



# Enhanced extraction of manganese from electrolytic manganese residue by electrochemical



Jiancheng Shu, Renlong Liu\*, Zuohua Liu, Hongliang Chen, Changyuan Tao

School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China  
Chongqing Key Laboratory of Chemical Process for Clean Energy and Resource Utilization, Chongqing 400044, China

## ARTICLE INFO

### Article history:

Received 31 May 2016  
Received in revised form 21 August 2016  
Accepted 30 August 2016  
Available online 31 August 2016

### Keywords:

Electrolytic manganese residue  
Extraction  
Manganese  
Electrochemical

## ABSTRACT

High-valent manganese was hard to be extracted from electrolytic manganese residues. To strengthen the extraction of Mn, electrochemical extraction method was investigated in this work. The mechanisms of the electrochemical extraction were examined along with the electrochemical performance of the reaction system via X-ray diffraction, scanning electron microscopy, X-ray Fluorescence, and BET. Results show that high-valent manganese can be reduced effectively under an electric field. The extraction efficiency of manganese reached 96.2% under the optimum conditions of current density 25 mA/cm<sup>2</sup>, 9.2 wt% H<sub>2</sub>SO<sub>4</sub>, solid-to-liquid ratio of 1:5, room temperature, 1:1.0 M ratio of Mn to Fe<sup>2+</sup> and 60 min extraction. The extraction efficiency of manganese is 51.8% higher than that attained under the same conditions without an electric field and Fe<sup>2+</sup>. Meanwhile, the manganese content in residue decreased from 2.34% to 0.09%.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Electrolytic manganese residue (EMR) is a solid waste found in filters after sulphuric acid extraction of manganese carbonate ore, which mainly contains manganese and ammonia nitrogen and seriously damages the ecological environment [1,2]. In recent years, China has been the top contributor in global electrolytic metal manganese production, accounting for over 98.5% of the total world capacity in 2014 [3]. At present, producing 1 ton of manganese would create 10–12 tons of EMR, and the situation has worsened as the grade of manganese ores declined with the depletion of mineral resources [4]. In China, the accumulated amount of EMR amount to more than 60 million tons in the past decades. EMR contains some hazardous metal elements and compounds, which not only seriously pollutes the surrounding soil and receiving water body but also massively occupies the land resources. Furthermore, the untreated discharge results in a huge loss of manganese element, for as high as 4%–7% w/w of manganese is contained [5]. Developing a non-hazardous EMR treatment method is extremely urgent, in which the extraction of manganese from EMR is the key to harmless treatment.

Presently, EMR is mainly used for the preparation of cement [6], solidification–delaying agent of cement [7], soil fertilizer, roadbed material, synthesis of zeolite [8,9], geopolymer [10]. Therein, extraction of

manganese and other hazardous materials is a significant subject for the utilization of EMR.

Some chemical and bioleaching methods have been used to extract manganese, but a few disadvantages come along, such as higher cost, complicated processes, low extraction efficiency, long operation period, strict requirement of extraction equipments and potential safe risk (Table 1). Electrochemical strengthen extraction technology, used for the release of metals from solid materials, has gotten great attentions, due to their high efficiency, low costs and few industrial requirements [11]. In recent years, electrochemical extraction was widely used for converter vanadium slag extraction [12], extraction copper [13], refractory Ore [14], refractory gold [15], heavy metal-polluted soil remediation [16], as well as recovery of manganese from electric arc furnace dust [17,18].

In this study, electrochemical extraction was applied for manganese extraction from EMR for the first time. The mechanisms of the extraction are discussed along with the factors associated with manganese extraction.

## 2. Experimental

### 2.1. Materials and methods

All solutions were prepared with deionized water with a resistivity greater than 18 MΩ cm<sup>-1</sup> (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. The EMR used in this study was supplied by Jiayuan Mining Co. Ltd. (Chongqing,

\* Corresponding author at: School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.  
E-mail address: [lrlees@126.com](mailto:lrlees@126.com) (R. Liu).

**Table 1**  
Comparison of various methods and extraction efficiency for recovery of manganese.

Methods	extraction efficiency	Reference
Potassium permanganate	75%	[19]
Glucose and saccharose and H <sub>2</sub> SO <sub>4</sub>	85%	[20]
Heated H <sub>2</sub> SO <sub>4</sub>	42.38%	[21]
Citric acid	57.28%	[22]
H <sub>2</sub> SO <sub>4</sub> -HCl mixture- ultrasonic	90%	[23]
Sulfur-oxidizing bacteria	93%	[24]
Pyrite-leaching bacteria	81%	

China). The pretreated EMR was passed through 80-mesh sieve. In general, EMR is a non-magnetic and insoluble fine black powder which likes sludge paste after absorbing moisture and changes into a kind of hard block when deposited for a long period. Chemical analysis of the EMR was carried out using X-ray fluorescence (XRF) and the result shows that the main constituents of EMR are SiO<sub>2</sub>, SO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and Fe<sub>2</sub>O<sub>3</sub> amounting to approximately 91% of the total composition (Table 2).

## 2.2. Experimental process

The experimental apparatus is a 200 ml beaker designed as the reactor. A plate-like dimensionally-stable-anode (DSA, Baoji ZhiMing Special Metal Co., LTD, China) with a surface area of 32 cm<sup>2</sup> (4 cm × 8 cm) (anode) and a stainless plate with an identical area (cathode) were fixed at a distance of 20 mm. The solution was stirred by a magnetic stirring. All experiments were conducted at room temperature otherwise specified. 30 g EMR, distilled water, concentrated sulfuric acid and FeSO<sub>4</sub>·7H<sub>2</sub>O supplying the Fe<sup>2+</sup> were added and stirred at the appropriate agitation speed for a required time. A direct current power supply (HangZhou Apple Instrument and Meter Co., Ltd., China) with a current range from 0 A to 3 A and a voltage range from 0 V to 30 V was applied. After a scheduled extraction time, the leachate was separated from the residue by vacuum filtration. To systematically investigate the effects of various experimental conditions on the extraction process, the experiments were conducted under different condition of acid concentration, extraction time, solid-to-liquid ratio, current density and effect of Fe<sup>2+</sup> addition.

## 2.3. Analysis methods

The concentration of manganese was determined by atomic absorption spectrophotometry (AAS; HITACHI 180/80, Japan) in flame. The main chemical compositions of EMR were determined by X-Ray Fluorescence (SHIMADZU, XRF-1800×). The surface morphologies of the EMR and samples were identified using a scanning electron microscopy (SEM, Tescan, Czech). The BET surface areas of the EMR were examined via a physisorption analyzer (ASAP2020, Micromeritics Instrument Corp., USA). The differences in the crystal phase of EMR were confirmed using an X-ray diffractometer (XRD, SHIMADZU-6000, Japan) with a Cu Kα radiation source under the conditions of λ = 0.15418 nm, 40 kV, and 40 mA at 10° to 90°.

## 3. Results and discussion

### 3.1. Effect of acid concentration

The effects of acid concentration on manganese extraction efficiency in different extraction are shown in Table 3. With the increase of H<sub>2</sub>SO<sub>4</sub> concentrations, the extraction efficiency of manganese increased, which

**Table 2**  
Chemical analysis of the EMR.

Chemical composition	SiO <sub>2</sub>	SO <sub>3</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	Other
EMR (wt.%)	34.65	26.40	14.78	1.32	8.21	7.01	0.75	2.72	3.02	1.14

**Table 3**  
Effect of acid concentration on manganese extraction efficiency.

	Acid concentration wt%				
	nil	3.7	7.4	9.2	11
Conditions	% Mn extraction				
Direct acid extraction (time 60 min, S/L <sup>a</sup> = 1:5)	10.1	31.0	37.2	44.4	46.9
Electrochemical extraction (time 60 min, S/L 1:5, Mn/Fe <sup>2+</sup> = 1:1.0)	45.3	63.9	83.2	85.8	87.3
Electrochemical extraction with Fe <sup>2+</sup> (time 60 min, S/L 1:5, Mn/Fe <sup>2+</sup> = 1:1.0, current density 25 mA/cm <sup>2</sup> )	47.4	65.3	88.9	96.2	96.3

<sup>a</sup> Solid-to-liquid ratio.

can be attributed to the fact that sufficient protons (H<sup>+</sup>) destroyed the EMR at high H<sub>2</sub>SO<sub>4</sub> concentrations. But when the H<sub>2</sub>SO<sub>4</sub> concentration is too high, it could not only lead to the increase of impurities in the solution, but also lead to waste. Therefore, 9.2 wt% H<sub>2</sub>SO<sub>4</sub> was recommended in the subsequent experiments. Moreover, the manganese extraction efficiency was higher using electrochemical extraction than direct acid extraction, and increased obviously when Fe<sup>2+</sup> was added into the EMR.

### 3.2. Effect of extraction time

The role of extraction time on the extraction efficiency of manganese is shown in Fig. 1. The results show that the manganese extraction efficiency increased rapidly with the increase of reaction time. The manganese extraction efficiency increased rapidly to 96.2% after 60 min electrochemical extraction with Fe<sup>2+</sup> (Mn/Fe<sup>2+</sup> = 1:1.0). The extraction efficiency for the three methods leveled off after 60 min, because some manganese accumulated on the surface of the unreacted particle cores and hindered the extraction ability after a long extraction time. Therefore, extraction time of 60 min was recommended.

### 3.3. Effect of current density

The effect of current density on manganese extraction was investigated from 0 to 35 mA/cm<sup>2</sup> for 60 min with a solid-to-liquid ratio of 1:5. In Fig. 2, as the current density increased from 5 to 25 mA/cm<sup>2</sup>, the manganese extraction efficiency increased from 41.0% to 85.8% by electrochemical extraction, and from 85.8% to 96.2% by electrochemical extraction with Fe<sup>2+</sup> (Mn/Fe<sup>2+</sup> = 1:1.0). However, extraction efficiency decreased at high current density. When the current density was low, electric field could promote the electrochemical reaction rate between Fe<sup>2+</sup>/Fe<sup>3+</sup> and Mn<sup>2+</sup>/MnO<sub>2</sub> and change the charge distribution on the surface of the gangue mineral, such as silicon dioxide, and dihydrate calcium sulfate, which prompted the particles collide with each other and released the manganese packaged in EMR. When the current density was too high, the cell voltage would rise, and the oxidation rate is higher than the reduction rate which could cause the decrease of manganese extraction efficiency [24]. Therefore, the current density should be set at 25 mA/cm<sup>2</sup>. The effect of current density by electrochemical extraction with Fe<sup>2+</sup> is similar.

### 3.4. Effect of solid-to-liquid ratio

The effect of solid-to-liquid ratio on manganese extraction was examined from 1:2 to 1:6 at 9.2 wt% H<sub>2</sub>SO<sub>4</sub>, extraction time 60 min. Fig. 3 shows that the extraction efficiency of manganese increased when the solid-to-liquid ratio increased to 1:5. Using direct acid

Download English Version:

<https://daneshyari.com/en/article/6477139>

Download Persian Version:

<https://daneshyari.com/article/6477139>

[Daneshyari.com](https://daneshyari.com)