

Beneficiation and Sulfuric Acid Leaching of Manganese Ore

Sukhbat Sandag-Ochir¹, Zagarzusem Tsedendamba¹, Orgilbayar Batkhuyag¹,
Jargalsaikhan Lkhasuren¹, Khasbaatar Dashkhuu^{1,2}, Sugir-Erdene Namsrai¹,
Baasanjav Dashtseren¹, Unursaikhan Buyannasan¹, Otgonjargal Enkhtur^{1,*}

¹ Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar, 13330, Mongolia

² Department of Chemical and Biological Engineering, School of Engineering and Applied Sciences, National University of Mongolia

*Corresponding author. Email: otgonjargale@mas.ac.mn

ABSTRACT

The beneficiation of low-grade manganese ore is investigated using applied magnetics separation, multi-gravity separator, shaking table, flotation methods, and sulfuric acid leaching. The manganese content in the ore sampled from the Unagad deposit is 17.31%. The best option and high result among beneficiation experiments is the use of a multi-gravity separator. Manganese leaching from the concentrate is investigated using H₂SO₄ and H₂O₂ as leaching and reducing agents. A study on the characterization of the main parameters such as agitation, reaction temperature, leaching time, H₂SO₄ concentration, H₂O₂ concentration, and liquid/solid mass ratio for increasing leaching of the manganese from the beneficiated samples was performed. The optimal leaching efficiency was 86.79% for manganese.

Keywords: Manganese ore, Flotation, Gravity, Acid leaching, Reductive leaching

1. INTRODUCTION

Manganese is one of the metals essential in many industrial food applications, fertilizer additives, dry battery cells, paint materials, and iron steel industries [1, 2]. Almost 90-95% of manganese in the form of its alloys is consumed in steel production. Generally, the production of manganese alloys requires ores with manganese content greater than 30% and a manganese/iron ratio greater than five [3]. Ores with a low manganese content (~12% or less) can be utilized in the production of manganese pig iron [4]. The gravity separation methods such as sink-float, jigging and tabling, and high-intensity magnetic separation are usually used to enrich manganese ores [5, 6]. Manganese ores are classified by mineral compositions as oxide, carbonate (rhodochrosite

MnCO₃), and mixed [7]. The main mineral components of the manganese ore are manganese oxides, hydroxides (pyrolusite MnO₂, psilomelane Ba(Mn²⁺)(Mn⁴⁺)₈O₁₆(OH)₄, jacobsonite MnFe₂O₄, manganite MnO(OH), and braunite Mn²⁺Mn³⁺₆[O₈|SiO₄] [8]. Each type of these manganese ores has a problem with selecting a proper concentration method, depending on the manganese minerals and constituents [9, 10]. In terms of the divalent manganese (Mn²⁺) soluble in water, manganese salts are generally obtained directly by acid leaching. If the manganese is insoluble in water (Mn⁴⁺), reducing agents are necessary to shift from (Mn⁴⁺) to the soluble (Mn²⁺) compounds [11]. Many researchers are investigating a reducing agent for the leaching of pyrolusite in an aqueous solution. The manganese ore from the Unagad deposit, Mongolia,

consists of the main pyrolusite with IV manganese valence, not soluble in water.

The acid reduction process of manganese leaching has emerged in recent years and stimulated a promising research interest as a cost-effective alternative method. The corresponding principle is that the reductants can convert insoluble MnO_2 of manganese ores into soluble MnO and further MnSO_4 in the acid solution without pre-calcination. Consequently, the acid leaching reduction method possesses the advantages of energy conservation and the one-step leaching process [12]. The research is aimed to develop a comprehensive method for optimal beneficiation of manganese ore and high-efficient leaching. Thus, it will be possible to exploit the Unagad manganese deposit by selecting the technology for the ore concentrating and obtaining concentrate that meets the standard requirements.

2. EXPERIMENTAL

2.1. Material

The manganese ore was sampled from the Unagad deposit, located in Airag soum, Dornogobi province of Mongolia [13]. A total of 300 kg samples were taken from the deposit and used for experimental research. In the flotation tests, oleic acid by the collector, the depressant sodium silicate, the frother pine oil, and sodium hydroxide were used by a pH adjuster. In the leaching tests, sulfuric acid and hydrogen peroxide were used as leaching reductants. The reagents were obtained from the Sinopharm chemical reagent Co., Ltd.

2.2. Magnetic Separation of Manganese Ore

Experiments on magnetic separation were conducted using an induction dry-rolled magnetic separator manufactured by “Roxmag Rafid” company. The primary ore sample was crushed to -1 mm, and concentration was performed by adjusting the current strength values of the separator to 0.5 A, 1 A, 1.5 A, 2 A, and 2.5 A. For magnetic separation tests, optimum conditions were 32 rpm roller speed, 5mm roller space, and concentrate receiving slope angle with 75 degrees.

2.3. Flotation Experiment of Manganese Ore

Flotation experiments were used the “XFD” flotation machine. After crushing and grinding, 500 g of the manganese ore sample was subjected to the flotation experiments in a 1.5 L flotation cell with a solid percentage of 30%. Adjusting the pH in the pulp

as 8.0 and mixing for 5 min and the depressant was conditioned for 5 min. Then collector has added to the pulp, and finally, pine oil was added with a conditioning time of 1 min. The flotation concentrate and tailing were filtered, dried, weighed, and analyzed by volumetric to determine manganese dioxide using lactic acid and ICP-OES methods.

2.4. Gravity Experiments of Manganese Ore

The test was performed by shaking table the sample preparation for the primary ore sample size of -2 mm, -1 mm, -0.6 mm, -0.3 mm, and -0.1 mm, respectively. In the grinding process, four manganese ore samples were prepared 60%, 70%, 80%, and 90%, passing -0.074 mm, respectively.

These fractions were subjected to multi-gravity separation experiments. For multi gravity separation tests, optimum conditions were 2 degree slope angle, 3 L/min washing water, and primary ore containing 0.074 mm fraction with 80%.

2.5. Leaching of Manganese Concentrates

At first, the manganese concentrate was dried in the drying oven to 65°C. The leaching experiments were carried out in closed glass flasks using 10 g concentrate and 200 g of 4 M H_2SO_4 , 1 M H_2O_2 , and mechanically mixed at 300 rpm at 40°C for 90 min, unless otherwise specified.

2.6. Effect of Agitation Rate

The effect of the agitation rate of Mn recovery from the manganese concentrate was carried out at an agitation rate ranging in 100-500 rpm using 3 M H_2SO_4 , a liquid/solid mass ratio of 20:1 at 40°C for 90 min, and 0.8 M H_2O_2 .

2.7. Effect of Leaching Time

The effect of leaching time on the leaching of Mn was carried out within the period range from 30 to 150 min with 3 M H_2SO_4 , 0.8 M H_2O_2 at a liquid/solid mass ratio of 20:1, 40°C, and agitation rate of 300 rpm.

2.8. Effect of Leaching Temperature

Four more leaching tests were performed to reduce thermal energy and leaching costs. The first leaching experiments were carried out at 20°C, 30°C, 40°C, 50°C, and 60°C. The other leaching conditions were fixed at 3 M H_2SO_4 , liquid/solid mass ratio of

20:1, 0.8 M H₂O₂, agitation rate of 300 rpm, and at 90 min.

2.9. Effect of H₂SO₄ Concentration

The effect of H₂SO₄ concentration, in the range 1–5 M, on leaching of Mn was studied using liquid/solid mass ratio of 20:1, at 40°C, 90 min, and 0.8 M H₂O₂ at an agitation rate of 300 rpm.

2.10. Effect of Liquid/Solid Mass Ratio

Leaching of Mn from pyrolusite by 4 M H₂SO₄, 1 M H₂O₂ at 40°C, agitation rate of 300 rpm, for 90 min was tested by varying the liquid/solid mass ratio from 10:1 to 30:1.

2.11. Analysis

The manganese content in the leach solution was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using the system iCAP 7200 ICP-OES Duo - Thermo Fisher Scientific. All chemical reagents employed were of analytical grade, and de-ionized water was used through the experiments whenever needed. The characteristics of the manganese ore were using mineralogy, the mineragraphic analysis, X-ray Fluorescence (Philips PW1800), and X-ray diffraction (Explorer 7000) analysis. The rock was selected from the manganese ore and prepared to a polished precise slice. The mineragraphic analysis of the rock was performed to identify ore minerals using a reflected light microscope.

3. RESULTS AND DISCUSSION

According to the results of mineralogical analysis, the manganese ore contains about 75-80% of non-ore minerals and 20-25% of ore minerals in 0.5-4.0 mm rocks. The dominant mineral was pyrolusite. The pyrolusite appears white-colored and has anisotropic characterization and prismatic and acerate appearance. Manganese minerals were in cement behavior in fine streaks of 0.05-0.7 mm wide and as monolithic mass covering the wide-area up to 7.5 mm². Mineragraphic analysis reveals the mineralogical compositions including hydro goethite, manganese minerals, and magnetite. The gangue minerals are constituted mainly by quartz, albite, orthoclase, microcline in manganese ore [13].

3.1. Beneficiation

3.1.1. The Magnetic Separation

The results of dry magnetic separation, flotation, and gravity separation experiments are shown in Figure 1.

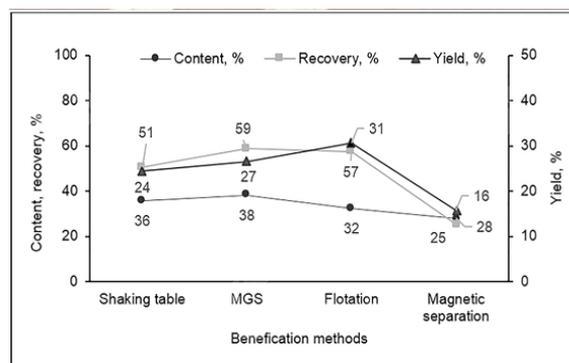


Figure 1. Results of beneficiation experiments

As a result of the experiments, the primary manganese ore with a grade of 17.31% and the yield was 15.7%, the content of concentrate was 28%, and the metal recovery was 25.45%. Manganese minerals (pyrolusite) have paramagnetic properties [14]. Paramagnetic materials can be concentrated in high-intensity magnetic separators. The concentrate content was lower than other experiments due to the low magnetic strength of the dry magnetic separator.

3.1.2. The Gravity Experiments

A multi-gravity separator (MGS) was applied to beneficiate manganese ore. Figure 2 shows the flow sheet and technology balance of multi-gravity separation. In terms of an MGS, a recovery concentrate, yield, and manganese content of enriched manganese ore were 58.83%, 26.57%, and 38.33%, respectively, when the grade of 0.074 mm fraction with 80% of manganese ore.

As a result of the shaking table tests, the manganese content in the concentrate was 35.84% and, the metal recovery and yield were 50.57% and 24.43%, respectively, for the manganese ore fraction with 0.3 mm size.

3.1.3. The Flotation Experiments

Manganese ore beneficiation tests were performed using the flotation method under the following conditions: the collector dosage with 900 g/t to 1700 g/t, the dosage of the depressant as 570 g/t to 870 g/t, and the frother with 900 g/t, pH value 8,

when the ore was ground to 60%, 70%, 80%, 90% passing -0.074 mm size. Beneficiation tests performed in the optimum conditions resulted in concentrate with Mn=32.37%, the recovery was 57.33%, and the yield was 30.6%.

The results of the above experiments show that the shaking table, MGS, and flotation beneficiation meet the requirements of YB/T319-2005 “AMn34” (Mn 32-36%). Multi gravity separator was better for high-performance metal recoveries and the contents than other experiments.

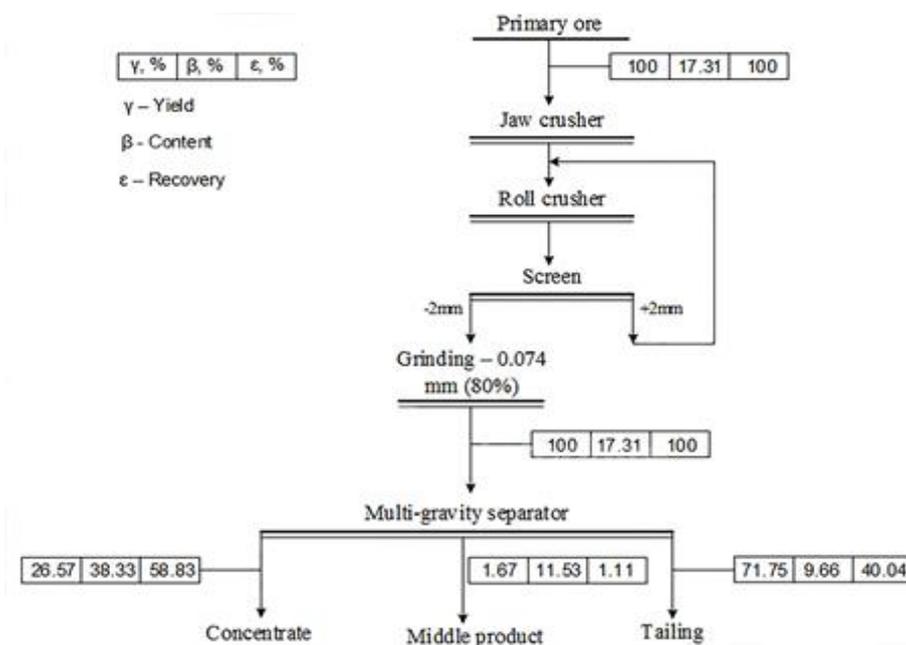


Figure 2. The flowsheet and technology balance of multi-gravity separation

MGS concentrate was selected as an agitation and leaching process sample. XRD indicated that two main manganese minerals characterize the manganese concentrate. Figure 3 presents the XRD pattern of the concentrate. Results showed that the concentrate mainly composed of pyrolusite MnO_2 and hausmannite was detected.

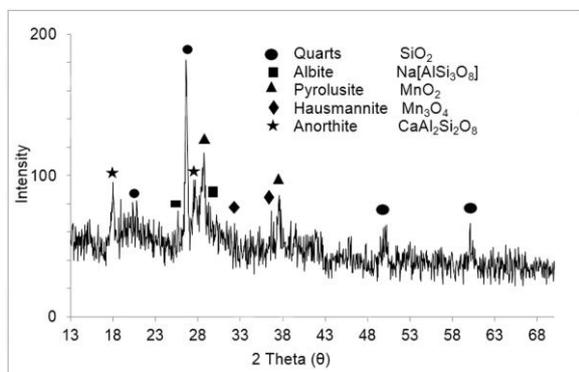


Figure 3. XRD pattern of manganese concentrate

3.1.4. Leaching Study

The purpose is to chemically dissolve manganese concentrate to separate manganese and increase manganese recovery efficiency.

3.1.5. Effect of Agitation Rate

In Figure 4a, the leaching of Mn increased as the agitation rate increased, and the leaching did not increase when the agitation rate was higher than 300 rpm. Therefore, subsequent experiments were performed at an agitation rate of 300 rpm to ensure that the influence of external mass transfer was tenuous.

3.1.6. Effect of Leaching Time

Figure 4b shows that at the first 30 min about 31.29% of the manganese leached. After 90 min, some 80.30% of manganese dissolved. The solubility increases slightly and stabilizes at 85.56-86.91% when the dissolution time was more than 90 min, so

it should be considered appropriate by taking the dissolution time as 90 min.

3.1.7. Effect of Leaching Temperature

In Figure 4c, when temperature increases, the leaching percent of Mn increases from 38.09% at 20°C to 84.20% at 40°C. It may be due to the accelerating reaction rate of MnO with H₂SO₄. However, at 50-60°C, the solubility of manganese stabilized and changed slightly. Due to the chemical reaction between manganese oxide and sulfuric acid, and it was recommended that the following tests be performed at 40°C.

3.1.8. Effect of H₂O₂ Concentration

To evaluate the effect of H₂O₂ the second series of leaching experiments was carried out using 3 M H₂SO₄. The other leaching conditions were fixed at liquid/solid mass ratio of 20:1, 40°C for 90 min, agitation rate of 300 rpm. Figure 4 d, shows that the concentration of H₂O₂ plays a critical role in the leaching process of Mn. According to the experimental results, the solubility of manganese reached 10.69-85.45% at a concentration of hydrogen peroxide 0.4-1 M.

3.1.9. Effect of H₂SO₄ Concentration

As shown in Figure 4e reveals that the leaching of Mn increases from 17.79% to 86.79% as H₂SO₄

concentration rises from 1 M to 4 M. This was followed by a more or less constant leached fraction of Mn with a further increase in H₂SO₄ concentration. However, the solubility of manganese was stabilized in 5 M solution of sulfuric acid.

These results indicated that the leaching percent increased with H₂SO₄ concentration, which accelerated leaching rates resulting from the high H₂SO₄ concentration [11, 15]. Further, high acid concentration will enhance the reduction of (Mn⁴⁺) to (Mn²⁺), as a result of the increase in hydrogen ion concentration, and subsequently (Mn²⁺) will be quickly released into the solution. Therefore, 4 M solution of sulfuric acid was considered to be the appropriate solvent concentration.

3.1.10. Effect of Liquid/Solid Mass Ratio

The data obtained are given in Figure 4f. It was observed that the content of the recovery of Mn increased rapidly with the increase in liquid/solid mass ratio from 10:1 to 20:1. At 10:1 of liquid/solid mass ratio, Mn extraction was too low because sulfuric acid was insufficient to obtain significant manganese dissolution. As the liquid/solid mass ratio increases, sulfuric acid was sufficient to leach manganese from the MGS concentrate. When the liquid/solid mass ratio was higher than 20:1, the leaching of Mn slightly increased since most manganese was leached into the solution to form an H₂SO₄ solution [16].

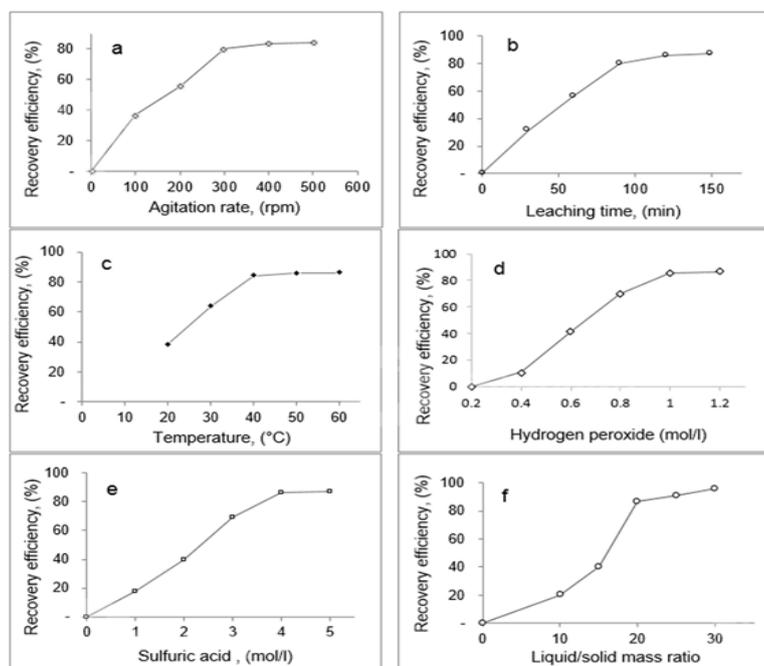


Figure 4. Results of manganese concentrate leaching

4. CONCLUSION

Manganese ore containing 17.31% can be beneficiated by gravity (shaking table and multi-gravity separator) and flotation to produce a standard manganese concentrate with 32.37-38.33%. Manganese ore of particle size distribution (80%-0.074 mm) can be beneficiated by a multi-gravity separator, and it was possible to produce concentrate with 26.57% yield, 58.83% metal recovery, and 38.33% manganese concentration.

This beneficiation was considering to be the most appropriate and most effective option for ore processing. The optimum condition of the leaching of manganese concentrate obtained for the sulfuric acid concentration as 4 M H₂SO₄, for the hydrogen peroxide concentration as 1 M H₂O₂, the liquid/solid mass ratio as 20:1, the leaching temperature was 40°C, the leaching time as 90 min, and the stirring speed as 300 rpm. Under these conditions, 86.91% of the manganese in the MGS concentrate was leached in an aqueous solution.

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