Preliminary Study on the Reductive Leaching of Manganese Ores using FeSO₄/Iron Powder as Reducing Agents under Room Temperature

Kofi Moro, Frank Haubrich, Mirko Martin

Abstract — The leaching of manganese (Mn) ore in sulphuric acid (H₂SO₄) under reductive conditions has been studied. The effects of leaching parameters such as ore/reductant mass ratio, acid concentration, ore particle size, solid/liquid ratio, leaching time and different reductant potential on the maximum recovery of manganese have been investigated. The optimal leaching conditions were ore/reductant mass ratio of 1:3.4, acid concentration of 10% v/v H₂SO₄, ore particle size of 63-200 µm, particle size of iron powder of <150 µm, solid/liquid ratio of 1:20, and leaching time of 1.5 hours at room temperature. A comparative analysis on the recovery of manganese ore was also investigated under the optimal leaching conditions for two different reductants, iron sulphate (FeSO₄) and iron powder. The maximum manganese recoveries at the optimal leaching conditions in the presence of FeSO₄ and iron powder are 80.6% and 95%, respectively. The results indicate that manganese can readily be leached during short time at room temperature. Furthermore, iron powder has a stronger reducing power compared to FeSO₄ with respect to manganese ore recovery.

Index Terms — Iron powder, Iron sulphate, Manganese ore, Reductive leaching, Sulphuric acid.

I. INTRODUCTION

Manganese is a transitional element which occurs naturally in rocks, soil and water. It forms about 0.1% of the earth's crust. In nature, it does not exist as free metal. However, it is found embedded in different minerals. Manganese has oxidation states ranging from -3 to +7. Manganese exists in most host minerals as Mn⁴⁺. Manganese is of great importance to wide range of industries especially in the metallurgical industry. Some of the metallurgical applications of manganese are steel, non-ferrous alloys [1], [2] and paint production [2]. Non metallurgical applications include dietary additives, fertilizers, dry cell batteries, animal feeds, colorants for bricks, textile dyes, and medicine [1]-[4]. The global increase in manganese consumption has led to increased manganese production. This has resulted in the depletion of high-grade manganese ores and to high interest in the extraction of manganese from low grade manganese ores

[5], [6]. Pyrometallurgical and hydrometallurgical routes are the two well-known processing methods for the extraction of manganese from manganese ores [7]. However, hydrometallurgical method is more preferable to pyrometallurgical method due to high energy consumption, high cost of operation and the release of poisonous gases into the environment causing air pollutant [7]. Manganese is insoluble in the +4 state but soluble in the +2 state. Therefore, insoluble manganese needs to be reduced to the soluble form in order to achieve recovery from its ore. This has resulted in many recent research works on the reductive leaching of manganese from low grade manganese ores [5], [8]. Most work focuses on the extraction of manganese in an acidic medium in the presence of reducing agents under varying leaching temperatures [9]-[11]. [12] conducted a study on the reductive leaching of manganese ores from Gabon and Xiangxi in dilute sulphuric solution in the presence of waste tea as a reductant. The extraction efficiencies were 100% and 99.8%, respectively under the following optimal conditions; Gabonese manganese oxide ore: manganese oxide ore to waste tea mass ratio of 10:1, sulfuric acid concentration of 2.5 mol/L, liquid/solid ratio, 7.5:1, leaching temperature of 368 K, time of 8 h; Xiangxi manganese oxide ore: manganese oxide ore to waste tea mass ratio of 10:1, sulfuric acid concentration of 1.7 mol/L, liquid/solid ratio of 7.5:1, leaching temperature of 368 K, time of 8 h [12]. Some of the leaching temperatures which have been employed are 30 °C [13], 29 °C [14], 48-55 °C [15] and so on. All of these leaching temperatures have resulted relative satisfactory recoveries based on the ore type. Considering the cost of energy consumed in the reductive leaching of low-grade ores under relatively elevated temperatures, it would be imperative to study the leaching of low-grade manganese ores under room temperature. Prior to this work, the authors found few studies and little information on the reductive leaching of manganese oxide ores under room temperature. The objective of the present study is to ascertain the necessary information on the optimum conditions and the reductive leaching kinetics of manganese metal in sulphuric acid [5] in the presence of FeSO₄ and metallic iron as reductants under room temperature.

II. MATERIALS AND METHODS

A. Materials

Manganese ore obtained from the Neue Hoffnung Stolln/Oberwildenthal dump near Eibenstock, Saxony, Germany was used as sample material. The ore was washed

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to remove any dirt or organic component that may interfere with subsequent processes. The washed sample was air dried for 24 h to preserve the natural composition of the sample. The manganese sample was crushed and ground using a laboratory scale jaw crusher and mill respectively. Pulverized manganese sample was classified into three different grain sizes by sieving with the aid of an electric shaker. The chemical and mineral compositions of the ore was analyzed using portable X-ray fluorescence spectrometer (XRF, BRUKER S1 Titan) and X-ray diffractometer system Orion Comet P2 (XRD Eigenmann GmbH) at the Mineralogical Laboratory of the TU Bergakademie Freiberg, Germany respectively. The chemical and mineralogical analysis results are shown in Table I and Fig. 1, respectively. The pregnant liquor was analyzed using photometric method with appropriate dilution. H_2SO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and iron powder were of analytical grade.

TABLE I: CHEMICAL ANALYSIS OF MANGANESE ORE

Component	Mass (%)
MnO	43.80
SiO_2	31.08
Ba	0.76
Co	0.40
P_2O_5	0.26
Pb	0.22
K_2O	0.21
TiO_2	0.14
CaO	0.14
Cu	0.11
Ce	0.10
Zn	0.07
Ag	0.01

Fig. 1. Qualitative XRD pattern of manganese ore.

B. Leaching Procedures

Pulverized manganese ore and calculated stoichiometric amount of FeSO_4 /iron powder was measured and introduced into a 100 mL air tight bottle. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added in the solid form. The required volume of H_2SO_4 solution was added to the mixture to form a suspension. Mixing of the solution was achieved by an overhead shaker with a shaking speed of 21 rpm. The mass of manganese ore used in all the experiments was 2 g. The leaching conditions such as FeSO_4 concentration, H_2SO_4 concentration, solid/liquid ratio, leaching time and particle size were varied to investigate the leaching kinetics of the ore under room temperature. After the leaching time, samples were taken and filtered using a

0.45 μm filter syringe. The filtrate was photometrically analyzed to determine the content of manganese leached. Batch leaching method was employed in the experiments.

III. RESULTS AND DISCUSSIONS

A. Effect of Ore/Reductant Mass Ratio

The effect of reductant/ore mass ratio was studied for the maximum recovery of manganese under the following conditions: particle size of 63-200 μm , solid/liquid ratio of 1:10 and leaching time of 24hrs, shaking speed of 21 rpm under room temperature. From equation (1) and the chemical composition of the ore, the stoichiometric amount of reductant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) needed to completely reduce $\text{Mn}^{(4+)}$ to $\text{Mn}^{(2+)}$ in 2 g of the manganese ore was calculated and used as the basis for all the experiments. In this particular test, the amount of ore/reductant was varied as follows; 1:0, 1:1.7, 1:3.4, 1:6.9 and 1:13.8. Below is Figure 2 showing the result. Mn recovery increases exponentially from 1.2% to 76.5% for ore/reductant mass ratio of 1:0 and 1:13.8, respectively. The lower recovery of manganese in the absence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ confirms the fact that, a reducing agent is required in the leaching of manganese from its ore [5]. 47.8% Mn recovery for ore/reductant mass ratio of 1:1.7 indicates that the quantity of reductant needed to completely be reduced Mn^{4+} to Mn^{2+} in the reduction process was insufficient. However, beyond ore/reductant mass ratio of 1:3.4 (Mn recovery of 75.6%), there was slight increase in Mn recovery owing to the fact that the reduction of tetravalent manganese to its bivalent state would have been completed. Therefore, increasing the quantity of the reductant dosage has little/no significant effect on the recovery of manganese. Therefore, ore/reductant mass ratio of 1:3.4 (stoichiometric amount; 6.8 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was recommended in this study.

Fig. 2. Effect of ore/reductant mass ratio on the recovery of manganese (ore particle size; 63-200 μm , 10% v/v H_2SO_4 ; Solid/Liquid ratio; 1:10, Shaking speed; 21 rpm, leaching time; 24hrs at room temperature; 24 °C).

B. Effect of Sulfuric Acid Concentration

The effect of sulphuric acid concentration on the leaching recovery of manganese was investigated under the following leaching parameters; particle size of 63-200 μm , ore/reductant mass ratio of 1:3.4, solid/liquid ratio of 1:10 and 24 h of leaching time under room temperature. The effect of acid concentration was investigated in the range of

5-20% v/v H_2SO_4 and the result is shown in Fig. 3. Fig. 3 shows clearly that increase in acid concentration resulted in the increase of Mn recovery from 29.3% to 73.2% for 5% and 20% H_2SO_4 , respectively. However, beyond 10% (v/v) H_2SO_4 (Mn recovery of 72.5%), there was no appreciable increase in Mn recovery despite the long leaching time. The dissolution of manganese is enhanced when there is an increase in the number of reaction surface sites which can be achieved by increasing acid concentration [16]. Furthermore, increasing acid concentration leads to an increase in H^+ ions resulting in a higher potential. This enhances redox reaction, hence an increase in Mn recovery [7]. For process optimization and to ease subsequent purification of the leached solution [3], 10% (v/v) H_2SO_4 was chosen for the subsequent tests.

Fig. 3. Effect of sulphuric acid concentration on the recovery of manganese (ore particle size; 63-200 μm , Ore/Reductant mass ratio; 1: 3.4, Solid/Liquid ratio; 1:10, Shaking speed; 21 rpm, leaching time; 24 h at room temperature; 24°C).

C. Effect of Ore Particle Size

In order to ascertain the effect of particle size on the recovery of manganese, the following size fractions 63-200, 200-500 and +500 μm were used. The other parameters were; acid concentration of 10% H_2SO_4 , solid/liquid ratio of 1:10, ore/reductant mass ratio of 1:3.4, leaching time of 24hrs and under room temperature. Fig. 4 indicates that, increasing particle size of the ore reduces the maximum Mn recovery. The highest and lowest Mn recovery were recorded at 71.9% and 51.2% for the particle size ranges of 63-200 μm and +500 μm , respectively. The smaller the particle size, the larger the reaction-surface area of the ore which resulted in a better solid-liquid contact of acid, reductant, and ore [7], [11] leading to the higher Mn recovery for the particle size range 63-200 μm .

Fig. 4. Effect of ore particle size on the recovery of manganese (10% (v/v) H_2SO_4 , Ore/Reductant mass ratio; 1: 3.4, Solid/Liquid ratio; 1:10, Shaking speed; 21 rpm, leaching time; 24hrs at room temperature; 24 °C).

D. Effect of Solid/Liquid Ratio

Maintaining particle size range of 63-200 μm , acid concentration of 10% v/v H_2SO_4 , ore/reductant mass ratio of 1:3.4, leaching time of 24 h, shaking speed of 21 rpm, under room temperature, the effect of solid/liquid ratio was studied by varying the ratio from 1:5 to 1:20. From Fig. 5, it can be observed that Mn recovery increased from 61.9% to 80.7% as the solid/liquid ratio increased from 1:5 to 1:20 respectively. This means that the quantity of acid needed to dissolve manganese from its ore was proportionally sufficient at 1:20 solid/liquid ratio. However, decreasing the volume of acid below the ratio of 1:20 could have resulted in the reduction of quantity of H^+ ions needed in the leach liquor hence low Mn recovery at lower solid/liquid ratio. To achieve higher recovery of manganese, solid/liquid ratio of 1:20 was recommended for the subsequent study.

Fig. 5. Effect of solid/liquid ratio on the recovery of manganese (ore particle size; 63-200 μm , 10% (v/v) H_2SO_4 , Ore/Reductant mass ratio; 1: 3.4, Shaking speed; 21 rpm, leaching time; 24hrs at room temperature; 24 °C).

E. Effect of Leaching Time

Leaching time was investigated to establish its effect on Mn recovery by varying the leaching time (0.5, 1, 1.5, 2, 3 and 24 h) and fixing the other leaching conditions at particle size range of 63-200 μm , acid concentration of 10% H_2SO_4 , solid/liquid ratio of 1:20, ore/reductant mass ratio of 1:3.4, shaking speed of 21 rpm, under room temperature. The result in Fig. 6 shows an initial sharp increase in Mn recovery at the initial stages from 72.3% to 80.6%. After this point, the Mn recovery remained steady, and the leaching recovery barely changed despite the long leaching time (24 h). This confirms a lot of literature works where maximum Mn recovery was achieved around the initial stages of leaching times. The optimum leaching time was however considered at 1.5 h in this study.

Fig. 6. Effect of leaching time on the recovery of manganese (ore particle size; 63-200 μm , 10% (v/v) H_2SO_4 , Ore/Reductant mass ratio; 1: 3.4, Solid/Liquid ratio; 1:20 Shaking speed; 21 rpm at room temperature; 24 °C).

F. Effect of Different Reductants

To confirm the work done by [10] with respect to the reductive role of Fe metal in the leaching of manganese ore, iron powder was used as a reductant in the sulphuric acid leaching of manganese ore. The results were comparatively analyzed with that of ferrous sulphate leaching of manganese. This was investigated under the following leaching conditions; particle size range of 63-200 μm , particle size of iron powder of $-150\ \mu\text{m}$, acid concentration of 10% H_2SO_4 , solid/liquid ratio of 1:20, ore/reductant mass ratio of 1:3.4, shaking speed of 21 rpm, 1.5 hours of leaching time under room temperature ($24\ ^\circ\text{C}$). Fig. 7 shows an impressive Mn recovery for iron powder over $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Mn recoveries were 95% and 80.7% for iron powder and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, respectively. [10] reported in their study that the dissolution of manganese metal is highly influenced by “the ratio of the activity of ferrous ion to that of ferric ion, $\alpha\text{Fe}^{2+}/\alpha\text{Fe}^{3+}$. Therefore, to maintain the high activity ratio of $\alpha\text{Fe}^{2+}/\alpha\text{Fe}^{3+}$ it is imperative to have metal iron in the leaching system to ensure a continuous regeneration of ferrous ions [10]. This could be the contributory factor to the high Mn recovery in the presence of iron powder.

Fig. 7. Effect of different reductant on the recovery of manganese (ore particle size; 63-200 μm , particle size of iron powder; $-150\ \mu\text{m}$, 10% (v/v) H_2SO_4 , Ore/Reductant mass ratio; 1: 3.4, Solid/Liquid ratio; 1:20 Shaking speed; 21 rpm, leaching time; 1.5hrs at room temperature; $24\ ^\circ\text{C}$).

IV. CONCLUSION

The reductive leaching of manganese ore in a mixture of sulphuric acid and FeSO_4 /iron powder under room temperature has been successfully studied. The results from the study indicate that manganese recovery increases with increasing H_2SO_4 concentration, ore/reductant ratio, solid/liquid ratio and leaching time. However, Mn recovery increases with decreasing ore particle size. Optimum recovery of manganese is best achieved at the initial stages of the leaching process since there is no significant change in recovery for extended leaching hours. The strong reducing power of iron powder in this study may provide a basis for the reductive leaching of manganese using iron scraps on the industrial scale. However, further studies and an intensive cost analysis should be considered prior to taking such decision.

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