

Carbonation precipitation of manganese from electrolytic manganese residue treated by CO₂ with alkaline additives

Hongliang Chen^{1, 2, a}, Renlong Liu^{1, b}, Qian Long^{2, c} and Zuohua Liu^{2, d}

¹ College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

² College of Chemistry and Chemical Engineering, Anshun University, Anshun 561000, China

^a 278631830@qq.com, ^b lrlcqu@163.com, ^c 759980003@qq.com, ^d liuzuohua@cqu.edu.cn

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Abstract. This work reports the results of carbonate precipitation of soluble manganese by CO₂ with alkaline additives with the aim of eliminating the harm caused by electrolytic manganese residue (EMR). Results showed that CaO exhibited a better performance for the precipitation of manganese which was converted to rhodochrosite (MnCO₃) by infrared spectra and XRD analyses and that the precipitation rate of manganese reached 99.99% at 800 mL/min CO₂ flow rate and 5% CaO for 20 min reaction time. The leached concentration of manganese of the treated EMR was reduced to 0.2 mg/L and the leached concentrations of heavy metals of the treated EMR were less than the discharge standard of China (GB8978-1996). Another interesting finding was that the pH value and the ORP of the treated EMR slurry were about 7 and 320 mV respectively, which favoured landfill and reuse of EMR.

1. Introduction

Electrolytic manganese metal (EMM) is a significant basic material used in metallurgy, aerospace, chemistry, etc. It is reported that China is the world's largest country of production, consumption and export of EMM [1]. With the increase of manganese demand in the global market, the development of EMM industry has been promoted recently, which results in many environment problems, especially the contamination of electrolytic manganese residue (EMR) [2]. EMR, a by-product of the electrolytic manganese metal process, is produced by the acid leaching, neutralization and pressure filtration treatment of manganese carbonate powder and contains an amount of soluble manganese [3]. At present, About 10-12 tons of EMR are discharged into the environment during the process of one ton of EMM production due to the decrease of manganese ore grade [4]. In China, about 10 million tons of EMR are discharged each year and the accumulated amount during the past many years is about 50 million tons [5-6]. Currently, The EMR is primarily dumped in the open field without pretreatment in China and the soluble manganese from the EMR can percolate through the soil in natural environment and seriously pollute the surface and ground water. Thus a large amount of EMR without pretreatment poses a serious threat to the surrounding environment and the health of the surrounding population. Therefore, the development of EMR disposal technologies is urgently needed for enterprises and society.

Some studies have focused on the treatment and reuse of EMR, which include recovery of manganese from the EMR [7-8], the direct use of the EMR to produce building materials [9-10] and the harmless pretreatment of the EMR [4]. Nevertheless, the EMR has not been used in quantity so far due to the poor mechanical performances and high concentrations of leached heavy metals [1, 11]. Accordingly, it is significantly necessary that a pretreatment technology immobilizes soluble manganese in the EMR. Owing to the high efficiency, low cost and simplicity during the process itself, carbonation technology has been used in the modification of material structures [12-13], the recovery of metal ions in wastewater [14], the harmless treatment of pollutants [15]. The carbonation precipitation of soluble manganese from the EMR by CO₂ favours the stability of EMR properties and its reuse: beneficiation-metallurgy, building material, road base, etc. The primary objective of this work was to evaluate the influences of different alkaline additives (NaOH and CaO) on the carbonation precipitation of manganese from the EMR, and to detect the changes of the

mineral characteristics and the leached heavy metals concentrations before and after carbonation with CO₂.

2. Materials and methods

The EMR samples were randomly obtained from a residue storage facility of an electrolytic manganese plant in Chongqing, China. After being mixed sufficiently, the residue was dried at 105 °C for 8 h. Then the dried residue was ground using a ball mill and sieved through an 80 mesh screen for experiments. Referring to the standard of NY/T 1377-2007, the pH value of the EMR measured by an acidimeter was 5.9. The nitric acid, perchloric acid, hydrochloride acid, phosphoric acid, sodium hydroxide, and calcium oxide used in these experiments were analytically pure. The applied CO₂ (with a purity of 99.99 %) was stored in a steel cylinder.

40 g residue sample, 80 mL distilled water and different amount of alkaline additives were mixed into a 250mL beaker with 800 mL/min CO₂ flow rate. Each experiment was run in triplicate for statistical accuracy, and the experimental data were averaged for reporting. The effect factors including different alkaline additives (NaOH and CaO), the amount of the additive (0 to 7 %) and reaction time (0 to 30 min) were investigated at normal pressure and 25 °C. The slurry pH and the oxidation-reduction potential (ORP) were detected during manganese precipitation. After reaction, air pump filtration was performed on the slurry and the leached residue was washed three times with distilled water. Filtered fluid and washing liquid were collected in volumetric flasks and prepared for flame atomic absorption spectrophotometric analysis to detect the concentrations of heavy metals ions.

The precipitation rate of manganese was calculated using Equation (1).

$$\zeta_{Mn} = \frac{m_t - m_e}{m_t} \times 100\% \quad (1)$$

Where ζ_{Mn} was the precipitation rate of manganese from the EMR (%), m_t is the mass of manganese in the raw EMR (mg), and m_e is the mass of manganese in the leached liquid after manganese precipitation (mg).

The oxidation-reduction potential (OPR) was measured using a platinum electrode in combination with an Ag/AgCl reference electrode. ORP data were also converted to E_h (potential related to the standard hydrogen electrode), using Equation (2), where E_r was the potential of the reference electrode, i.e. +199 mV at 25 °C when an Ag/AgCl reference electrode was used [16].

$$E_h = ORP + E_r \quad (2)$$

The pH value of the EMR slurry was measured by an acidimeter (pHS-25, INESA, China). The chemical components of raw EMR were analyzed using an X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan). The manganese-bearing minerals of the treated EMR were detected by Fourier transform infrared spectrometer (IRPrestige-21, shimadzu Japan) and X-ray diffractometer (X'Pert PRO Panalytical, Holland). Determination of manganese and other metals in the filtrate was conducted using a flame atomic absorption spectrophotometric (180-80, Hitachi, Japan).

3. Results and Discussion

3.1 Characterization of raw EMR

The major chemical components of the raw EMR determined by XRF analysis included O (47.39 %), Si (15.32 %), S (13.05 %), Ca (9.26 %), Mn (2.07 %), Mg (1.83 %), Cu (0.01 %), Zn (0.01 %), etc. Figure 1a shows that the manganese phases of the EMR were mainly MnSO₄·H₂O and (NH₄)₂Mn(SO₄)₂·6H₂O which were likely to dissolve in water to produce Mn²⁺ and polluted the surface and ground water. Table 1 displays the heavy metals concentrations of the raw EMR by means of leaching test (GB 5085.3-2007). The concentration of manganese was 1552.4 mg/L and over 310 times as high as the discharge standard of China (GB8978-1996).

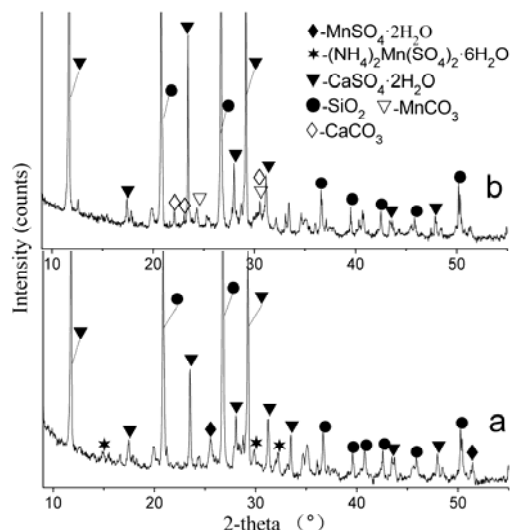


Figure 1. XRD diffractograms of the raw EMR (a) and the treated EMR (b) (◆- $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, ★- $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, ▼- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, ●- SiO_2 , ▽- MnCO_3 , ◇- CaCO_3)

3.2 Effects of different alkaline additives

Figure 2 presents that alkaline additives (NaOH and CaO) effectively improved the precipitation rate of manganese from the EMR by CO_2 under the conditions of 30 min reaction time and 800 mL/min CO_2 flow rate. It could be observed that the precipitation rates of manganese increased with the increased amount of the alkaline additives. This was attributed to the fact that the soluble manganese was precipitated as manganese-bearing carbonate minerals by CO_2 under the action of NaOH or CaO which improved the pH value of the EMR slurry [17]. In addition, it was found that the precipitation rates of manganese with CaO were higher than with NaOH. The probable reason for this was that CaO produced gentler hydrolysis [18] and brought about a sustainable and higher pH value in the slurry for most of reaction time (as described in Figure 3), while NaOH caused only a higher pH value at the beginning of the reaction. The optimal rate reached 99.99% at the CaO mass fraction more than 5%. However, the precipitation rate of manganese was merely 99.89%, when the mass fraction of NaOH increased to 7%.

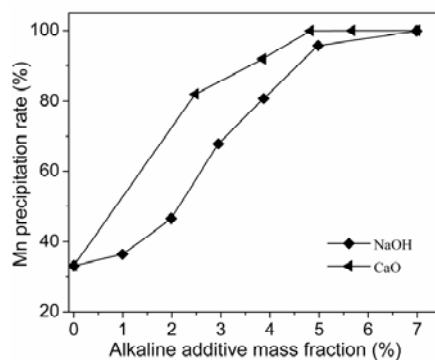


Figure 2. Effect of different alkaline additives on the manganese precipitation

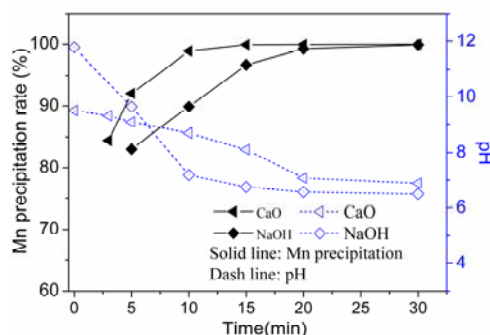


Figure 3. Effects of reaction time on the manganese precipitation and the pH value

Figure 3 demonstrates the effect of time on the precipitation of manganese at 800 mL/min CO_2 flow rate with 5% CaO and 7% NaOH, respectively. It was worth noting that the precipitation rates of manganese with CaO were more than 99.99% after 20 min and the precipitation rate with NaOH was only 99.89% for 30 min reaction time. Additionally, the pH values of the EMR slurry were almost constant after 20 min for CaO and NaOH respectively and the pH value stabilised at approximately 7 for CaO, although the pH value of the slurry with CaO was higher than with NaOH due to the slower release of hydroxyl anion from the hydrolysis of CaO. Seeing that CaO was applied widely in the restoration and remediation of polluted soils, where it promoted reactions such as flocculation, ion exchange, lime carbonisation and clay mineral dissolution between the polluted soil and its pore water [19] and the price of per ton of CaO was about one-fifth of NaOH, CaO was a preferable choice as the additive to precipitate manganese from the EMR by CO_2 .

Figure 4 shows the ORP change of reaction process at 800 mL/min CO_2 flow rate with 5% CaO. The ORP of the raw EMR slurry was 403 mV (Figure 4a). When CaO and CO_2 were added to the slurry, the ORP decreased rapidly to 277 mV (Figure 4b) and continued to reduce to a minimum of 133 mV about 4 min ((Figure 4c). This occurrence was associated with the alkalinity effect of CaO exceeding the acid effect of CO_2 . Afterward, the ORP began to increase and stabilised at approximately 320 mV after 20 min, which showed that the acid effect of CO_2 played a main role. Figure 5 presents that when the pH value and the ORP were about 7 and 320 mV respectively, the produced manganese-bearing carbonate minerals existed stable.

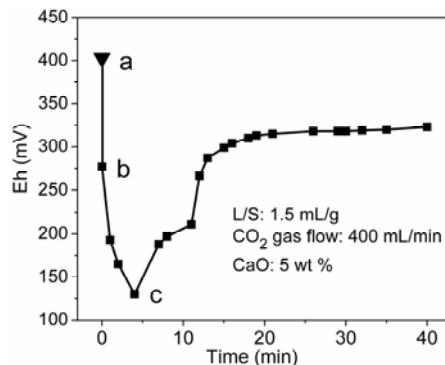


Figure 4. Effect of reaction time on the ORP

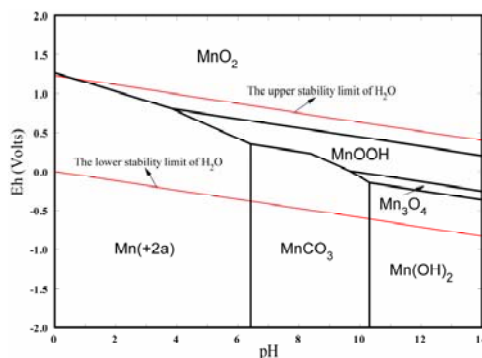


Figure 5. Eh-pH diagram for manganese carbonate formation

3.3 Mineral characteristics change of manganese

Figure 6 shows the infrared spectra of the EMR before and after manganese precipitation by CO_2 with 5% CaO. With increased reaction time, the infrared spectral bands of the treated EMR were intensified at 1418 cm^{-1} , 864 cm^{-1} , and 725 cm^{-1} and basically stabilized after 20 min. The band at 1418 cm^{-1} was the characteristic absorption band for carbonate minerals and was caused by stretching C-O vibrations [20]. The band at 864 cm^{-1} was caused by bending O-C-O vibrations [21]. The band at 725 cm^{-1} was associated with the manganese. Similarly, Silva et al. found that the infrared characteristic spectra of manganese carbonate produced in mine water was at 724 cm^{-1} [22]. The XRD analysis (as shown in Figure 1b) showed that the soluble manganese from the EMR was mainly converted to rhodochrosite (MnCO_3). The chemical reactions of soluble manganese treated by CO_2 with CaO in the EMR slurry were Equations (3) to (5).

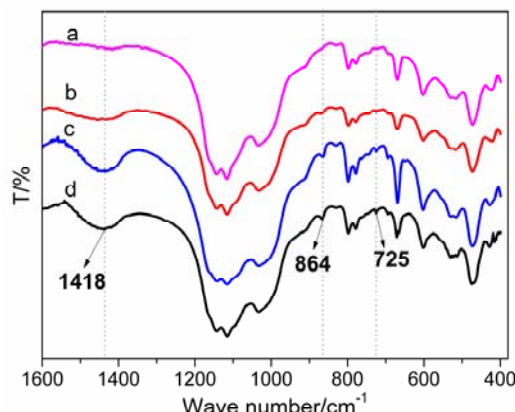


Figure 6. Infrared spectra of treated EMR (a: the raw EMR, b: 4 min reaction time, c: 20 min reaction time, d: 30 min reaction time)

3.4 Leaching Test

Leaching experiments were conducted to test the leached metals concentrations from the treated EMR by means of leaching test (GB 5085.3-2007). Table 1 displays the leached metals concentrations of the treated EMR. The leached concentration of manganese of the treated EMR was reduced to 0.2 mg/L and was lower than the discharge standard of China (GB8978-1996). In addition, the leached concentrations of other heavy metals were lower than the discharge standard of China.

Table 1. Leached metals concentrations before and after carbonation precipitation

Parameters		Ca	Mg	Na	K	Mn	Zn	Cu	Co
Leached metals concentrations (mg/L)	The raw EMR	386.3	105	91.3	65	1552.4	0.35	0.09	0.13
	After carbonation precipitation	383.1	28.1	125.6	101.9	0.2	0.03	0.08	0
	Wastewater discharge standard of China	-	-	-	-	5.0	5.0	2.0	-

“-” represents the unrequired value in the standard.

4. Conclusions

The EMR contained an amount of soluble manganese and could not be directly buried and used as building materials. Carbonate precipitation by CO_2 with CaO could convert soluble manganese to rhodochrosite ($MnCO_3$) and decrease effectively the leached concentration of manganese from the EMR to 0.2 mg/L. In addition, the pH value and the ORP of the EMR slurry after manganese precipitation were about 7 and 320 mV, respectively, and the concentrations of leached heavy metals of the treated EMR were less than the discharge standard of China, which favoured landfill and reuse of EMR.

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