

Leaching of Manganese Ores Using Ghalab as Reductant in H₂SO₄ Solution

T. A. A. El Barbary*

Chemical and Electrical Lab, Ore Technology Division, Central Metallurgical Research & Development Institute email tarekmmmm2012@yahoo.com

Abstract

In this study, molass deposit was used as reductant for sulfuric acid leaching of manganese ore from Abu Zeniema Sinai, Egypt. X-ray diffraction of representative sample revealed the presence of manganese pyrolusite (MnO₂) structure. Lines of lower but still appreciable intensities indicate the presence of hematite (Fe₂O₃), goethite (α -FeO(OH)), corundum (Al₂O₃), calcite (CaCO₃) and quartz (SiO₂). Thus the ore is mainly formed from pyrolusite, hematite, and goethite. X-ray diffraction and energy dispersive spectroscopy analyses indicated that the examined manganese ore was pyrolusite in nature. Four process parameters were investigated in the present study including the amount of ore, sulphuric acid concentration, molass deposit concentration and leaching temperature. Manganese extraction of 85 wt% was achieved leaching time of 60 min at 85 °C using 22% H₂SO₄ concentration and 10% of molass deposit. The results demonstrate that molass deposit are a low cost, renewable, and non-hazardous reducing agent for manganese leaching under mild acid conditions in comparison to the other available reagents.

Keywords: *manganese ore, characterization, leaching, Molass deposit*

Introduction

Manganese is an important element with several industrial applications such as steel, non-ferrous alloys, and paints production. Its non-metallurgical uses include fertilizers, animal feeds, and colouring agent for bricks, textile dyes, and medicine [1]. With increasing demand for manganese and gradual depletion of high grade manganese ore, various routes have been tried to develop an economic and efficient process to recover manganese from low-grade manganese dioxide ores[2] (Haifeng et al.,2010). Low and medium-grade ores of manganese usually contain phosphorous, iron, and silica, rendering these ores unsuitable for usual industrial applications [1]. Manganese occurs in nature mostly as pyrolusite (MnO₂) which is stable in acidic and alkaline media. Therefore, extraction of manganese from such a source has to be carried out under reducing conditions [3]. Low-grade manganese dioxide ore can be treated by reductive acid leaching using different kinds of reducing agents and acids [1]. Coal is used as a reductant in traditional technology in order to convert manganese dioxide to manganese oxide which can be leached by sulfuric acid. This

method produces smoke, dust, oxysulfide, and nitrogen oxides which greatly pollute the environment. Additionally, this method requires reaction temperature over 800 °C, which is too high for most of the reactors [4].

Several other reducing agents have also been used traditionally in different acidic media e.g. pyrite, ferrous sulfate, aqueous sulfur dioxide, and hydrogen peroxide. Some of the reducing agents used as SO₂, may be harmful for the environment. Therefore, many investigators focused on reductive leaching of manganese dioxide ores using organic reductants mainly carbohydrates like glucose, sucrose, lactose, and oxalic acid. The use of organic reductant to leach manganese dioxide ores has been reported to be simple and efficient under mild temperature conditions (<90 °C) [5], however the cost of reductant and the high consumption rate limit the commercial applications of this technique[6].

Biomass can be used as a cheap and effective reductant to reduce manganese oxide ore at temperatures below 450 °C with a degree of reduction more than 95%. Moreover, the amount of CO₂ released during the roasting process is equal to the amount absorbed during biomass growth, and this is a zero emission process for biomass fuel[7]. Adopting of a zero-waste approach, carbohydrates from agriculture wastes are characterized by being low-cost, renewable, and non-hazardous and can be used for manganese leaching under mild acidic conditions [8]. Among the biomass wastes, sawdust, cane molasses, corncob, cornstalks, rice husk, wheat stalks, bagass, bamboo, and shredded papers have been considered as environmentally friendly and low-cost reducing agents for reduction of manganese dioxide ore [9]. In order to extract manganese efficiently and economically using waste materials, the hydrometallurgical treatment of low-grade manganese ore has attracted much attention in recent years [10].

In the present work, Molass deposit was used as a reducing agent in a dilute sulfuric acid medium to extract manganese from manganese ores. In this process, Molass deposit was hydrolyzed to release glucose and fructose under acidic condition so that manganese dioxide could be reduced at a low temperature. The use of molasses deposit for reduction of manganese dioxide is a simple, low cost, and economical method in comparison to the other available

raw reductants. Using this method, manganese could be extracted up to about 85% [6].

Materials and methods

Manganese ore was obtained from Abu Zeneima, Sinai, Egypt. The ore contains 50.710 % MnO, 26.89 % Fe₂O₃, and 2.417% CaO. The ore was crushed, ground and passed through 149 and 74 μm sieves.

The leaching experiments were carried out in a 400 cm³ glass round bottle placed in water bath, stirred using mechanical stirrer. Concentrated H₂SO₄ was mixed thoroughly with weighed amount of Molass (0 to 20%) to release the glucose and fructose into the acid. After 15 min, the weighed amount of ore (1 to 50 g) powder was transferred to the pulp. The leaching experiments were carried out using different amounts of manganese ore amount, acid concentration, molasses deposit, at various temperatures.

Ghallab or "Honey Suppress"

During sugar refining from sugar cane juice, and after separation of sugar crystals and black honey fraction (molass), thick residue is deposited on the bottom of the molass tank. This residue which has pasty nature is deep brown in colour and rich in succarides. It is sold against low price to local inhabitants as sweet source whereby it is moulded into certain shape and sun-dried.

Results and discussion

X-ray Diffraction

X-ray diffraction pattern of the studied sample is shown in Figure (1). The x-ray diffraction pattern shows that the strongest line having the relative maximum intensity corresponds to typical pyrolusite (MnO₂) structure. Lines of lower but still appreciable intensities indicate the presence of hematite (Fe₂O₃), goethite (αFeO(OH)), corundum (Al₂O₃), calcite (CaCO₃) and quartz (SiO₂). Thus the ore is mainly formed from pyrolusite, hematite, and goethite.

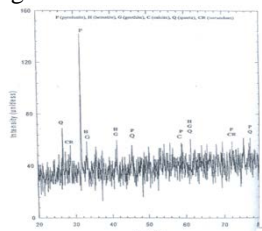


Fig. 1. XRD pattern of manganese ore showing peaks of Pyrolusite, Hematite and Quarandom.

Effect of manganese ore amount

The effect of ore amount from 1 up to 50 g of ore amount was studied. It was found that by using the amount of increase in ore the reduction of manganese increases up to 22.5% then start to decrease. Tests were carried out at room temperature for 60 minute with a concentration of molass deposit 10%, the results are

plotted in Figure 2.

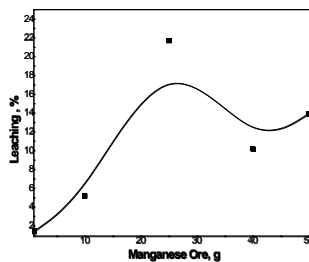


Figure 2: The Effect of manganese ore amount on the dissolution of manganese

Effect of Molass deposit amount

Keeping the same concentration of sulfuric acid (20%), leaching time of 60 min for 22.5 g of ore at room temperature, the influence of molass deposit on leaching efficiency was investigated in details. The variation in leaching efficiency of manganese and other elements with the amount of molass are shown in Fig. 3. This experiment demonstrates that the leaching efficiency of manganese is increased with the increase in the amount of molass deposit. The leaching efficiency of manganese increased up to 85% when the amount of molass was increased to 10 g. This was the highest leaching efficiency of manganese achieved. Therefore, 10 g of molasses deposit are considered the optimal parameter.

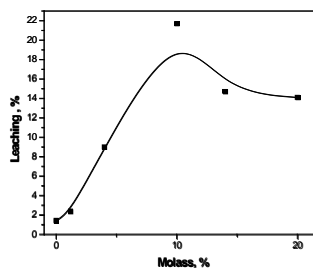


Figure 3: Effect of molasses deposit on manganese reduction

Effect of acid concentration

The effect of sulphuric acid concentration on the leaching of manganese from its ore has been studied. It was found that the acid concentration reaches to 22.5% and start to decrease due to the oxidation effect of sulphuric acid where it reaches to 21.7 and starts to decrease with the high concentration of sulphuric acid. The data are plotted in Figure 4.

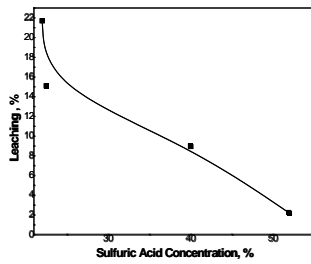


Figure 4: Effect of acid concentration on Manganese reduction

Effect of temperature

Keeping the molass amount fixed at 5 g, sulfuric acid concentration at 22%, leaching time of 60 min, ore amount of 25 g and particle size of 74 μm , the influence of temperature on leaching efficiency was investigated. Two leaching experiments were carried out at room temperature and 85°C. The result obtained is given in Fig. 5 showing variation of manganese reduction with temperature. It is observed that by increasing with increasing temperature, manganese recovery after 60 min leaching increased from 21.7% to 85%. [11].

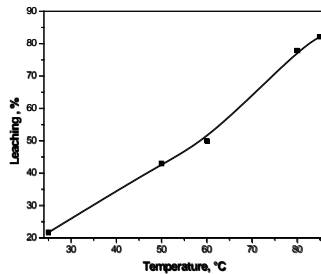


Figure 5: Effect of Temperature on Manganese reduction

Conclusion

In this study, a manganese ore from Abu Zeneima, Sinai, Egypt was leached using predetermined concentration of H_2SO_4 in the presence of molasses deposit as reductant. The investigated factors were temperature, ore amount and molasses deposit amount. The best operating conditions giving the highest manganese content were 85°C, 25g ore, leaching time of 60 min, H_2SO_4 concentration of 20% and 10% molass deposit. Under these conditions a maximum manganese recovery of 85% has been achieved. The present results indicated that with the variation of temperature the rate of leaching efficiency increased. Manganese extraction from manganese ore strongly depends on the reaction temperature.

References

[1] F. PAGNANELLI, G. FURLANI, P. VALENTINI, F. VEGLIO, L. TORO, 2004, Leaching of low-grade manganese ores by using nitric acid and glucose: optimization of the operating conditions, *Hydrometallurgy*, 75, 157-167.

[2] S. HAIFENG, L. HUAIKUN, W. FAN, L. XIAOYAN, W. YANXUAN, 2010, Kinetics of reductive leaching of low-grade pyrolusite with molasses alcohol wastewater in H_2SO_4 , *Chinese Journal of Chemical engineering*, 18(5), 730-735.

[3] D. HARIPRASAD, B. DASH, M.K. GHOSH, S. ANAND, 2007, Leaching of manganese ores using sawdust as a reductant, *Minerals Engineering*, 20, 1293-1295.

[4] Z. CHENG, G. ZHU, Y. ZHAO, 2009, Study in reduction-roast leaching manganese from low-grade manganese dioxide ores using cornstalk as reductant, *Hydrometallurgy*, 96, 176-179.

[5] D. HARIPRASAD, B. DASH, M.K. GHOSH, S. ANAND, 2009, Mn recovery from medium grade ore using a waste cellulosic reductant, *Indian Journal of Chemical Technology*, 16, 322-327.

[6] X. TIAN, X. WEN, C. YANG, Y. LIANG, Z. PI, Y. WANG, 2010, Reductive leaching of manganese from low-grade manganese dioxide ores using corncob as reductant in sulfuric acid solution, *Hydrometallurgy*, 100, 157-160.

[7] H. ZHANG, G. ZHU, H. YAN, T. LI, Y. ZHAO, 2013, The mechanism on biomass reduction of low-grade manganese dioxide ore, *The Minerals, Metals and Materials Society and ASM International*.

[8] T.A. LASHEEN, M.N., EL-HAZEK, A.S. HELAL, W. EL-NAGAR, 2009, Recovery of manganese using molasses as reductant in nitric acid solution, *International Journal of Mineral Processing*, 92, 109-114.

[9] H. ZHANG, G. ZHU, H. YAN, Y. ZHAO, T. LI, X. FENG, 2013, Reduction of low-grade manganese dioxide ore pellets by biomass wheat stalk, *Acta Metallurgica Sinica*, 26 (2), 167-172.

[10] X. CHAO, X. LONGJUN, P. TIEFENG, C. KUN, Z. JING, 2013, Leaching process and kinetics of manganese in low-grade manganese ore, *Chinese Journal of Geochemistry*, 32, 222-226.

[11] S. ALI, Y. IQBAL, U. FAROOQ, S. AHMED, Leaching of Manganese ores using corncob as Reductant in H_2SO_4 Solution, *physicochem. Probl. Miner. Process* 52(1), 2016, 56-65.