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RESEARCH ARTICLE

Immobilization of Mn and NH_4^+-N from electrolytic manganese residue waste

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Abstract The objective of this work was the immobilization of soluble manganese (Mn) and ammonium nitrogen (NH_4^+-N) leached from electrolytic manganese residue (EMR). Immobilization of Mn was investigated via carbonation using carbon dioxide (CO_2) and alkaline additives. NH_4^+-N immobilization was evaluated via struvite precipitation using magnesium and phosphate sources. Results indicated that the immobilization efficiency of Mn using CO_2 and quicklime (CaO) was higher than using CO_2 and sodium hydroxide (NaOH). This higher efficiency was likely due to the slower release of OH^- during CaO hydrolysis. The immobilization efficiency of Mn was >99.99 % at the CaO:EMR mass ratio of 0.05:1 for 20-min reaction time. The struvite precipitation of NH_4^+-N was conducted in the carbonated EMR slurry and the immobilization efficiency was 89 % using $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ at the Mg:P:N molar ratio of 1.5:1.5:1 for 90-min reaction time. A leaching test showed that the concentrations of Mn and NH_4^+-N in the filtrate of the treated EMR were 0.2 and 9 mg/L, respectively. The combined immobilization of Mn and NH_4^+-N was an effective pretreatment method in the harmless treatment of the EMR.

Keywords Electrolytic manganese residue · Mn · NH_4^+-N · Carbonation · Struvite precipitation

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Introduction

Electrolytic manganese metal (EMM), widely used in metallurgy, aerospace, chemical processing, etc., is an important basic material. It is reported that China is the world's largest country of production, consumption, and export of EMM (Du et al. 2014). With the increase of Mn demand in the global market, the development of EMM industry has been promoted recently. The quick development results in various environment problems, especially the contamination from electrolytic manganese residue (EMR) (Duan et al. 2010). 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. The EMR contains high concentrations of soluble Mn and NH_4^+-N (Chen et al. 2015). At present, ~10–12 t of EMR are discharged into the environment during the production of 1 t of EMM (Zhou et al. 2013). In China, about 10×10^6 t of EMR are discharged into the environment each year and the accumulated amount during the past many years is about 50×10^6 t (Duan et al. 2010; Zhou et al. 2014). Currently, EMR is primarily dumped into the environment without pretreatment in China. Such a large amount of EMR poses a serious threat to the surrounding environment and the population. Therefore, the development of EMR disposal technologies is urgently required.

Studies have reported about the disposal and utilization of the EMR. Feng et al. (2006) used EMR as a cement setting retarder. Liu et al. (2012) used EMR as supplementary cementitious materials. Li et al. (2007) used burned EMR and fly ash as complex additives for cement. Applications of EMR as soil amendment and roadbed backfill were also investigated (Lan 2006; Xu 2001). Nevertheless, these applications could not be generalized in practice due to the low quantity of added EMR and the leaching of Mn and NH_4^+-N. The extraction of metals from the EMR was also investigated. Ouyang et al. (2007)

reported that the extraction efficiency of Mn reached 57.3 % using citric acid as the leaching reagent assisted with ultrasound. Yao et al. (2003) added glucose and saccharose into a sulfuric acid solvent to extract Mn, resulting in an extraction efficiency of 85 %. Xin et al. (2011) obtained a 93 % extraction efficiency of Mn from the EMR using sulfur-oxidizing bacteria. Owing to the high cost and complicated procedures, these technologies could not be applied in practice. Currently, the landfill treatment of EMR is still a primary choice for EMM industries. It is significantly necessary that the EMR is pretreated to immobilize soluble Mn and NH_4^+-N before the landfill treatment.

In view of high efficiency and low cost, the stabilization/solidification technology is extensively applied to the harmless disposal of various pollutants (Bednarik et al. 2005). The contaminants can be immobilized in the solid waste materials. The strength of the waste materials can also be enhanced. This technology is favorable to the application of these waste materials to landfill, building materials, and roadbeds. CaO and NaOH are typical additives used for decreasing metal mobility and leachability. Several studies reported that CaO and NaOH were effective additives to stabilize heavy metals (Zhou et al. 2013; Guo et al. 2006), because these additives were easily soluble and available for reactions. One drawback of these additives is the unacceptable increase of pH (>10) (Zhou et al. 2013), because a high proportion is required to add to waste materials. Additionally, previous studies reported the removal of NH_4^+-N using magnesium and phosphate sources in landfill leachate and wastewater (Huang et al. 2014; Stolzenburg et al. 2015).

The objective of this work was to immobilize (1) soluble Mn from EMR by CO_2 with alkaline additives and (2) NH_4^+-N via struvite precipitation using magnesium and phosphate sources. In addition, mechanisms of the Mn immobilization via carbonation and the struvite precipitation of NH_4^+-N were characterized and the optimal conditions were determined. The advantages of this study were the utilization of greenhouse gas (CO_2) by converting soluble Mn into Mn carbonate that can be recovered further by flotation (Zhou et al. 2015) and direct immobilization of NH_4^+-N via struvite precipitation in the EMR slurry.

Materials and methods

Materials

The EMR was obtained from a residue storage facility at an electrolytic manganese plant in Chongqing, China. After being thoroughly mixed, the residue was dried to constant weight at 105 °C. The dried residue was then ground to a powder with a ball mill and sieved through an 80-mesh screen (180 μm) for testing. Analytical grade CaO (≥98 %) and NaOH (≥96 %) were used as alkaline additives. CO_2 was collected from the ore leaching process of electrolytic manganese production and used to immobilize Mn. Analytical grade $MgCl_2 \cdot 6H_2O$ and MgO were used as magnesium sources, and $Na_3PO_4 \cdot 12H_2O$ was used as a phosphate source.

Table 1 The chemical components of raw EMR as determined by XRF

Elements	Content (%)	Elements	Content (%)
O	47.39	Fe	3.89
Si	15.32	Mn	2.07
S	13.05	Mg	1.83
Ca	9.26	Na	0.61
Al	4.14	NH_4^+-N	0.55

Immobilization of Mn via carbonation

The experiments were conducted at room temperature with a jar test apparatus. For each experiment, 20-g ground EMR, 40-mL distilled water, and different amount of alkaline additives were mixed into a 250-mL beaker with 0.8-L/min CO_2 flow rate. Each experiment was run in triplicate for statistical accuracy, and mean values were reported. To determine the effect of different alkaline additives (CaO and NaOH):EMR mass ratios on the immobilization of Mn, comparative tests were carried out by changing alkaline additives:EMR mass ratios in the range of 0.01:1–0.075:1. Additionally, the effect of reaction time on the immobilization of Mn was measured

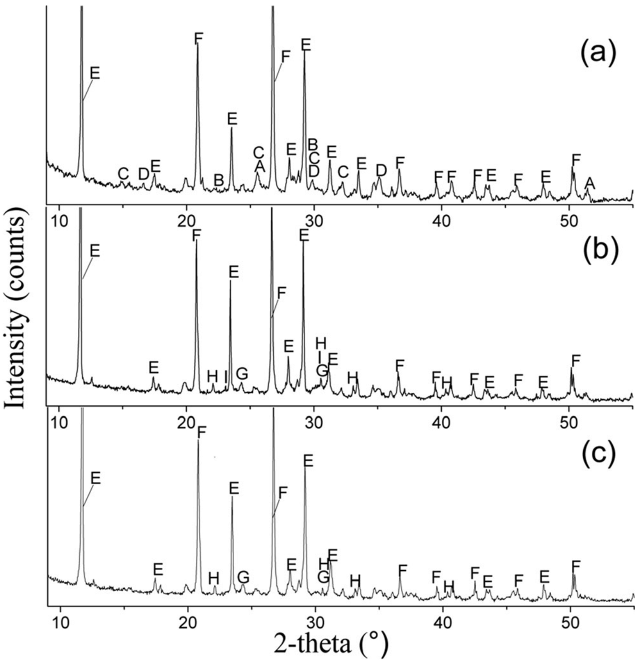


Fig. 1 The diffractograms of the raw EMR (**a**), the carbonated EMR using CO_2 + CaO (**b**), and the carbonated EMR using CO_2 + NaOH (**c**) (A-$MnSO_4 \cdot H_2O$, B-$(NH_4)_2SO_4$, C-$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, D-$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, E-$CaSO_4 \cdot 2H_2O$, F-$SiO_2$, G-$MnCO_3$, H-$CaMg(CO_3)_2$, and I-$CaCO_3$)

under different alkaline additives. The optimized experimental conditions, including an alkaline additive, the alkaline additive:EMR mass ratio, and reaction time, were determined based on the experimental results.

Immobilization of NH_4^+-N via struvite precipitation

After the immobilization of Mn from the EMR at the optimized conditions, immobilization experiments of NH_4^+-N were carried out using $MgCl_2 \cdot 6H_2O + Na_3PO_4 \cdot 12H_2O$ and $MgO + Na_3PO_4 \cdot 12H_2O$, respectively. The immobilization efficiency of NH_4^+-N was determined at the different Mg:P:N molar ratios. In addition, the effects of reaction time on the immobilization of NH_4^+-N, concentration of P, and stability of Mn carbonate formed by CO_2 with the alkaline additive were investigated. After the Mn and NH_4^+-N immobilization under optimum conditions, a leaching experiment was conducted under the conditions of a water:treated EMR mass ratio of 10:1, 8-h vibration time, and 16-h resting time according to the leaching standard designed by Chinese government (GB 5085.3-2007).

Calculation of immobilization efficiency

After each experiment, the treated sample was discharged from the reactor. Air pump filtration was performed to collect the filtrate in a 0.2-L flask for analyses. The immobilization efficiency of Mn (ζ) and the immobilization efficiency of NH_4^+-N (η) were defined by Eqs. (1) and (2), respectively.

$$\zeta = (n - n_t) \big/ n \times 100\ \% \tag{1}$$

$$\eta = (m - m_t) \big/ m \times 100\ \% \tag{2}$$

where n and n_t were the Mn mass (mg) in the raw EMR and the filtrate from the treated EMR, respectively, and m and m_t were the NH_4^+-N mass (mg) in the raw EMR and the filtrate, respectively.

Characterization

The chemical components of the raw EMR were analyzed using an X-ray fluorescence (XRF) spectrometer (XRF-1800, Shimadzu, Japan). The pH of the slurry was measured

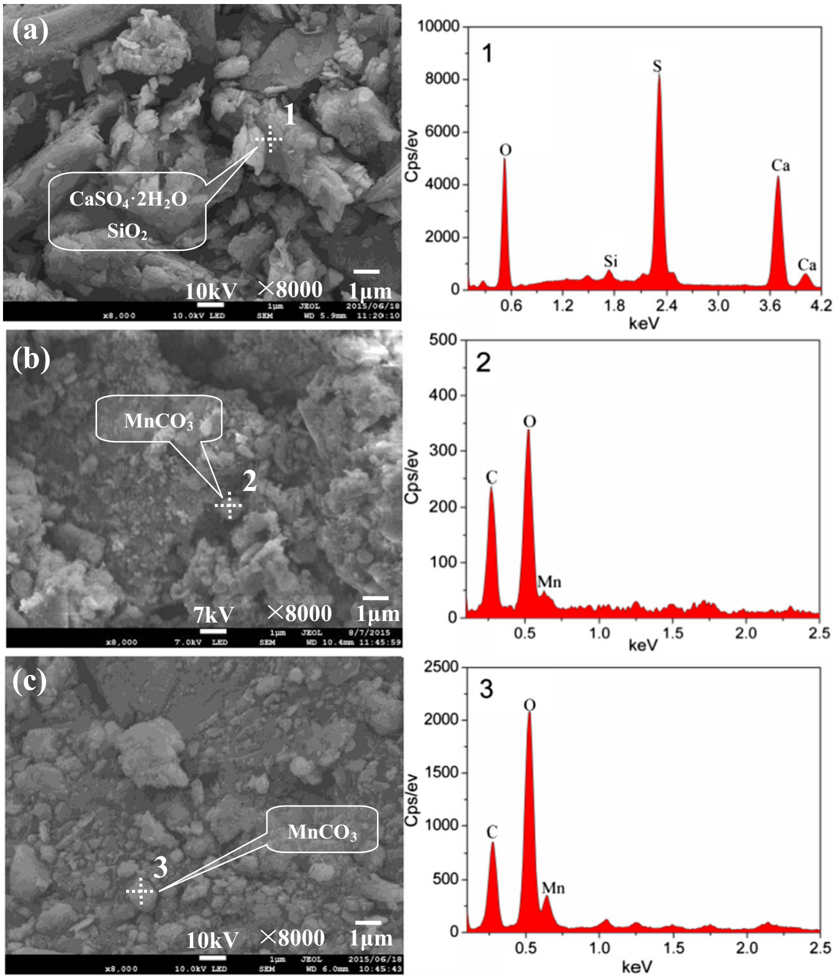


Fig. 2 The SEM micrographs of the raw EMR (**a**), the carbonated EMR using CO_2 + CaO (**b**), and the carbonated EMR using CO_2 + NaOH (**c**)

using a pH meter (pHS-25, INESA, China). The EMR slurry after treatment was filtered and the solid phase was dried at 35 °C for 48 h. X-ray diffractometer (XRD) technique (X'Pert PRO, Panalytical, Holland), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy system (EDS; ∑IGMA + X-Max20, Zeiss, Germany) were used to characterize the treated EMR. Mn concentration in the filtrate was determined using a flame atomic absorption spectrophotometer (180-80, Hitachi, Japan). The concentrations of NH_4^+-N and P were determined using a UV-Vis spectrometer (UV-8000S, Shanghai Metash, China) at wavelengths of 420 and 700 nm, respectively.

Results and discussion

Characterization of raw EMR

The major chemical components of the raw EMR determined by XRF analysis were presented in Table 1. The contents of Mn and NH_4^+-N, respectively, accounted for 2.07 and 0.55 %. Crystalline phases of the raw EMR primarily consisted of $MnSO_4 \cdot H_2O$, $(NH_4)_2SO_4$, $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, $CaSO_4 \cdot 2H_2O$, and SiO_2 (Fig. 1a). Regular cylindrical particles and particles in irregular shape overlapped randomly and loosely (Fig. 2a). A small amount of irregular floccule residues were observed in the spaces formed by the particles. A leaching experiment of the raw EMR was conducted under the conditions of a water:EMR mass ratio of 2:1, 8-h mixing time. The results indicated that Mn (7135 mg/L) and NH_4^+-N (2768 mg/L) were the major contaminants in the filtrate. The production of these contaminants was attributed to the incomplete pressure filtration of Mn^{2+} and NH_4^+-N that was added to the ore slurry to adjust the pH during the electrolytic manganese production (Xu et al. 2014). A small fraction of Mn^{2+} and most NH_4^+-N were leached into the EMR after the pressure filtration and formed $MnSO_4 \cdot H_2O$, $(NH_4)_2SO_4$, $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, etc. (Fig. 1a). These compounds could be dissolved in water, and the dissolved Mn^{2+} and NH_4^+-N posed serious threats to the environment (Li et al. 2014a). In addition, the observation of $MnSO_4 \cdot H_2O$, $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, and $(NH_4)_2SO_4$ indicated that Mn

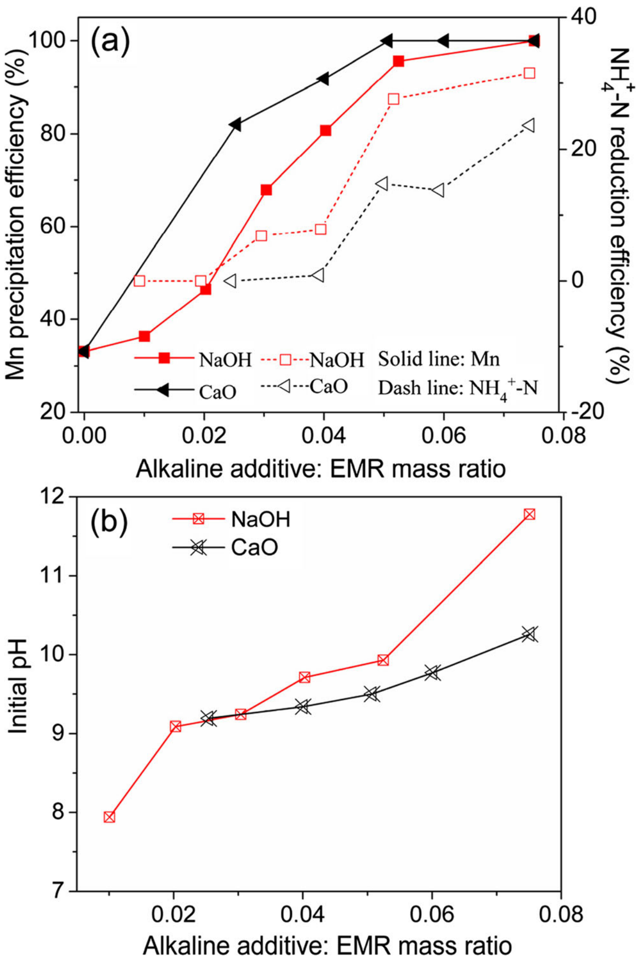


Fig. 3 The effects of alkaline additive, EMR mass ratios on Mn immobilization and NH_4^+-N volatilization (**a**) and the change of the initial pH (**b**)

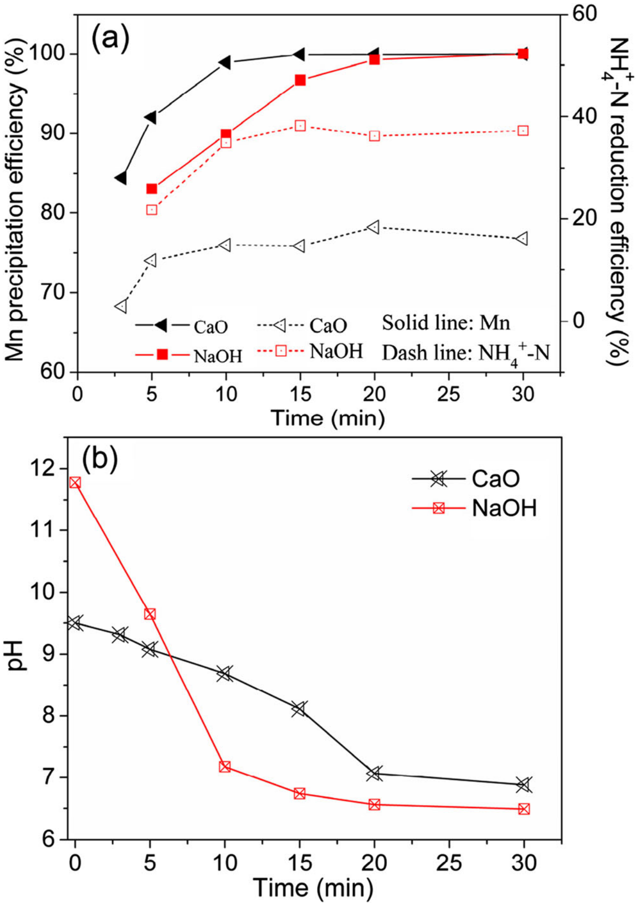


Fig. 4 The effects of time on Mn immobilization and NH_4^+-N volatilization (**a**) and the change of the pH (**b**)

and NH_4^+-N were in crystalline forms in EMR, which was inconsistent with previous studies (Du et al. 2015; Zhou et al. 2013).

Immobilization of Mn

Figure 3 shows the results of Mn immobilization by CO_2 with alkaline additives (CaO and NaOH) under different alkaline additives:EMR mass ratios, 30-min reaction time, and 0.8-L/min CO_2 flow rate. The immobilization efficiency of Mn was only 33.1 % when CO_2 was bubbled into the EMR slurry without alkaline additives. The immobilization efficiency of Mn increased when the mass ratios of alkaline additives:EMR increased. The immobilization efficiency of Mn using CO_2 + CaO was higher than using CO_2 + NaOH. The immobilization efficiency reached 99.99 % when the CaO:EMR mass ratio was greater than 0.05:1. The immobilization efficiency of Mn using CO_2 + NaOH was 99.99 % when the ratio of NaOH:EMR was 0.075:1. For the immobilization of Mn in same mass, more mass of NaOH is required than CaO.

More NH_4^+-N was volatized using NaOH than using CaO at the same dosage during the Mn immobilization (Fig. 3a). This observation was due to the higher initial pH of the EMR slurry mixed using NaOH than using CaO (Fig. 3b). NH_4^+ could be converted to NH_3 which evaporated under a higher pH (Bonmati and Flotats 2003; Gustin and Marinsek-Logar 2011). The release of OH^- from the hydrolysis of CaO was slower and resulted in a higher pH of the EMR slurry after 7-min reaction time (Fig. 4b), which was the main reason that the Mn immobilization efficiency using CO_2 + CaO was higher than using CO_2 + NaOH.

Figure 1b presents the diffractogram of the carbonated sample under the conditions of the CaO:EMR mass ratio of 0.05:1, 30-min reaction time, and 0.8-L/min CO_2 flow rate. The loss of X-ray reflections for $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, and $(NH_4)_2SO_4$ was observed in the carbonated sample. The observation indicated that the minerals from the raw EMR reacted with CO_2 and CaO to form $MnCO_3$ (Fig. 2b) and $CaMg(CO_3)_2$, of which the X-ray reflections were identified in the carbonated sample. The occurrence reactions were described by Eqs. (3)–(7). The peaks of $CaSO_4 \cdot 2H_2O$ and SiO_2 existing in the raw EMR were also detected, which demonstrated that these phases were resistant to the carbonation. In addition, the slight increase of intensity of X-ray peaks for $CaSO_4 \cdot 2H_2O$ was attributed to the formation of additional $CaSO_4 \cdot 2H_2O$

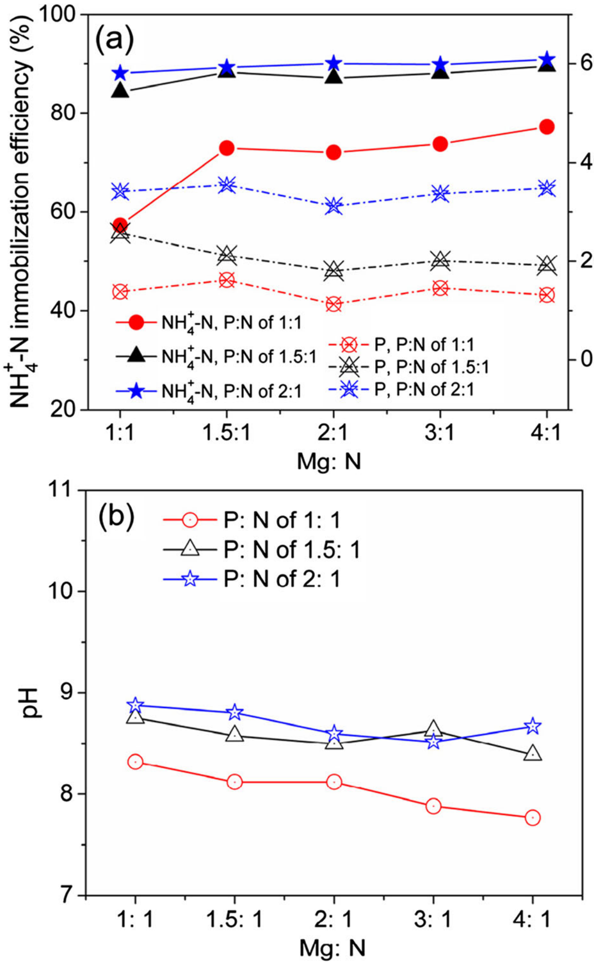


Fig. 5 The performance of struvite precipitation at different Mg:P:N molar ratios using $MgCl_2 \cdot 6H_2O + Na_3PO_4 \cdot 12H_2O$ (**a**) and the change of the pH (**b**)

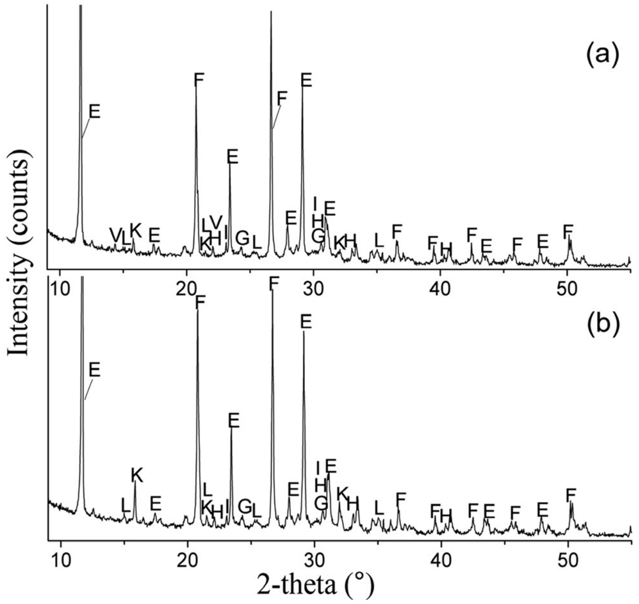
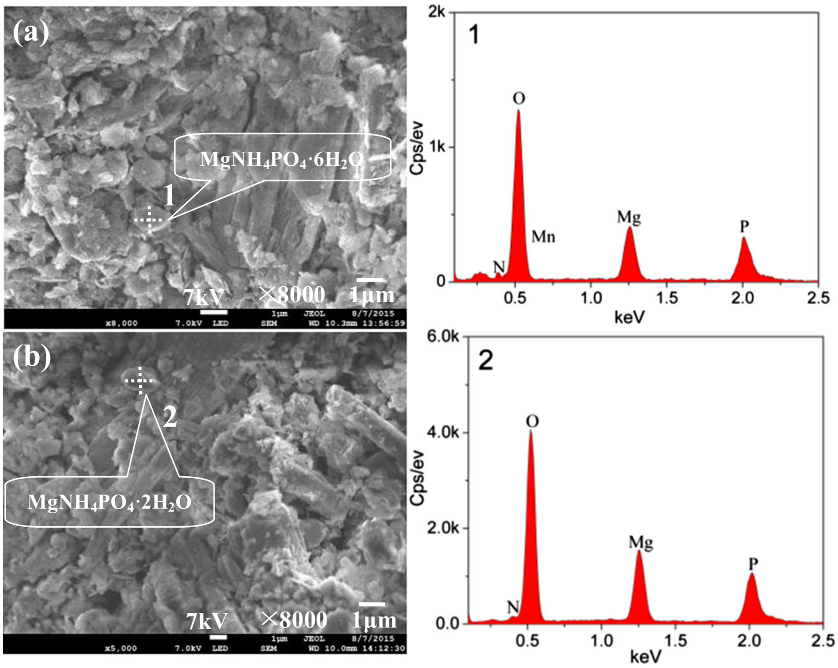


Fig. 6 The diffractograms of the treated EMR using $MgCl_2 \cdot 6H_2O + Na_3PO_4 \cdot 12H_2O$ (**a**) and the treated EMR using $MgO + Na_3PO_4 \cdot 12H_2O$ (**b**) (E-$CaSO_4 \cdot 2H_2O$, F-SiO_2, G-$MnCO_3$, H-$CaMg(CO_3)_2$, I-$CaCO_3$, K-$MgNH_4PO_4 \cdot 6H_2O$, L-$Ca_3(PO_3)_2$, and V-$Mg_3(PO_3)_2$)

Fig. 7 The SEM micrographs of the treated EMR using $MgCl_2 \cdot 6H_2O + Na_3PO_4 \cdot 12H_2O$ (**a**) and the treated EMR using $MgO + Na_3PO_4 \cdot 12H_2O$ (**b**)



(Eqs. (4)–(6)). $(NH_4)_2SO_4$, which was observed partly in the raw EMR and formed partly by carbonation process, was almost dissolved in the slurry, except the volatilization of a fraction of NH_4^+-N (Fig. 4a).

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{3}$$

$$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O + CO_2 + Ca(OH)_2 \rightarrow MnCO_3 + (NH_4)_2SO_4 + CaSO_4 \cdot 2H_2O + 5H_2O \tag{4}$$

$$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O + 2CO_2 + 2Ca(OH)_2 \rightarrow CaMg(CO_3)_2 + (NH_4)_2SO_4 + CaSO_4 \cdot 2H_2O + 6H_2O \tag{5}$$

$$MnSO_4 \cdot H_2O + CO_2 + Ca(OH)_2 \rightarrow MnCO_3 + CaSO_4 \times 2H_2O \tag{6}$$

$$CO_2 + Ca(OH)_2 \rightarrow {}^{2}CaCO_3 + H_2O \tag{7}$$

Figure 1c displays the diffractogram of the carbonated sample under the conditions of the NaOH:EMR mass ratio of 0.075:1, 30-min reaction time, and 0.8-L/min CO_2 flow rate. Similar to the diffractogram in Fig. 1b, the X-ray reflections for $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, and $(NH_4)_2SO_4$ disappeared in the carbonated sample, and the peaks of $MnCO_3$ (Fig. 2c) and $CaMg(CO_3)_2$ were identified in the carbonated sample. The generation of $MnCO_3$ resulted from CO_2 and NaOH reacting with $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$, as shown by Eqs. (8) and (9). Additionally, the formation of $CaMg(CO_3)_2$ was related with a certain amount of $CaSO_4 \cdot 2H_2O$ subjected to desulfating by NaOH to form $Ca(OH)_2$ (Eq. (10)), which further reacted with CO_2 and $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ (Eq. (11)) at the beginning of

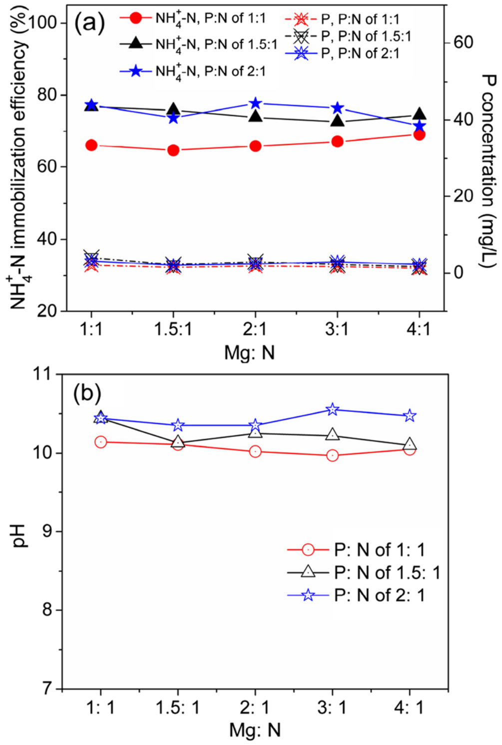


Fig. 8 The performance of struvite precipitation at different Mg:P:N molar ratios using $MgO + Na_3PO_4 \cdot 12H_2O$ (**a**) and the change of the pH (**b**)

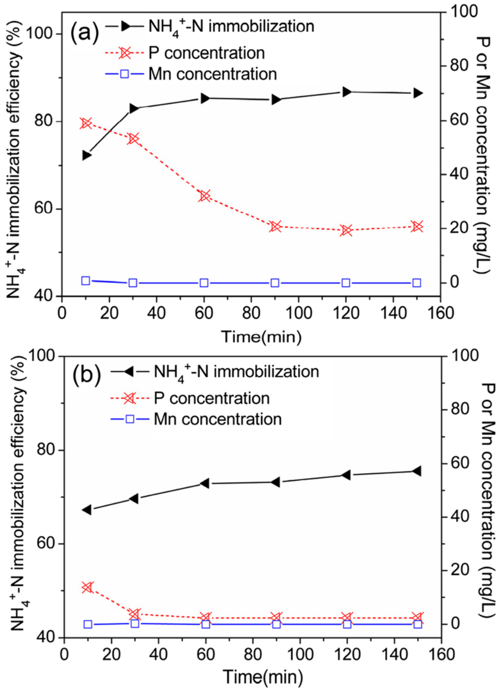


Fig. 9 The effects of time on NH_4^+-N immobilization and P concentration using $MgCl_2 \cdot 6H_2O + Na_3PO_4 \cdot 12H_2O$ (**a**) and $MgO + Na_3PO_4 \cdot 12H_2O$ (**b**), respectively

the reaction where the EMR slurry had a higher pH (Bang et al. 2014).

$$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O + CO_2 + 2NaOH \rightarrow MnCO_3 + (NH_4)_2SO_4 + Na_2SO_4 + 7H_2O \tag{8}$$

$$MnSO_4 \cdot H_2O + CO_2 + 2NaOH \rightarrow MnCO_3 + Na_2SO_4 + 2H_2O \tag{9}$$

$$CaSO_4 \cdot 2H_2O + 2NaOH \rightarrow Ca(OH)_2 + Na_2SO_4 + 2H_2O \tag{10}$$

$$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O + 2CO_2 + Ca(OH)_2 + 2NaOH \rightarrow CaMg(CO_3)_2 + (NH_4)_2SO_4 + Na_2SO_4 + 8H_2O \tag{11}$$

Figure 4a demonstrates the effect of time on the immobilization of Mn from the EMR at 0.8-L/min CO_2 flow rate with the CaO:EMR mass ratio of 0.05:1 and the NaOH:EMR mass ratio of 0.075:1, respectively. The immobilization efficiency of Mn using CO_2 + CaO was higher than using CO_2 + NaOH within 30-min reaction time. Twenty-minute reaction time was adequate to immobilize 99.99 % Mn using CO_2 + CaO. As shown in Fig. 4b, the pH of the EMR slurry was almost constant after 20-min reaction time, although the pH of the slurry using CO_2 + CaO was higher than using CO_2 + NaOH after 7-min reaction time due to the slower release of OH^- from the hydrolysis of CaO. In addition, The NH_4^+-N reduction efficiency of the EMR slurry using CO_2 + NaOH was higher than using CO_2 + CaO, implying NaOH resulting in more NH_4^+-N volatilization which led to more hazard for environment. In view of the higher Mn immobilization efficiency and the lower cost, CaO was more suitable as the alkaline additive for immobilizing Mn. The optimized experimental conditions were the CaO:EMR mass ratio of 0.05:1, 20-min reaction time, and 0.8-L/min CO_2 flow rate.

Immobilization of NH_4^+-N

Prior to immobilization of NH_4^+-N from the EMR slurry, soluble Mn was immobilized by CO_2 + CaO under the optimized experimental conditions. The efficiencies and characteristics of two ways of immobilizing NH_4^+-N in the EMR slurry were compared directly using $MgCl_2 \cdot 6H_2O + Na_3PO_4 \cdot 12H_2O$ and $MgO + Na_3PO_4 \cdot 12H_2O$, respectively. Figure 5 presents the results of NH_4^+-N immobilization directly using $MgCl_2 \cdot 6H_2O + Na_3PO_4 \cdot 12H_2O$ at different Mg:P:N molar ratios with 90-min reaction time. The immobilization efficiency of NH_4^+-N for the P:N molar ratios of 1.5:1 and 2:1 were similar when the molar ratio of Mg:N ranged from 1:1 to 4:1. The lowest efficiency was

Table 2 The comparison of correlative studies of the EMR harmless treatment

Reagents	Experiment objectives	Leached toxic substance concentrations of the treated EMR	Notes	References
CO_2, CaO, $MgCl_2 \cdot 6H_2O$, and $Na_3PO_4 \cdot 12H_2O$	Immobilizing Mn and NH_4^+-N	0.2 mg/L Mn and 9 mg/L NH_4^+-N	Immobilizing NH_4^+-N via struvite precipitation and obtaining a modest pH in the EMR	This paper
Quicklime	Immobilizing heavy metals	0.036 mg/L Mn	NH_4^+-N was not studied	Zhou et al. (2013)
CaO	Stabilizing Mn and removing NH_4^+-N	0.32 mg/L Mn and 5.35 mg/L NH_4^+-N	Transforming NH_4^+-N into NH_3 released into the air and obtaining a higher pH in the EMR	Du et al. (2014)
Calcium sulfide	Immobilizing Mn	0.05 mg/L Mn	NH_4^+-N was not studied	Li et al. (2014b)
Modified sulfur and sand	The EMR as filler in sulfur concrete	0.05 mg/L Mn	NH_4^+-N was not studied	Yang et al. (2014)

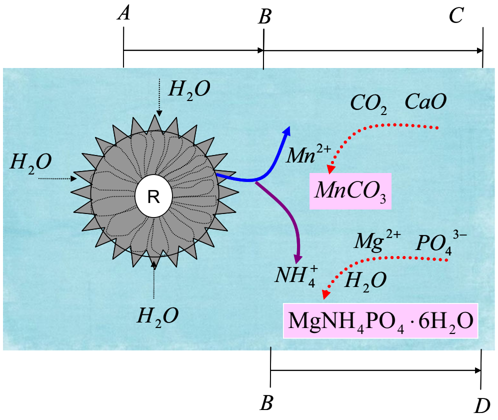


Fig. 10 The mechanisms of EMR treatment (R represents a particle of EMR)

observed when the molar ratio of P:N was 1:1. The highest efficiency of NH_4^+-N immobilization was 89 % when the molar ratio of Mg:P:N was 1.5:1.5:1. When the molar ratio of Mg:P:N was greater than 1.5:1.5:1, the immobilization efficiency of NH_4^+-N showed little change, but the remaining P concentration increased with the increase of P:N molar ratio (Fig. 5a). The product of NH_4^+-N immobilization was the struvite ($MgNH_4PO_4 \cdot 6H_2O$) as determined by laboratory tests (Figs. 6a and 7a), suggesting the reaction shown by Eq. (12). The Ca^{2+} from $CaSO_4 \cdot 2H_2O$ in the EMR likely competed for PO_4^{3-} by forming $Ca_3(PO_4)_2$ precipitation (Fig. 6a). This competing process could explain the lower NH_4^+-N immobilization efficiency when the molar ratio of P:N was 1:1 (Huang et al. 2014; Le Corre et al. 2005). Additionally, the pH of the EMR slurry (Fig. 5b) with the Mg:P:N molar ratio of 1.5:1.5:1 was 8.6, which favored the stabilization of struvite precipitation. Similarly, Li et al. (1999) reported that the optimum pH for struvite precipitation was in the range of 8.5–9.0 in landfill leachate.

$$(NH_4)_2SO_4 + 2MgCl_2 + 2Na_3PO_4 + 6H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O + Na_2SO_4 + 4NaCl \qquad (12)$$

Figure 8 displays the results of NH_4^+-N immobilization directly using MgO + $Na_3PO_4 \cdot 12H_2O$ at different Mg:P:N molar ratios with 90-min reaction time. The immobilization efficiency of NH_4^+-N using MgO + $Na_3PO_4 \cdot 12H_2O$ was lower than using $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ when the molar ratios of P:N were 1:1, 1.5:1, and 2:1, respectively. This observation could be attributed to pH > 10 (Fig. 8b), because the higher pH could increase the solubility of struvite (Nelson et al. 2003) and even give rise to the stripping of part NH_4^+-N (Zhou et al. 2013). Additionally, extra Na_3PO_4 could react with added MgO to form $Mg_3(PO_4)_2$ at the higher pH (Fig. 6b), which lowered the concentration of P (<3 mg/L; Fig. 8a). The product of NH_4^+-N immobilization using MgO + $Na_3PO_4 \cdot 12H_2O$ was the struvite ($MgNH_4PO_4 \cdot 6H_2O$) determined by XRD and SEM-EDS analyses (Figs. 6b and 7b).

Figure 9 presents the effects of time on the NH_4^+-N immobilization and P concentration using $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ and MgO + $Na_3PO_4 \cdot 12H_2O$, respectively. The stabilization of NH_4^+-N using $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ started at 60 min and the efficiency was 89 %, while P concentration was stable at 20 mg/L in the EMR slurry at 90 min (Fig. 9a). The NH_4^+-N immobilization efficiency using MgO + $Na_3PO_4 \cdot 12H_2O$ (Fig. 9b) was stable at ~73 % after 60 min. Additionally, for NH_4^+-N immobilization using two ways, undetectable Mn concentrations in the filtrates indicated that newly formed Mn carbonate was not decomposed. Thus, the optimized conditions for NH_4^+-N immobilization were using $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$, 90-min reaction time, and the Mg:P:N molar ratio of 1.5:1.5:1.

Leaching test

After the immobilization of Mn and NH_4^+-N under the optimized conditions, the concentrations of Mn and NH_4^+-N in the filtrate decreased from 7135 to 0.4 mg/L and from 2768 to 302 mg/L, respectively. The lowered concentration of NH_4^+-N in the filtrate could further be removed by electrochemical methods (Li et al. 2009; Lei et al. 2009). In order to test the leached toxic substance concentrations from the treated EMR

Table 3 The market prices of the chemicals

Chemicals	Market price ($/kg)	Mn immobilization ($/kg EMR)		NH_4^+-N immobilization ($/kg EMR)	
		CaO + CO_2	NaOH + CO_2	$MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$	MgO + $Na_3PO_4 \cdot 12H_2O$
CaO	0.61	0.031	–	–	–
NaOH	0.92	–	0.069	–	–
$MgCl_2 \cdot 6H_2O$	0.46	–	–	0.055	–
MgO	2.76	–	–	–	0.066
$Na_3PO_4 \cdot 12H_2O$	0.66	–	–	0.149	0.149
Total	–	0.031	0.069	0.204	0.215

which was dumped subsequently in landfill site, a leaching experiment was conducted according to the leaching standard designed by Chinese government (GB 5085.3-2007). The results showed that the concentrations of leached Mn, NH_4^+-N, and P in the leached fluid were only 0.2, 9, and 0.4 mg/L, respectively. This study could immobilize both soluble Mn and NH_4^+-N in the EMR slurry in comparison with other EMR harmless studies shown in Table 2.

Mechanism analysis

Although CaO could reduce the leaching of Mn (Du et al. 2015), CO_2 further decreased the leachability of Mn and nudged the transformation of Mn compounds to Mn carbonate. After the combined treatment of Mn and NH_4^+-N via immobilization, the pH of the EMR slurry was ~8.6, and this value could stabilize the structures of Mn carbonate and struvite precipitation (Li et al. 1999). In addition, the contaminant of NH_4^+-N from the EMR was seldom investigated, although it led to the environment pollution. The combination treatment of Mn carbonation and NH_4^+-N precipitation was an effective exploration for the immobilization of contaminants from the EMR. The mechanisms could be divided into three steps (Fig. 10). Firstly, Mn^{2+} and NH_4^+-N of $MnSO_4 \cdot H_2O$, $(NH_4)_2SO_4$, $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, and $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ in the EMR were released into the slurry (the process of $A \rightarrow B$). Secondly, Mn^{2+} reacted with CO_2 and CaO to form Mn carbonate (the process of $B \rightarrow C$). Thirdly, the struvite precipitation ($MgNH_4PO_4 \cdot 6H_2O$) of NH_4^+-N was formed after adding $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ (the process of $B \rightarrow D$).

Economic analysis

An economic evaluation of the immobilization of contaminants in the EMR was performed. In the assessment, seeing that CO_2 was collected from the ore leaching process of electrolytic manganese production and need not be purchased, the cost of other chemicals used in the EMR treatment was considered. The market prices of the used chemicals were obtained from the trading platform of Alibaba, and the results were shown in Table 3. The cost of the chemicals for the Mn immobilization using CO_2 + CaO was calculated as \$ 0.031/kg EMR. This value was less than using CO_2 + NaOH. The cost of the chemicals for NH_4^+-N immobilization using $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ was \$ 0.204/kg EMR, which was slightly less than using MgO + $Na_3PO_4 \cdot 12H_2O$. The cost of the immobilization of Mn and NH_4^+-N using CO_2 + CaO and $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ was \$ 0.235/kg EMR, which is less than other chemical combinations.

Conclusions

A large amount of soluble Mn and NH_4^+-N in the EMR pose serious threats to the environment. This study showed an effective method for the immobilization of contaminants from the EMR. The Mn immobilization was conducted by using greenhouse gas (CO_2) with the alkaline additives. The immobilization efficiency of Mn using CO_2 + CaO was higher than using CO_2 + NaOH. The efficiency was >99.99 % at the CaO:EMR mass ratio of 0.05:1 and 20-min reaction time. The NH_4^+-N immobilization was conducted by magnesium and phosphate sources. The immobilization efficiency of NH_4^+-N using $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ was higher than using MgO + $Na_3PO_4 \cdot 12H_2O$. The immobilization efficiency was 89 % under the optimized conditions, which were the Mg:P:N molar ratio of 1.5:1.5:1 and 90-min reaction time. The Mn was immobilized to form Mn carbonate and the NH_4^+-N was immobilized to form struvite. An economic evaluation shows that the cost of the immobilization of Mn and NH_4^+-N in the EMR using CO_2 + CaO and $MgCl_2 \cdot 6H_2O$ + $Na_3PO_4 \cdot 12H_2O$ was less than other chemical combinations.

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