

Oxidative Fusion and Alkaline Leaching for Manganese Extraction from Low Grade Silicate Ore

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Abstract. Manganese silicate is one of manganese mineral which is barely exploited for mineral processing and extraction compared to other manganese minerals such as pyrolusite, psilomelane and rhodochrosite. Manganese silicate ore could not directly be leached out in the hydrometallurgical extraction process due to strong bonding between silicon and manganese. At the same time, traditional high-temperature treatment (pyrometallurgy) was unfavorable in terms of high consumption of energy and additives (flux). Therefore, in this research fusion pre-treatment would be proposed to break Mn-silicate bonding using NaOH, in a relatively lower temperature than the traditional pyrometallurgical process for common manganese ore. Fusion pre-treatment of manganese silicate would produce intermediate compound sodium manganate (Na_2MnO_4), which is easily leached using a mildly alkaline solution. The effect of manganese silicate ore/NaOH mass ratio, fusion temperature, fusion time, leaching pulp density, and leaching time on the Mn recovery would be investigated and discussed. Optimum parameters for Mn recovery (94 %) obtained were manganese silicate ore/NaOH ratio 1, fusion temperature 500 °C, fusion time 1 h, leaching pulp density 7 %, and leaching time 5 min.

INTRODUCTION

Manganese (Mn) is an element with wide application. Most Mn mined would be processed as steel raw material, while the rest would be used to supply electronic, battery, and chemical industries [1]. High demand for Mn encouraged the development of the mineral processing industry in Indonesia. Mn resources are scattered through Indonesia, which unfortunately is difficult to develop due to small size deposits and lower grades. The most common Mn minerals found in Indonesia include MnO_2 (pyrolusite), MnCO_3 (rhodochrosite) and to lesser extent $(\text{Ba},\text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ (psilomelane) and MnSiO_3 (pyroxmangite). To meet steel industry's specification, ore as a raw material must have a minimum Mn content of 40 % (high grade), which is processed by a high treatment method (pyrometallurgy) [2].

To obtain high-grade ore, selective mining is practiced, which unfortunately produced low-grade Mn ore as wastes. In the long term, this waste could pose a hazard to the environment. Low-grade Mn ore could be processed using a chemical method (hydrometallurgy) [3–8] to produce Mn salts, which could be used as chemicals in various industries. However, hydrometallurgical method could only process common Mn minerals including pyrolusite, rhodochrosite, and psilomelane. Mn silicate such as pyroxmangite on the other hand, could not be processed using this method due to mineral stability to chemical attacks at atmospheric conditions. The pyrometallurgical method could solve the problem, but it would be impractical due to the very low content of Mn in raw materials.

To solve the problem, alkali fusion pre-treatment will be proposed. The pre-treatment has successfully treated silicate material to leach out certain valuable metals for example rare earth elements from fly ash [9], vanadium and tungsten from spent catalyst [10], thorium from tin slag [11] and zirconium from zircon sand [12]. The advantage of this method is the working temperature, which is far lower (< 700 °C) than the temperature used for traditional

manganese pyrometallurgy [13]. During fusion, NaOH as additive would melt and hypothetically attack Mn silicate mineral to produce manganate salts (MnO_4^{2-}) which is easily soluble in mild leaching condition, according to reaction:



This research reaction would test alkaline fusion efficacy and leaching to recover Mn from Mn silicate ore (MS). Parameters investigated included mass ratio between NaOH as fusion agent and MS, fusion temperature, fusion time, and pulp density during leaching and leaching time.

MATERIALS AND METHOD

Manganese ore used in this study was obtained from local mines in Tanggamus Regency, Lampung Province, Indonesia. XRD analysis in previous study [8] revealed the mineral composition to be oxide (magnetite and magnesiochromite) and silicates. Mn silicate phases in the ore consist of manganese garnet ($\text{Ca}_{1.3}\text{Mg}_{0.1}\text{Mn}_{0.8}\text{Fe}_{0.8}\text{Al}_2(\text{SiO}_4)_3$) and pyroxmangite (MnSiO_3), which portion were 21 % and 15 %, respectively, according to Rietveld analysis. Chemicals used: sodium hydroxide and hydrochloric acid were obtained from Merck, Darmstadt, Germany in analytical grade. MilliQ water was used throughout the experiment. MS ore was crushed and sieved, which fraction 44-53 micron would be used in further fusion and leaching studies. Typically, 0.5 gr MS was mixed with NaOH in nickel crucible. MilliQ water was added to form MS-NaOH slurry, which was then dried in an oven at 120 °C for 12 h. The mixture was then introduced into a muffle furnace for fusion. After that, the fusion product was leached using NaOH 2 M. Mn in NaOH leachate was determined using AAS (Shimadzu AA7000). Mn recovery (R, %) was calculated using equation 2:

$$R(\%) = \frac{CxV}{mxG} \times 100\% \quad (2)$$

where:

- C : Mn concentration in leachate (mg/L)
- V : leachate volume (L)
- m : Mn ore mass (g)
- G : Mn grade in ore (mg/g)

RESULTS AND DISCUSSION

Effect of Mn Silicate ore/NaOH Mass Ratio

The effect of the mass ratio of MS and NaOH to the MN recovery was studied in the range of 1-4. Constant variables included fusion temperature 500 °C, fusion time 1 h, leaching pulp density 7 % (using NaOH 2 M), and leaching time 30 min. Figure 1 shows that mass ratio 1 yielded 66 % Mn recovery, while higher mass ratio did not significantly increase the recovery. Compared to the controlled experiment (without the addition of NaOH), the fusion and leaching produced 17 % Mn recovery. This demonstrated that the addition of NaOH as a fusion agent significantly improved Mn extraction.

Effect of Fusion Temperature

Effect of fusion temperature was studied between 300 and 700 °C while constant variables included NaOH/MS mass ratio 1, fusion time 1 h, leaching pulp density 7 % using NaOH 2 M, and leaching time 30 min. Results show a sharp increase of Mn recovery from 8 % Mn recovery at 300 °C to 56 % recovery at 400 °C (Fig. 2). Further expansion in fusion temperature caused a minor increase in Mn recovery to 71 % at 700 °C.

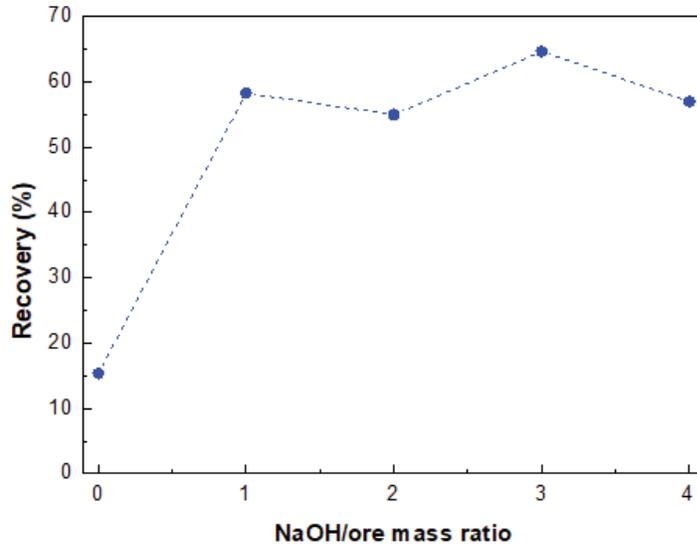


FIGURE 1. Effect of NaOH/Mn ore to the Mn recovery.

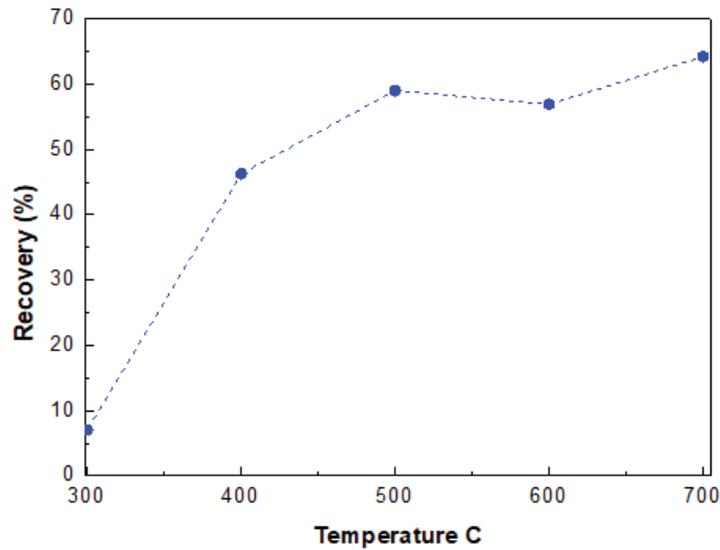


FIGURE 2. Effect of fusion temperature to Mn recovery.

Effect of Fusion Time

The effect of fusion time was studied at 15, 30, 60, 120, and 180 min. NaOH/MS mass ratio, fusion temperature, leaching pulp density, and leaching time were set constant at 1, 500 °C, 7 %, and 30 min, respectively. Results in Fig. 3 indicate the optimum fusion time to be 60 min (57 % recovery), which longer fusion time did not significantly increase Mn recovery.

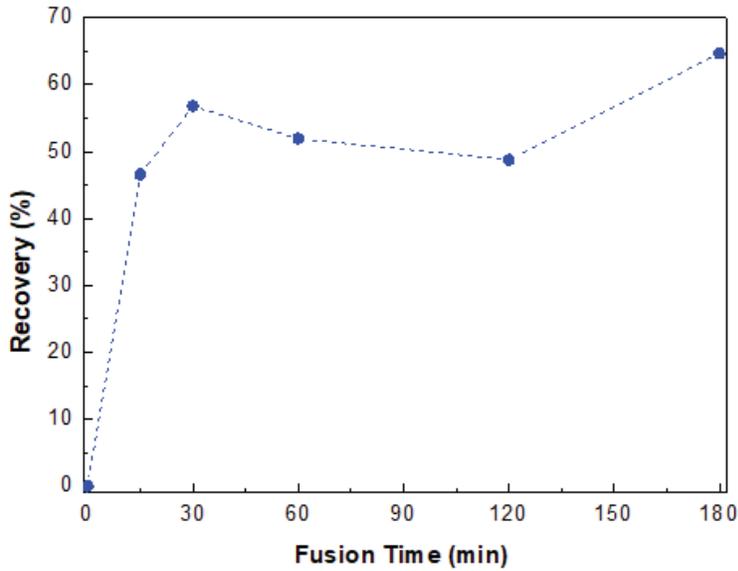


FIGURE 3. Effect of fusion time to Mn recovery.

Effect of Leaching Pulp Density

Constant variables applied in the pulp density effect study were NaOH/MS mass ratio 1, fusion temperature 500 °C, fusion time 1 h and leaching 30 min. Pulp density varied between 4 and 20 % (using NaOH 2 M), which results are depicted in Fig. 4. The figure shows the optimum pulp density to be 7 % (Mn recovery 73 %).

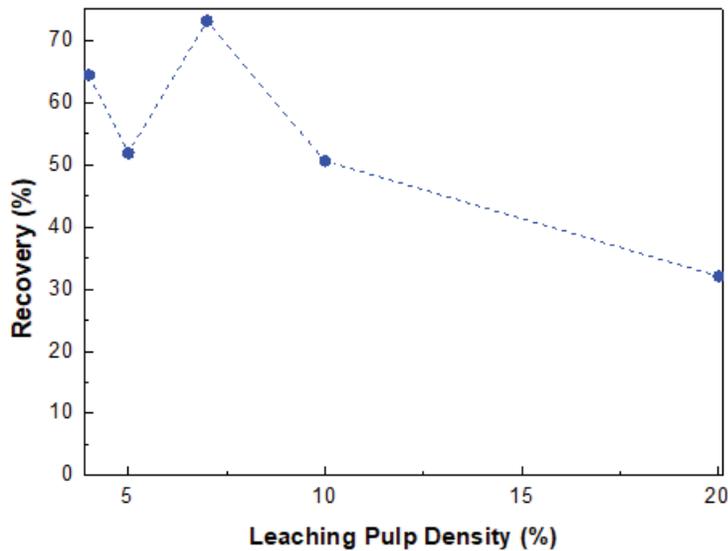


FIGURE 4. Effect of fusion time to Mn recovery.

Effect of Leaching Time

The effect of leaching time was studied from 5 to 60 min, which constant variables included NaOH/MS mass ratio 1, fusion temperature 500 °C, fusion time 1 h, and leaching pulp density 7 %. Figure 5 demonstrated that more prolonged leaching resulted in lower Mn recovery. Therefore, 5 min leaching was considered as the optimum leaching time. This was probably due to disproportionation of manganate to permanganate and insoluble MnO₂, according to reaction 3:

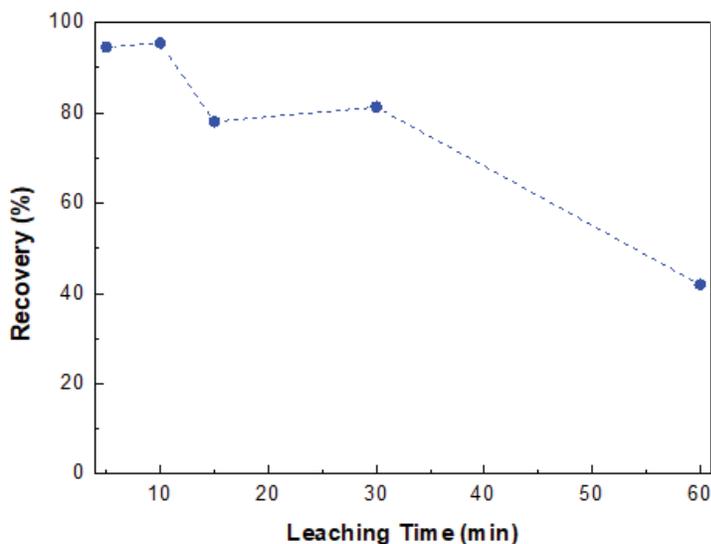


FIGURE 5. Effect of leaching time to Mn recovery.

CONCLUSIONS

Alkaline fusion and leaching successfully recovered Mn from Mn silicate, which traditionally could not be processed using common hydrometallurgical leaching as other manganese minerals i.e., MnO₂. During fusion, insoluble Mn silicate was transformed into manganate, which is soluble and could be leached at the mild condition. Optimum conditions to obtain Mn (94% recovery) are NaOH/Mn ore mass ratio 1, fusion temperature 500 °C, fusion time 1 h, leaching pulp density 7% (using NaOH 2 M), and leaching time 5 min. Shorter leaching time is preferable to prevent disproportionation of manganate into permanganate and insoluble MnO₂.

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