Effect of ore mineralogy on the reductive-leaching of manganese ores

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Abstract. Manganese ores from Waykanan region (WK ore) contain pyrolusite (MnO₂) as major minerals, whereas the main minerals in manganese ore from Tanggamus region (TG ore) are iron manganese silicide. The effects on manganese extraction of leaching reagents without reductant, leaching temperature of non-reducing leaching, and reducing agents of sulfuric acid leaching were determined to investigate the leaching performances of the two manganese ores. Manganese leaching efficiency from WK ore is always higher than that from TG ore under the same leaching conditions. The mineral contents of the ores significantly affected the leaching performances and mineral dissolution behaviors of the samples.

1. Introduction

Manganese plays an important role in many fields, such as steel production, preparation of dietary additives, fertilizers, cells, and fine chemicals [1,2,3,4,5,6,7,8,9,10,11,12,13]. Many efforts have applied recently to develop a commercial hydrometallurgical process to recover manganese from various manganese ores because most manganese products are produced from hydrometallurgical processes. Reductive leaching is one of the most important methods for extracting manganese from manganese ores. Some reductants such as molasses, biomass, sugar, oxalic acid, etc. have been applied in the leaching of manganese ores using acids mainly inorganic acids as the acidic medium and leaching reagents [14,2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13].

Indonesia has potential manganese ore resources that are distributed in some islands. They are widely distributed and spread among the islands of Sumatera, Kalimantan, West Java, Yogyakarta, East Java, and East Nusa Tenggara. The properties of manganese ores from every area may differ, depending on the sample origins; this is also the case for Indonesian manganese ores. The chemical and mineral compositions of manganese ores from different origins or even from different depths in one area can vary significantly. Therefore different leaching efficiency and leaching behavior might be occured, even though the similar method was used. Leaching rates and products will depend not only on the leaching conditions but also on the mineralogy of ores [15]. Specific mineralogical research should therefore always be conducted when a new manganese ore sample is found.
The aim of this study was to obtain a better understanding of the comparative mineral characterization of the ores, leaching performances, and mineral dissolution behavior of different Indonesian manganese ores from two different mining areas in Lampung Province, under atmospheric-reductive-leaching conditions using sulfuric acid and various reducing agents. This is important in the design of alternative techniques for treating such ores. The findings of the study can be adopted for leaching of other manganese ores from different locations. The leaching processes of manganese and iron from two different manganese ores by applying several leaching parameters were demonstrated to investigate the effect of reducing agents and leaching parameters on the leaching efficiency and leaching behaviour of each manganese ore.

2. Materials and Method

2.1. Materials
Manganese ores were originated from two mining areas i.e. Way Kanan (WK ore) dan Tanggamus (TG ore) in Lampung Province, Indonesia. The samples (WK ore and TG ore) were mineralogically and chemically characterized. X-ray fluorescence (XRF, Epsilon 3XLE, PANalytical, Netherland) was used to determine the chemical compositions of these samples. The mineral phases of the raw ore samples were identified by X-ray diffraction (XRD, X’Pert 3 Powder, PANalytical, Netherland), using CuKα radiation, in the 2θ range 5° to 80°. Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS; JEOL, USA) was used to determine the nickel contents of the different minerals by metal mapping.

2.2. Reductive Leaching method
To evaluate the leachability of mangan from two different manganese ores, the ores with particle size of <75 µm were acid leached (5% w/v of pulp density) by sulfuric acid (various concentrations) using various reducing agents at 150 rpm of shaker speed, 30°C of leaching temperature, and 8 hours of leaching period. Analytical-grade of all chemicals (Wako Pure Chemicals Industries, Ltd., Tokyo, Japan and Sigma-Aldrich, Germany) were used to prepare the solutions. Ultrapure water with a resistivity of 18 ΩM was used throughout this work. Reducing agents used in the experiments were molasses, glucose, fructose, cane sugar, sodium sulfite, tannic acid, oxalic acid, citric acid, black tea, green tea, cellulose, sawdust of candlenut shell, sawdust of Acacia wood, sawdust of coconut shell, sawdust of Albizia chinensis wood, and hydrogen peroxyde. Liquid samples after leaching were analyzed by Induced Couple Plasma-Optical Emission Spectroscopy (ICP-OES; Perkin Elmer 8500, Waltham, MA, USA) to calculate metal concentrations in the pregnant leaching solution.

3. Results and Discussion

3.1. Comparison of ores characterization
XRF analyses in Table 1 show that manganese ores used have different chemical compositions. WK ore has higher manganese content (36.77%) than TG ore (12.5), while the iron content of TG ore (11.02%) is greater than that of WK ore (6.59%). In addition, Si and Al content in both samples are similar. Figure 1 shows the XRD pattern of WK ore and TG ore. From this figure, it can be seen that major minerals in WK ore are quartz and pyrolusite (MnO₂), while TG ore contains quartz and Fe₂MnSi. Manganese in both samples is incorporated in different minerals. Figures 2 and 3 present the metal mapping of each sample respectively by SEM/EDS analysis. Figure 2 shows that manganese in WK ore is closely associated with oxygen as manganese dioxide (MnO₂), whilst from figure 3, it can be seen that manganese in TG ore is incorporated with iron.

| Sample  | Elements (wt %) |
|---------|----------------|
|         | Si  | Mn   | Fe  | S   | Al  |
| WK ore  | 4.13| 36.77| 6.59| 0.31| 0.45|
| TG ore  | 6.89| 12.50| 11.02| 0.59| 0.69|
Figure 1. XRD pattern of manganese ores (a) WK ore; (b) TG ore
Figure 2. SEM/EDS metal mapping of TG ore
### Table 1: Elemental Composition of WK Ore

| Element | Wt%  |
|---------|------|
| O       | 38.13|
| Al      | 2.06 |
| Si      | 2.31 |
| K       | 0.25 |
| Mn      | 45.76|
| Fe      | 9.81 |
| Pb      | 1.68 |
| Total   | 100.00|

**Figure 3.** SEM/EDS metal mapping of WK ore
3.2. Effect of reagents on the non-reducing leaching

Leaching reagent is one of the most important parameters on the effectiveness and behavior of leaching. The effects of leaching reagents on the manganese recovery of this study were studied for concentration each acid of 1 M at 30°C, 150 rpm shaker speed, 8 hours of leaching period, and atmospheric pressure using <75 μm ore particle size and 5% (w/v) pulp density. Two manganese ores (WK ore and TG ore) were used to investigate the comparison of manganese leaching behavior with different leaching reagents. Figure 4 shows that without reducing agents, both manganese ores were very difficult to be leached by all leaching reagents.

![Figure 4](image_url)

**Figure 4.** Manganese recoveries on the leaching of manganese ores (WK ore and TG ore) by various leaching reagents (acid concentration: 1M, pulp density: 5%, shaker speed: 150 rpm, temperature: 30°C, leaching period: 8 hours)

3.3. Effect of temperature on the non-reducing leaching

From the previous experiment, it can be seen that leaching reagents did not affect to the manganese leaching recoveries for both samples although the types of major manganese minerals contained in them were different. In order to increase the manganese recovery, a higher leaching temperature was used. The effects of leaching temperatures on the manganese recovery of this study were studied for sulfuric acid concentration of 1 M, 150 rpm shaker speed, 8 hours of leaching period, and atmospheric pressure using <75 μm ore particle size and 5% (w/v) pulp density with three various leaching temperatures (30, 50, 70°C). The results (Fig. 5) show that for both samples, manganese leaching efficiencies were not affected by leaching temperature. There were no significant changes when the leaching temperature were increased. Whereas usually the temperature greatly affects the leaching results and increases the recovery value, but in this study, the increasing temperature from 30°C to 50°C and 70°C actually shows a decrease in manganese recovery value. It can concluded that the increase of temperature in the non-reducing leaching of manganese ore does not affected to the increase of manganese recovery.
Figure 5. Manganese recoveries on the leaching of manganese ores (WK ore and TG ore) by various leaching temperatures (acid concentration: 1M, pulp density: 5%, shaker speed: 150 rpm, temperature: 30°C, leaching period: 8 hours)

3.4. Effect of various reducing agents on the sulfuric acid leaching

In some references, it was found that reducing agent was required in the leaching of manganese from manganese ore due to the stability of manganese in the manganese ore. The effect of various reducing agents on the sulfuric acid leaching of pyrolusite ore from WK ore and TG ore was conducted using 1 M sulfuric acid concentration at 30°C, 150 rpm shaker speed, 8 hours of leaching period, and atmospheric pressure using <75 μm ore particle size and 5% (w/v) pulp density. Sixteen reducing agents were used in this study that were molasses, glucose, fructose, cane sugar, sodium sulfite, tannic acid, oxalic acid, citric acid, black tea, green tea, cellulose, sawdust of candlenut shell, sawdust of Acacia wood, sawdust of coconut shell, sawdust of Albizia chinensis wood, and hydrogen peroxide. The results presented in Figure 6 show that the manganese leaching are strongly dependent on the reducing agents. The best reducing agents that produce the greatest manganese recoveries in both samples were tannic acid and oxalic acid. From this figure, it can also be found that manganese recovery from WK ore was higher than it from TG ore when tannic acid, oxalic acid, sodium sulfite, and cane sugar were used as reducing agents. However, manganese recovery from TG ore was greater than it from WK ore when the other reducing agents were used. In addition, figure 7 shows that iron was also leached simultaneously during leaching. This iron should be separated after leaching process if the manganese product is needed in the pure form.
Figure 6. Manganese recoveries on the leaching of manganese ores (WK ore and TG ore) by various reducing agents (acid concentration: 1M, pulp density: 5%, shaker speed: 150 rpm, temperature: 30°C, leaching period: 8 hours).

Figure 7. Comparison manganese and iron recoveries on the leaching of manganese ores (WK ore and TG ore) by various reducing agents (acid concentration: 1M, pulp density: 5%, shaker speed: 150 rpm, temperature: 30°C, leaching period: 8 hours) (a) WK ore (b) TG ore.
4. Conclusion
The chemical contents of the ores indicated that both samples were typical low-grade manganese ores. The mineral composition of both samples differs. The WK ore contains quartz and pyrolusite as the main minerals, whereas the major phases in TG ore are quartz and diiron manganese silicide. The maximum leaching efficiency of manganese was achieved from WK ore (100%) and TG ore (66%) under the same leaching conditions, i.e., sulfuric acid concentration 1 M, leaching temperature 30 °C, leaching time 8 hours, ore particle size <75 μm, shaking speed 150 rpm, and pulp density 5% (w/v) using tannic acid as well as oxalic acid (2.5% w/v) as reducing agents. Manganese leaching rate from WK ore is always higher than that from TG ore under the same leaching conditions. From this study, it can be concluded that ore mineralogy is significantly affected to the leaching behaviour and leaching efficiency of manganese ore.

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