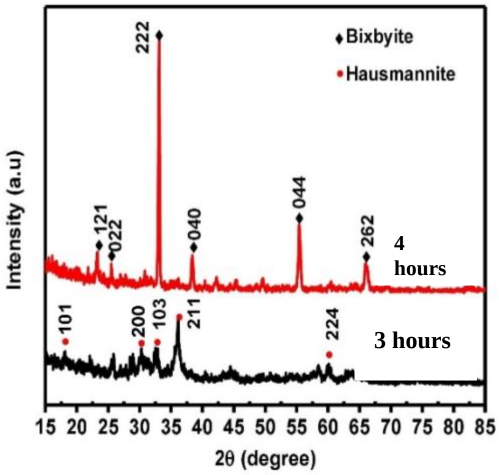
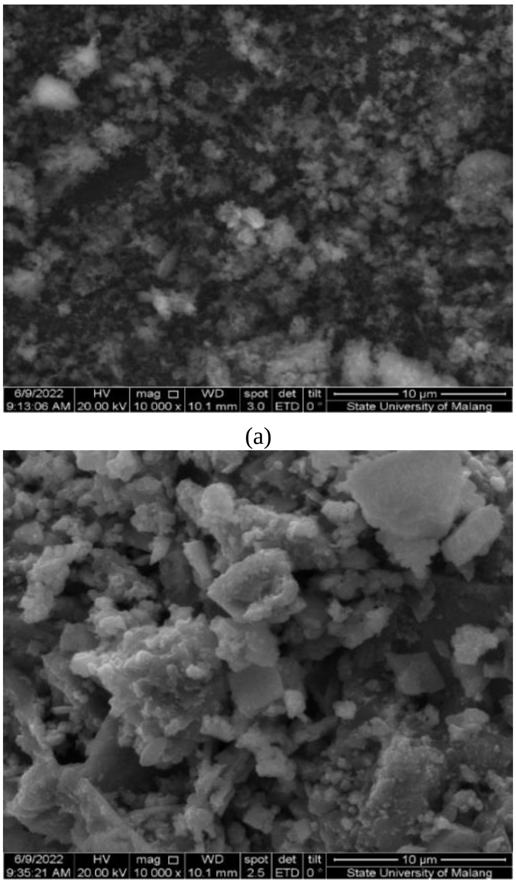


Figure 3. X-ray diffraction patterns for Mn recovered from manganese ores with holding time calcination of 3 and 4 hours

Other Mn_2O_3 phase peaks formed at 2θ, ~23.139°; ~26.781°; ~38.235°; ~55.183° and ~65.791° correspond to the crystal planes (121), (022), (040), (044), and (262), respectively.



(a)

(b)

Figure 4. SEM images of the sample with holding time calcination at (a) 3 hours, and (b) 4 hours

Meanwhile, in samples with a calcination holding time of 4 hours, the manganese phase formed was dominated by the bixbite (Mn_2O_3) phase.

Figure 4 shows the microstructure of the samples using 3 and 4 hours of calcination holding times (Figs. 4(a) and 4(b)), which were characterized by using SEM with 1000x magnification. The sample using 3 hours of holding times calcination showed the morphologically formed plate particles (Figure 4(a)). Meanwhile, the sample using 4 hours of holding times calcination showed the morphology of the bixbite oxide phase (Mn_2O_3) in the form of flake particles that were evenly distributed (Fig. 4(b)).

4. CONCLUSION

The recovery of manganese ores obtained from West Sumbawa Regency, West Nusa Tenggara, Indonesia, using reeds (Imperata Cylindrica) as the reducing agent, has been successfully investigated. Increasing the temperature of the calcination process generates an increased percentage of manganese from 79.58% to 87.38%. Increasing the calcination temperature also changes the structure of the sample. In addition, putting temperature variation in the calcination process produces different morphological patterns.

Increasing the holding time of the calcination process generates an increased percentage of manganese from 83.88% to 89.24%. Besides, increasing the holding time also changes the structure obtained from the sample. Furthermore, different holding times in the calcination process produce different morphological patterns.

ACKNOWLEDGMENT

The authors thank the Sumbawa University of Technology for the laboratory facilities.

REFERENCES

[1] C. Sudjoko, "Strategi pemanfaatan kendaraan listrik berkelanjutan sebagai solusi untuk mengurangi emisi karbon," *Jurnal Paradigma: Jurnal Multidisipliner Mahasiswa Pascasarjana Indonesia*, vol. 2, no. 2, pp. 54-68, 2021. Doi: 10.22146/jpmmpi.v2i2.70354

[2] V. Mathew, B. Sambandam, S. Kim, K. Sungjin, S. Park, S. Lee, M. H. Alfaruqi, V. Soundhararajan, S. Islam, D. Y. Putro, J. Y. Hwang, Y. K. Sun, and K. Jaekook, "Manganese and vanadium oxide cathodes

for aqueous rechargeable zinc-ion batteries: a focused view on performance, mechanism, and developments," *ACS Energy Lett.*, vol. 5, no. 7, pp. 2376-2400, 2020. Doi: 10.1021/acsenergylett.0c00740.

[3] M. H. Alfaruqi., S. Islam, D. Y. Putro, V. Mathew, S. Kim, J. Jo, K. Seokhun, Y. K. Sun, K. Kwangho, and K. Jaekook, "Structural transformation and electrochemical study of layered MnO_2 in rechargeable aqueous zinc-ion battery," *Electrochim. Acta*, vol. 276, pp. 1-11, 2018. Doi:10.1016/j.electacta.2018.04.139.

[4] S. Islam, M.H. Alfaruqi, J. Song, S. Kim, D.T.Pham, J. Jo, K. Seokhun, V. Mathew, J.P. Baboo, Z. Xiu and K. Jaekook, " Carbon-coated manganese dioxide nanoparticles and their enhanced electrochemical properties for zinc-ion battery applications, " *Journal of energy chemistry, vol.* 276, pp. 815-819, 2017.

[5] R. Farzana, K. Hassan, and V. Shajwalla, " Manganese oxide synthesized from spent Zn-C battery for supercapacitor electrode application," scientific reports, *vol.* 9, pp. 1-12, 2019.

[6] M. J. Pereira, M. M. F. Lima, and R. M. F. Lima, "Calcination and characterisation studies of a Brazilian manganese ore tailing," *Int. J. Miner. Process.*, vol. 131, pp. 26-30, 2014. Doi:10.1016/j.minpro.2014.08.003.

[7] F. F. Wu, H. Zhong, S. Wang, and S. F. Lai, "Kinetics of reductive leaching of manganese oxide ore using cellulose as reductant," *J. Cent. South Univ.*, vol. 21, no. 5, pp. 1763-1770, 2014. Doi:10.1007/s11771-014-2122-1.

[8] S. Xiong , X. Lia, P. Liua, S. Haoa, F. Haoa, Z. Yinb, and J. Liu "Recovery of manganese from low-grade pyrolusite ore by reductively acid leaching process using lignin as a low cost reductant," *Miner. Eng.*, vol. 125, pp. 126-132, 2018. Doi: 10.1016/j.mineng.2018.06.003.

[9] S. Ali, Y. Iqbal, K. Ahmad, and B. Afridi, "Phase, microstructure and beneficiation of manganese ore by acid leaching," *Journal of Minerals and Materials Characterization and Engineering*, vol. 6, no.1. pp. 60-71, 2018. Doi:10.4236/jmmce.2018.61006.

[10] S. D. Kartikasari, S. Nurhatika, and A. Muhibuddin, "Potensi alang-alang (Imperata cylindrica) dalam produksi etanol menggunakan bakteri zymomonas mobilis," *Jurnal Sains dan Seni ITS*, vol. 2, no. 2, 2013. Doi:10.12962/j23373520.v2i2.3741.

[11] L. Lan, Q. Li, G. Gu, H. Zhang, and B. Liu, "Hydrothermal synthesis of γ-MnOOH nanorods and their conversion to MnO_2, Mn_2O_3, and Mn_3O_4 nanorods," *J. Alloys Compd.*, vol. 644, pp. 430-437, 2015. Doi: 10.1016/j.jallcom.2015.05.078.

[12] I. W. Eltara, F. Widyawati, S. Bahtiar, and S. Hidayat, "Sintesis manganese ferrite dengan metode mechanical alloying dari bijih mangan alam," *Hexagon Jurnal Teknik dan Sains*, vol. 3, no. 1, pp. 29-33, 2022. Doi:10.36761/hexagon.v3i1.1345.