Journal of Electroanalytical Chemistry 788 (2017) 165–174

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electric field enhancement in leaching of manganese from low-grade manganese dioxide ore: Kinetics and mechanism study

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ARTICLE INFO

Article history:
Received 26 September 2016
Received in revised form 10 January 2017
Accepted 6 February 2017
Available online 07 February 2017

Keywords:
Low-grade manganese dioxide ore
Kinetics
Mechanism
Electric filed enhancement

ABSTRACT

In this work, hydrometallurgical leaching process intensified by electric field for leaching manganese from low-grade manganese dioxide ore was developed to increase the leaching efficiency of manganese. The leaching kinetics and mechanism were studied. The leaching parameters on manganese extraction, such as concentration of $FeSO_4$, concentration of H_2SO_4, liquid to solid ratio, leaching temperature, current density, were studied. The results showed that the leaching efficiency of Mn could reach up to 98.2% under the optimum conditions of 0.65 M $FeSO_4$, liquid–solid ratio of 5.5 mL/g, 1.6 M H_2SO_4, current density of 900 A/m^2, temperature of 353 K. The leaching process followed the shrinking core model, the reaction rate was controlled by diffusion through a product layer. The macroscopic kinetic equation of the leaching process was

$$1-\frac{2}{3}X-1-X^{\frac{2}{3}} = 5.67 \times 10^{-3}[FeSO_4]^{1.419}\ [H_2SO_4]^{1.686}\ ({}^{l}/{}_{s})^{1.239}\ (j)^{0.777}\ \exp({}^{-19.68}/{}_{RT})t$$

and the Ea (apparent activation energy) was 19.68 kJ/mol. During the leaching process, the newly formed Fe^{3+} that generated from the oxidation of ferrous on manganese dioxide surface was reduced to Fe^{2+} by electric field to ensure the Fe^{2+} in the solution keeps at a high level. The cycling of Fe^{3+} and Fe^{2+} ensured the high leaching efficiency of manganese during the process and reduced the dosage of the reducing agent.

1. Introduction

Manganese (Mn) is a strategically important element, which has been widely used in many important fields including steel production, non-ferrous metallurgy, battery, fertilizers, dietary additives, colorants as well as medicines [1–4]. Manganese is generally produced by electrolysis of manganese sulphate which is prepared by leaching manganese ore in sulfuric acid [4,5]. As high-grade manganese ores are exhausted gradually, recently much attention has been paid to the recovery of manganese from low-grade manganese resources recently. Developing efficient and economical processes to recover Mn from low-grade manganese dioxide ore (MDO) is urgently needed, particularly in China [2,6]. However, the extraction of manganese from MDO must be carried out by converting the tetravalent manganese oxides to bivalent forms [7–9], because of the strong stabilization of the manganese dioxide both in acid and alkaline oxidizing conditions. Generally speaking, such ores can be treated either by reduction roasting followed by acid leaching or directly by reductive acid leaching using different reducing agents [2,6,10]. The reductants used for reduction roasting–acid leaching include coal, graphite, sulfur and cornstalk [10–13]. These above methods, however, not only generate plenty of smoke dust, but also require a high reaction temperature. Therefore, these processes for exploiting manganese oxide ores are characterized as high production costs, energy consumption and serious environmental pollution. As for the directly reductive leaching methods, there are also some reducing agents, such as pyrite, iron(II) sulphate, carbohydrates, biogas residual, biomass, cellulose, bagasse, and sawdust, have been reported to be used in the leaching process [1,14–21]. The main problems with these hydrometallurgical processes are the purification of the leaching solution, high production cost, high dosage of reducing agent, low leaching efficiency, etc. In contrast, electric field strengthening leaching technology, releasing metals from solid materials, has been paid great attentions due to their higher efficiency, lower costs, environmental friendly and few industrial requirements [22]. In recent years, hydrometallurgical leaching process intensified by electric field are widely used for leaching vanadium from converter vanadium slag [23–25], leaching copper [26], refractory ore [27], refractory gold [28], heavy metal-polluted soil remediation, as well as recovering manganese from electric arc furnace dust [29,30]. However, few available ways on the extraction of manganese from low-grade MDO enhanced by electric field was reported.

This work focuses on a novel hydrometallurgical leaching process intensified by electric field for the leaching of manganese from low-grade MDO. The leaching kinetic and mechanism of the hydrometallurgical process are discussed along with the factors associated with manganese extraction.

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http://dx.doi.org/10.1016/j.jelechem.2017.02.009
1572-6657/

2. Materials and methods

2.1. Materials

All solutions were prepared with deionized water with a resistivity greater than 18 MΩ cm^{-1} (HMC-WS10). All chemical reagents (analytical grade) in this study were purchased from Chongqing Boyi Chemical Reagent Co., Ltd., China and used without further purification.

Low-grade MDO used in this work was obtained from Guangxi province, China. The ore sample was dried in an oven and then grounded to the required particle size of −74 μm. Sample characterizations by XRF and XRD were showed in Table 1 and Fig. 1. The XRF results showed that the ore contained 17.35 wt% manganese. From XRD pattern, the manganese minerals was formed of MnO_2 (ramsdellite), quartz pyroxmangite ($MnSiO_3$), quartz (SiO_2) and gismondine ($CaAl_2Si_2O_8 \cdot 4H_2O$).

2.2. Procedure and equipment

2.2.1. Leaching experiments

Leaching experiments were carried out in a glass beaker immersed in thermostatically controlled water bath with mechanical stirrer. On the top of the beaker there were two electrodes, an anode and a cathode, both of them were made of quaternary alloy, Pb/Ag/Ca/Sr (Fig. 2). The electrodes were fixed by spacers that were made of PVC. In a typical experiment, proper amount of MDO and $FeSO_4$ were added into a certain concentration of H_2SO_4 solution when the expected temperature was reached. And then, the power supply was turned on and adjusted to the needs of current. The rate of agitation was kept constant (500 rpm) in all the experiments. After the required contact time, the filtrate was separated from the residue by vacuum filtration. The leaching efficiency was calculated by referring the amount of leached manganese in the liquor to its original input quantity.

2.2.2. Voltammetric studies

The behavior of the ore during the leaching process was observed using cyclic voltammetric technique. This study was carried out in a conventional three electrode glass cell placed in a thermostatically controlled water bath using CHI660D (Shanghai Chenhua, China). The platinum pieces (1.5 cm × 1.5 cm) were used as the counter electrodes. Standard calomel electrode (SCE) was taken as the reference electrode. To assemble the working electrode (Fig. 3), manganese dioxide was directly pressed in the ore hold hole (diameter = 8 mm, depth = 6 mm), and then pressed for 30 min under 8 MPa pressure. The surface of the electrode was smoothed with a spatula and the excess pasting on the edges was removed. Voltammetric scans were performed in the potential range of 0.5 to −1.5 V to 0.5 V vs SCE at a scan rate of 10 mV/s.

2.3. Analytical methods

Atomic absorption spectrophotometry (AAS; HITACHI 180/80, Japan) in flame was used to determine the concentration of manganese. X-ray fluorescence (XRF, Shimadzu Lab Center XRF-1800) was used to analyze the main chemical compositions of MDO and leaching residue. Mineral composition was analyzed by a D/Max-2500 X-ray diffractometer (XRD; Rigaku, Japan) with a Cu Kα radiation source under the conditions of λ = 0.15418 nm, 40 kV, and 40 mA at 5– 70°. Surface morphology and elemental composition of the manganese deposits were analyzed through field emission scanning electron microscopy (FESEM; JSM-7800F, Japan).

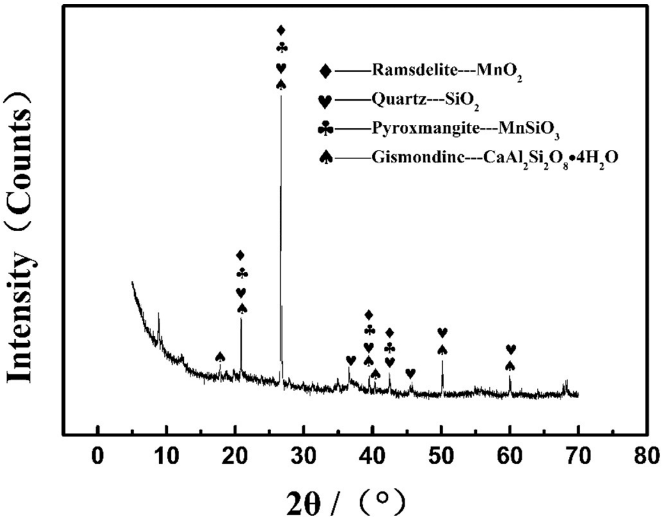

Fig. 1. XRD of manganese dioxide ore.

3. Results and discussion

3.1. Effect of initial concentration of ferrous

To investigate the effect of initial concentration of Fe^{2+} on the leaching efficiency of Mn from low grade MDO, five concentrations range from 0 to 0.7 M were carried out in all experiments. As seen in Fig. 4, manganese still had certain leaching when the concentration of Fe^{2+} was 0 M, for MDO had certain solubility in sulfuric acid and the electric field played an important role in direct reducing manganese dioxide to Mn^{2+}, the reactions most likely as Eqs. (1) to (3) [19]. The results showed that the addition of reductant Fe^{2+} could greatly enhance the reduction leaching of manganese. Fig. 4 also indicated that the leaching of manganese increased with the increasing of initial concentration of Fe^{2+} varied from 0.40 to 0.65 M.

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 4H_2O \quad (1)$$

$$MnO_2 + H^+ + e^- = MnOOH \quad (2)$$

$$MnOOH + 3H^+ + e^- = Mn^{2+} + 2H_2O \quad (3)$$

3.2. Effect of initial concentration of H_2SO_4

The effect of the initial sulfuric acid concentration was examined at 0.65 M $FeSO_4$, 5 mL/g liquid-solid ratio, 700 A/cm^2 current density, temperature 353 K; and the results were presented in Fig. 5. When the initial acid concentration was 1 M, the maximum leaching efficiency of Mn was only about 72.8%. Increasing initial acid concentration to 1.6 M, about 93.6% Mn could be extracted. It was indicated that the initial acid concentration had a significant effect on the leaching efficiency of manganese. It might because of the pH dependent oxidizing capacity of MnO_2. The increasing concentration of H^+ helped MnO_2 to improve the oxidizing capacity ($\varphi^{\circ}_{MnO2/Mn2+} = 1.224 + 0.118lg[H^+]$). The increased oxidizing capacity of MnO_2 can enhance both the direct reduction of manganese dioxide on electrode and the reduction by Fe^{2+}. Fig. 5 also showed that the leaching efficiency from MDO with acid initial

Table 1
Main element composition of the ore by XRF analysis.

Component	O	Si	Mn	Fe	Al	Mg	Ca	P	S	Ni	Co	Sr	Others
wt%	41.35	23.28	17.35	6.13	5.98	1.32	0.31	0.17	0.04	0.04	0.03	0.05	3.95