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Simultaneous immobilization of NH₄⁺ and Mn²⁺ from electrolytic manganese residue using phosphate and magnesium sources

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Immobilization of contaminants from electrolytic manganese residue (EMR) is essential for the safe stacking and reuse of EMR. This study provides experiment results for the simultaneous immobilization of NH_4^+ and Mn^{2+} from EMR using $Na_3PO_4 \cdot 12H_2O$ and $MgSO_4 \cdot 7H_2O$ (PS) agents, as well as $Na_3PO_4 \cdot 12H_2O$ and MgO (PO) agents. The optimum reaction conditions, characteristics of immobilization, mechanism and the economy of alternative chemicals were determined and are discussed. The results indicated that the immobilization efficiencies of NH_4^+ and Mn^{2+} were 92.4% and 99.9% respectively under the following conditions: a $MgSO_4 \cdot 7H_2O$: $Na_3PO_4 \cdot 12H_2O$: EMR mass ratio of 0.113 : 0.175 : 1, a CaO : EMR mass ratio of 0.03 : 1 and a reaction time of 1 h using PS agents. The concentration of NH_4^+ in the leach liquor reduced from 1264 to 98 mg L^{-1} after immobilization. The concentration of heavy metal ions decreased sharply in the leach liquor and met the Integrated Wastewater Discharge Standard of China (GB8978-1996). The characteristics of immobilization indicated that NH_4^+ was immobilized to form $NH_4MgPO_4 \cdot 6H_2O$ and that Mn^{2+} was immobilized to form $Mn_5(PO_4)_2(OH)_4$, $Mn_3(PO_4)_2 \cdot 3H_2O$ and $Mn(OH)_2$. An economic evaluation showed that using PS agents had lower associated cost than using PO agents.

1. Introduction

Electrolytic manganese residue (EMR) is an industrial waste product from electrolytic metal manganese (EMM) plants which is discharged from the process of sulfuric acid leaching of manganese carbonate, neutralization of ammonia and the pressure filtration treatment of mineral pulp. Currently, about 10–12 metric tons of EMR are derived from each EMM plant for every metric ton of EMM produced.[1] In China, these EMM plants discharge up to 10 million tons of EMR into the environment each year and the accumulated amount is over 60 million tons during the past few years.[1,2] As the grade of manganese carbonate ore falls, the amount of EMR discharged increases further for the production of every metric ton of EMM, which causes further environmental and human health problems. At present, owing to the shortage of reutilization techniques for EMR, it is primarily transported to the stockyard for stacking without undergoing any preprocessing.[3,4] There is a great quantity of heavy metal ions from the raw ore and NH_4^+ from the neutralization process of EMM in EMR products. In addition, EMR possesses the following characteristics, fineness, high humidity, viscosity and toxicity.[5] These characteristics cause serious threat to the surrounding environment and the surface and ground water. It is crucial to exploit reusability technology and find harmless disposal methods for EMR.

Some research has been previously conducted on the reuse of EMR, including preparation of adsorbents,[6,7] photocatalytic materials[8] and soil fertilizers,[9] production of fillers for sulfur cement concrete,[2] granulated blast furnace slag cement,[10] steam-autoclaved bricks,[11,12] road beds[13] and quasi-sulphoaluminate cementitious materials,[14] the recovery of valuable metals[1] and so on. Owing to the reduced amount of EMR added, and the process instability and high cost, few studies have reported the industrial utilization of EMR. To date, the harmless disposal of EMR has remained the main focus, before the stacking and reuse of EMR. Some compounds, such as quicklime, carbonates, phosphates, caustic magnesia,[15] sodium hydroxide,[16] carbon dioxide[3] and so forth, were used to immobilize the heavy metal ions in EMR, although with less consideration of the NH_4^+ in EMR.

Owing to operational simplicity, low cost, the availability in large amounts and the ability to treat pollutants in a large scale operation, stabilization/solidification technology has been extensively applied to the harmless disposal of various pollutants.[17] Solidification or immobilization prompts a reduction in the potential hazards from the waste by converting the contaminants into their least soluble, mobile or toxic form and

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also imparts some strength to the waste, which is favorable for their utilization or stacking. Ammonium from the leachate is removed by forming a struvite precipitation with phosphate and magnesium sources of magnesite,[18] MgO[19] and MgCl$_2$·6H$_2$O,[20] and heavy metal ions from soil[21] and waste ash[22] are immobilized by the phosphate. The objective of this study was to propose a novel and low cost method for the immobilization of NH$_4^+$ and heavy metal ions from EMR. The optimum reaction conditions, characteristics of immobilization, mechanism and the economy of alternative chemicals are discussed and determined. The results of this study results are conducive to harmless disposal, prior to the stacking and reuse of EMR.

2. Materials and methods

2.1 Materials

EMR was collected from a residue storage facility at an EMM plant in Chongqing, China. Before immobilization, the residue sample was dried to a constant weight at 80 °C. The dried residue sample was ground using a ball mill and sieved using a screen with a 180 μm bore diameter for all experiments. The chemicals used were of analytical grade, CaO, MgSO$_4$·7H$_2$O, MgO,Na$_3$PO$_4$·12H$_2$O and so forth, and deionized water was used in the process of contaminant immobilization.

2.2 Immobilization process for contaminants

A series of experiments were conducted at room temperature using a convoluted shaking table. Each trial was run in triplicate for statistical accuracy, and the trial data were averaged for reporting. The treated sample was poured from the reactor at a specified time and air pump filtration was used to collect the leach liquor for further analyses. Contaminants of EMR were immobilized using Na$_3$PO$_4$·12H$_2$O and MgSO$_4$·7H$_2$O (or PS, for short) agents, as well as Na$_3$PO$_4$·12H$_2$O and MgO (or PO, for short) agents. CaO was used to increase the alkalinity of the EMR slurry. A 10 g residue sample was used and the water : EMR mass ratio was 4 : 1 in each trial. The effect of different Mg : NH$_4^+$ (1 : 1–4 : 1) and P : NH$_4^+$ (0.5 : 1–2 : 1) molar ratios, the dose of added CaO (0–1 g) and the reaction time (0.5–4 h) were evaluated. The P concentration and the pH of the treated EMR slurry were examined. In addition, the immobilization efficiencies of NH$_4^+$ and Mn^{2+} at specified times, the concentrations of contaminants and the economic analysis under the optimum conditions were measured. The immobilization efficiencies of NH$_4^+$ (η) and Mn^{2+} (ζ) were defined respectively using eqn (1) and (2).

$$\eta = (m - m_t)/m \times 100\% \tag{1}$$

$$\zeta = (n - n_t)/n \times 100\% \tag{2}$$

In which m and m_t are the NH$_4^+$ mass (mg) in the raw EMR and the leach liquor of the treated EMR at the specified time, respectively. Both n and n_t are the Mn^{2+} mass (mg) in the raw EMR and the leach liquor of the treated EMR at the specified time, respectively.

2.3 Characterization

The pH of the EMR slurry was measured using a pH meter (pHS-25, INESA, China). The chemical compositions of the raw EMR samples were determined using an X-ray fluorescence (XRF) spectrometer (XRF-1800, Shimazu, Japan). The phase compositions and the morphology characteristics of the raw EMR and the treated EMR were analyzed using an X-ray diffractometer (XRD) technique (X'Pert PRO, Panalytical, Holland), a scanning electron microscopy (SEM) and an energy dispersive X-ray spectroscopy system (EDS) ($\sum$IGMA+X-Max20, Zeiss, Germany). The concentration of Mn^{2+} and other metal ions in the leach liquor were measured using a flame atomic absorption spectrophotometer (180-80, Hitachi, Japan). The concentrations of NH$_4^+$ and P were measured by a UV-vis spectrometer (UV-8000S, Shanghai Metash, China) at wavelengths of 420 nm and 700 nm, respectively.

3. Results and discussion

3.1 Characterization of raw EMR

The major chemical compositions of the raw EMR determined using X-ray fluorescence analysis are shown in Table 1, amounting to 98.2% of the total amount of the sample. Fig. 1 shows that the crystalline phases of the raw EMR mainly included MnSO$_4$·H$_2$O, (NH$_4$)$_2$SO$_4$, (NH$_4$)$_2$Mn(SO$_4$)$_2$·6H$_2$O, (NH$_4$)$_2$Mg(SO$_4$)$_2$·6H$_2$O, CaSO$_4$·2H$_2$O, SiO$_2$ and so forth. The compounds of NH$_4^+$ and Mn^{2+} were easily dissolved in water. In Fig. 2, the SEM image indicates that the regular cylindrical particles and the irregular shaped particles are overlapped randomly and loosely. A leaching experiment of the raw EMR was conducted with a water : EMR mass ratio of 4 : 1 and an 8 h mixing time. The results (shown in Table 2) stated that the concentrations of NH$_4^+$ and Mn^{2+} were 1264 mg L^{-1} and 3518 mg L^{-1} respectively and that trace amounts of the heavy metal ions were detected, of which the concentrations were at low levels. Thus, the main contaminants of the EMR sample were NH$_4^+$ and Mn^{2+}.[15]

3.2 Effect of the different molar ratios of the immobilizing agents

Immobilization of NH$_4^+$ and Mn^{2+} from EMR was carried out using PS agents and PO agents respectively, under the conditions of a 10 g residue sample, 0.3 g mass of CaO, and a 1 h reaction time. Fig. 3a shows that the efficiency of NH$_4^+$ immobilization increased from 46.9% to 93.5% and that the efficiency of Mn^{2+} immobilization increased from 98.3% to 99.9% as the

Table 1 Chemical compositions of raw EMR

Element	Content (%)	Element	Content (%)
O	47.39	Mn	2.35
Si	15.32	Mg	1.83
S	13.05	Na	0.61
Ca	9.26	Ti	0.34
Al	4.14	Sr	0.04
Fe	3.89	Zn	0.01
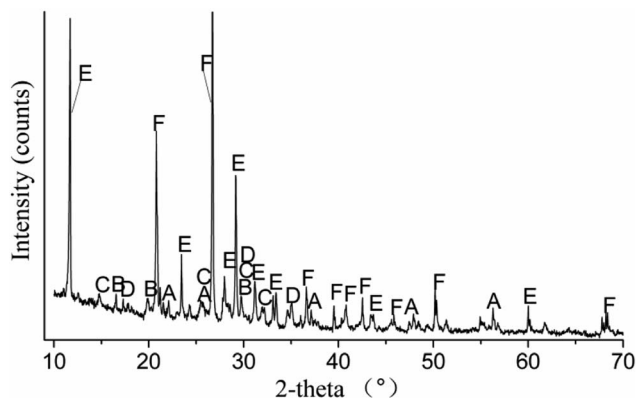
Fig. 1 X-ray diffraction patterns for raw EMR (A − $MnSO_4 \cdot H_2O$, B − $(NH_4)_2SO_4$, C − $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, D − $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, E − $CaSO_4 \cdot 2H_2O$, F − SiO_2).

molar ratio of $Mg : NH_4^+$ increased from $1:1$ to $3:1$ and the $P : NH_4^+$ molar ratio increased from $0.5:1$ to $2:1$ using PS agents. The efficiency of NH_4^+ and Mn^{2+} immobilization increased slightly when the molar ratio of $Mg : NH_4^+$ was greater than $1.5:1$ and the molar ratio of $P : NH_4^+$ was over $1.5:1$. In addition, as shown in Fig. 3b, the concentration of P from the leach liquor increased in proportion to the $P : NH_4^+$ molar ratio and was inversely proportional to the $Mg : NH_4^+$ molar ratio. The concentration of P was over 3.3 mg L^{-1} with a $P : NH_4^+$ molar ratio of $2:1$, which implied that excess PO_4^- was insignificant to the immobilization of contaminants in EMR. To avoid secondary pollution, the molar ratio of $P : NH_4^+$ was kept lower than $2:1$. By contrast, the optimum molar ratio of $Mg : P : NH_4^+$ should be $1.5:1.5:1$ (*i.e.*, $MgSO_4 \cdot 7H_2O : Na_3PO_4 \cdot 12H_2O : EMR$ mass ratio of $0.113:0.175:1$) to allow immobilization efficiencies of 92.4% NH_4^+ and 99.9% Mn^{2+}.

Fig. 4a shows the results of the immobilization of NH_4^+ and Mn^{2+} from EMR using PO agents under the following conditions: 10 g residue sample, 0.1 g CaO mass, and a 2 h reaction time. The efficiency of NH_4^+ immobilization increased from 79.4% to 86.7% with an increase of the $Mg : NH_4^+$ and $P : NH_4^+$ molar ratios. The immobilization efficiency of NH_4^+ with a $P : NH_4^+$ molar ratio of $2:1$ increased slightly compared to that of a $P : NH_4^+$ molar ratio of $1.5:1$ at the same $Mg : NH_4^+$

ratio. At $Mg : NH_4^+$ molar ratios of greater than $3:1$, the efficiency of NH_4^+ immobilization was almost constant at an invariable $P : NH_4^+$ molar ratio. Additionally, Mn^{2+} was immobilized almost completely with a $1:1$ $P : NH_4^+$ molar ratio. Thus, the optimum molar ratio of $Mg : P : NH_4^+$ was $3:1.5:1$ (*i.e.*, $MgO : Na_3PO_4 \cdot 12H_2O : EMR$ mass ratio of $0.037:0.175:1$), in which the immobilization efficiencies of NH_4^+ and Mn^{2+} were 83.5% and 99.9% respectively, with a P concentration of the leach liquor of under 0.5 mg L^{-1} (as shown in Fig. 4b).

3.3 Effect of the dose of CaO and the reaction time

The immobilization of NH_4^+ and Mn^{2+} from EMR are influenced by the pH.[15,23] To adjust the pH of the EMR slurry, different doses of CaO with PS agents or PO agents were added to the EMR samples.

Fig. 5a shows that the immobilization of NH_4^+ and Mn^{2+} were influenced by adding CaO using PS agents under the following conditions: 10 g residue sample, a water : EMR mass ratio of $4:1$, and a $Mg : P : NH_4^+$ molar ratio of $1.5:1.5:1$. The efficiency of the NH_4^+ immobilization firstly increased and decreased later with an increase in the dose of CaO within the same reaction time, the maximum value obtained was 92.4% over a 1 h reaction time. This was attributed to using the appropriate pH. As shown in Fig. 5b, the pH of the EMR slurry after completion of the reaction was raised as the dosage of the added CaO increased at the specified time. When the dose of added CaO was 0.3 g, the pH of the EMR slurry ranged from 9.66 to 9.13 with a reaction time from 0.5 to 4 h, which allowed the NH_4^+ to form deposits and to be immobilized. A higher pH resulted in the conversion of NH_4^+ into NH_3 and allowed it to escape from the EMR, which could cause secondary pollution. Ahmet Gunay reported that the minimum solubility of struvite in a reaction product was observed in the range of pH 8.8–9.4.[18] The efficiency of Mn^{2+} immobilization remained constant in general when the dose of added CaO was greater than 0.3 g and the reaction time was over 1 h. To summarize, the optimum conditions were 0.3 g of added CaO (*i.e.*, CaO : EMR mass ratio of $0.03:1$) and a 1 h reaction time using PS agents.

Fig. 6a shows that the immobilization of NH_4^+ and Mn^{2+} were influenced by the added CaO using PO agents at a $Mg : P : NH_4^+$ molar ratio of $3:1.5:1$. The efficiency of the
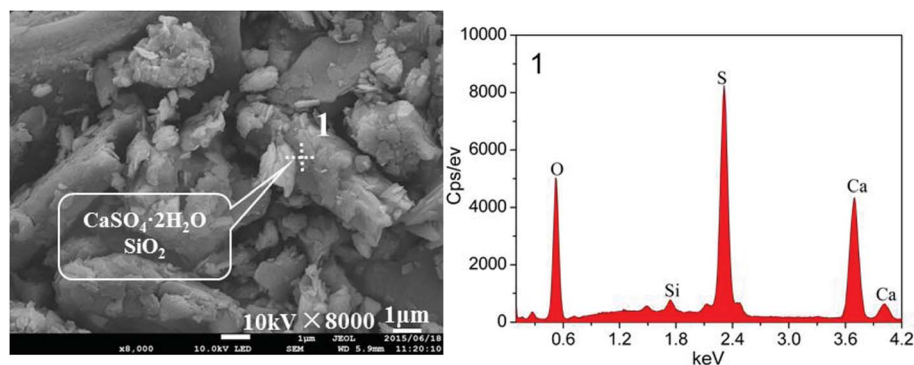

Fig. 2 An SEM micrograph of the raw EMR.

Table 2 Leaching compositions of EMR

Parameter	Concentration (mg L^{-1})			Parameter	Concentration (mg L^{-1})		
	Raw EMR	PS agents	PO agents		Raw EMR	PS agents	PO agents
NH_4^+	1264	98	207	Zn^{2+}	2.2	0.21	0.36
Mn^{2+}	3518	1.3	0.7	Cu^{2+}	0.6	0.16	0.08
Ca^{2+}	966	1977	1286	Co^{2+}	0.3	0.11	0.10
Mg^{2+}	263	517	181	Pb^{2+}	0.13	0.05	0.07
K^+	132	213	174	Cd^{2+}	0.06	0.03	—

NH_4^+ immobilization first increased and then decreased as the dose of added CaO was increased at the same reaction time. The maximum efficiency was 83.5% when the amount of added CaO was 0.1 g and the reaction time was 2 h. Adding further CaO (>0.3 g) gave rise to a higher pH (as shown in Fig. 5b) and a lower efficiency of the immobilization of NH_4^+, which was due to higher pH of the slurry of EMR which was unfavorably to forming NH_4^+ deposits.[24] As shown in Fig. 5a, the immobilization of Mn^{2+} was weakly influenced by the amount of added CaO. When the reaction time was greater than 1 h, the efficiency of the Mn^{2+} immobilization was 99.9%. Thus, the optimum conditions for the immobilization of NH_4^+ and Mn^{2+} using PO agents were less than 0.1 g of added CaO (*i.e.*, an CaO : EMR mass ratio of 0.01 : 1), a 2 h reaction time, and

a MgO : $Na_3PO_4 \cdot 12H_2O$: EMR mass ratio of 0.037 : 0.175 : 1. The Mg : NH_4^+ molar ratio when using PO agents was greater than those used for the PS agents to give the optimum conditions for the immobilization of the contaminants. This was due to the slow release of Mg^{2+} from MgO. The hydrolysis reaction of MgO released OH^- and resulted in a reduced amount of CaO being added during the immobilization process when using PO agents compared with PS agents.

3.4 Analysis of the mechanism

The crystalline phases of the treated EMR samples using PS agents and PO agents were analyzed using XRD technology. As shown in Fig. 7a and b, the loss of the X-ray diffraction peaks for $MnSO_4 \cdot H_2O$, $(NH_4)_2SO_4$, $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ and
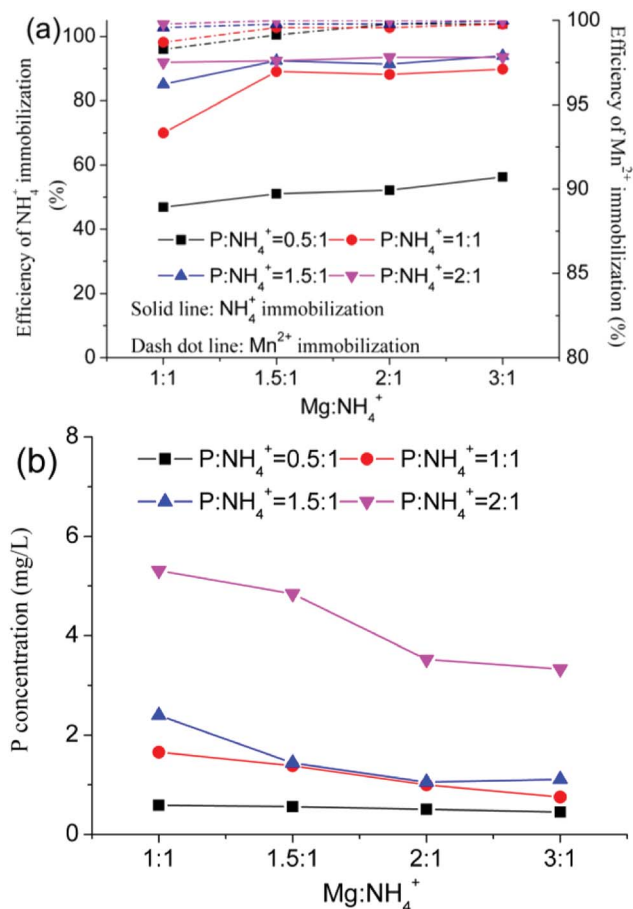

Fig. 3 Immobilization of contaminants (a), and the change in the P concentration (b) using PS agents.
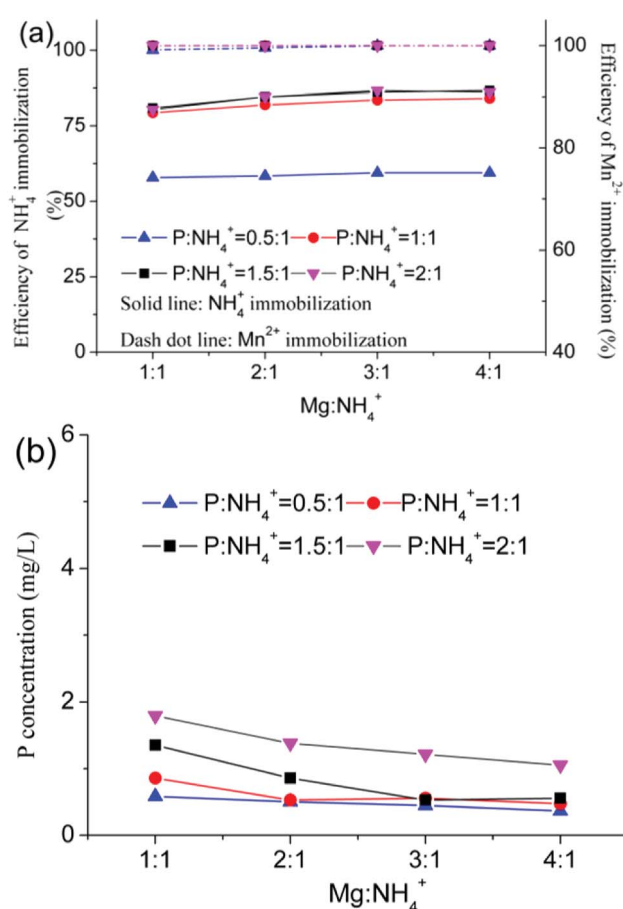

Fig. 4 Immobilization of contaminants (a), and the change in the P concentration (b) using PO agents.
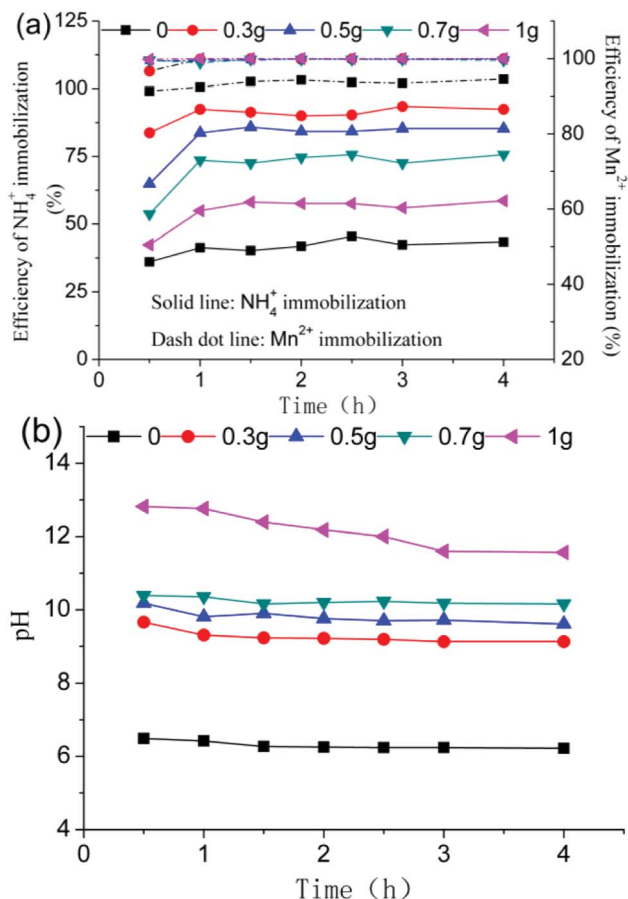
Fig. 5 Immobilization of contaminants (a), and the pH change (b) at different doses of CaO using PS agents.
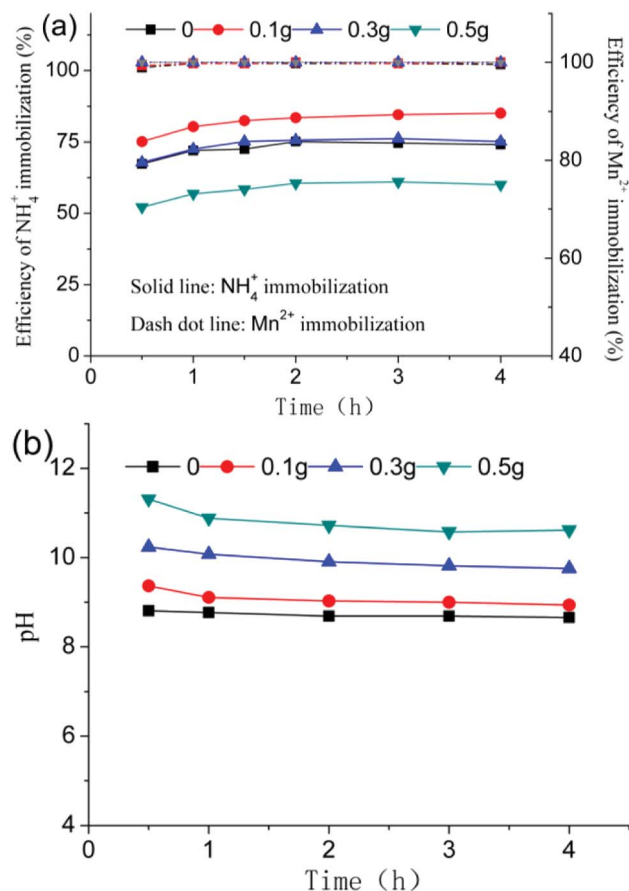

Fig. 6 Immobilization of contaminants (a), and the pH change (b) at different doses of CaO using PO agents.

$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ was observed in the treated samples. The diffraction peaks for $NH_4MgPO_4 \cdot 6H_2O$, $Mn_5(PO_4)_2(OH)_4$, $Mn(OH)_2$, $Mn_3(PO_4)_2 \cdot 3H_2O$, $Mg_2(PO_4)(OH)$, $Mg(OH)_2$ and $Ca_3(PO_4)_2$ were discovered in the treated samples. The peaks of SiO_2 were detected both in the raw EMR (Fig. 1) and the treated samples, indicating that the compound could not be changed using immobilizing agents.

The SEM micrographs and EDS data for the point analysis of the treated EMR samples using PS and PO agents respectively are displayed in Fig. 8. The results demonstrated that the crystalline and amorphous phases overlapped and were linked to each other. The number of regular cylindrical particles from the treated EMR using PS and PO agents respectively declined obviously, compared to the raw EMR data shown in Fig. 2. This meant that the micro-morphology of $CaSO_4 \cdot 2H_2O$ could be changed by the immobilization reaction.[25] EDS analysis determined that the formed phase of $NH_4MgPO_4 \cdot 6H_2O$ was linked to NH_4^+ immobilization and the formed phase of $Mn_5(PO_4)_2(OH)_4$, $Mn_3(PO_4)_2 \cdot 3H_2O$ and $Mn(OH)_2$ were linked to Mn^{2+} immobilization. The main equations for the reaction that used PO agents (eqn (3)–(10)) and those using PS agents (eqn (4)–(10)) are given below. Schematic illustrations of the proposed mechanisms of the PS and PO agents are shown in Fig. 9 and are based on the reaction equations.
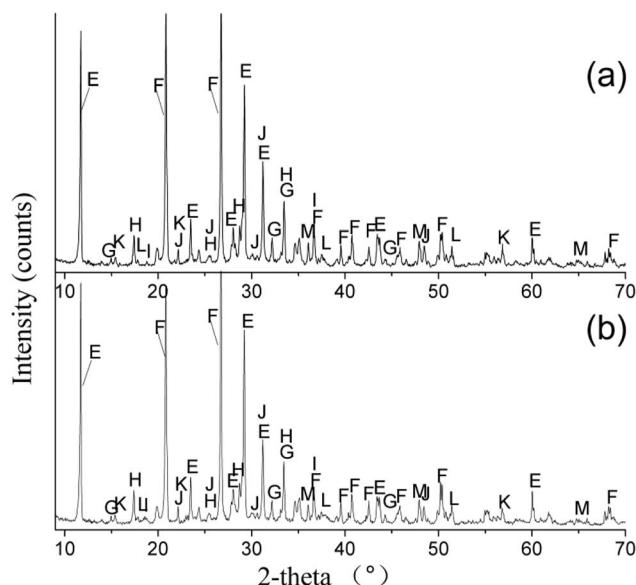

Fig. 7 X-ray diffraction patterns of the treated EMR (E − $CaSO_4 \cdot 2H_2O$, F − SiO_2, G − $NH_4MgPO_4 \cdot 6H_2O$, H − $Mn_5(PO_4)_2(OH)_4$, I − $Mn(OH)_2$, J − $Mn_3(PO_4)_2 \cdot 3H_2O$, K − $Mg_2(PO_4)(OH)$, L − $Mg(OH)_2$, M − $Ca_3(PO_4)_2$) using PS agents (a) and PO agents (b).
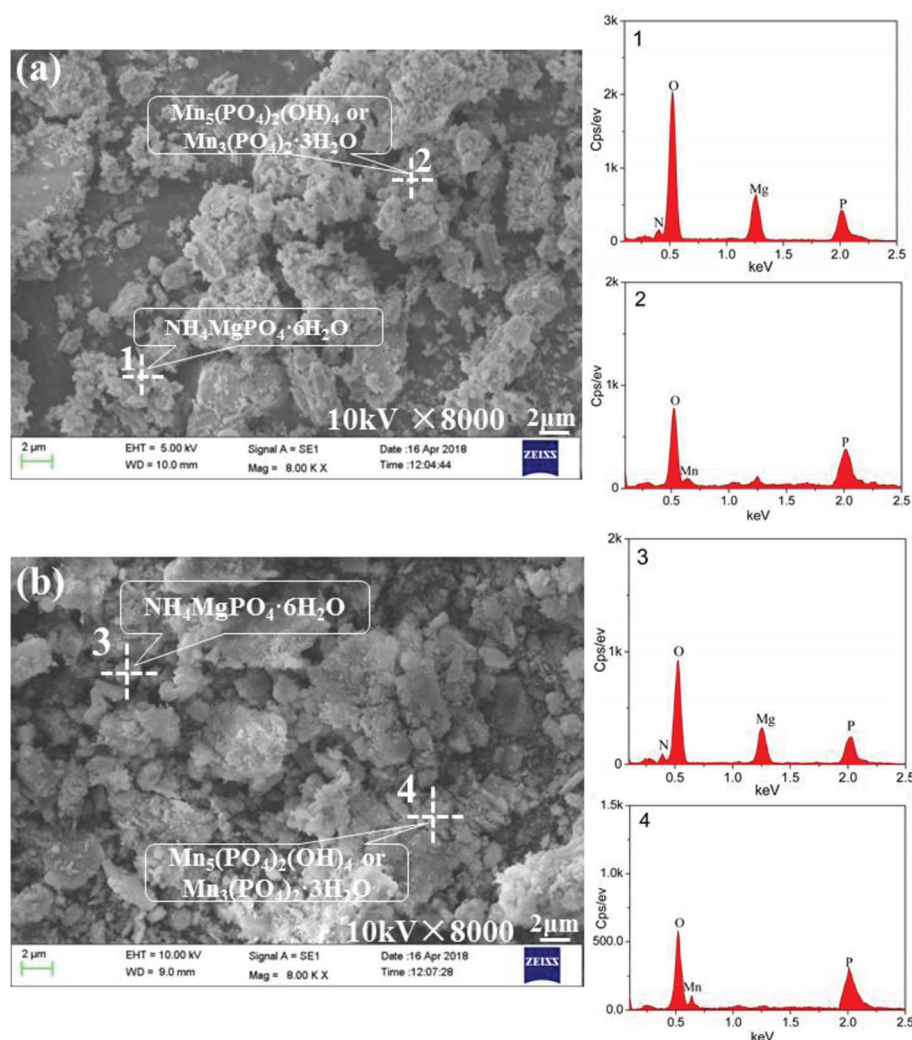
Fig. 8 SEM micrographs of the treated EMR samples using PS agents (a) and PO agents (b).
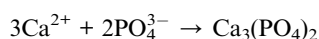
$$MgO + H_2O \rightarrow Mg(OH)_2 \rightarrow Mg(OH)^+ + OH^-$$
$$\rightarrow Mg^{2+} + 2OH^- \tag{3}$$

$$2Mg^{2+} + PO_4^{3-} + OH^- \rightarrow Mg_2PO_4(OH) \tag{4}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \rightarrow Ca(OH)^+ + OH^-$$
$$\rightarrow Ca^{2+} + 2OH^- \tag{5}$$

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \tag{6}$$

$$3Mn^{2+} + 2PO_4^{3-} + 3H_2O \rightarrow Mn_3(PO_4)_2 \cdot 3H_2O \tag{7}$$

$$5Mn^{2+} + 2PO_4^{3-} + 4OH^- \rightarrow Mn_5(PO_4)_2(OH)_4 \tag{8}$$

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2 \tag{9}$$

$$NH_4^+ + Mg^{2+} + PO_4^{3-} + 6H_2O \rightarrow NH_4MgPO_4 \cdot 6H_2O \tag{10}$$
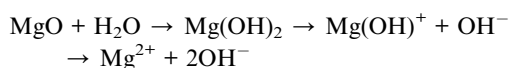
By contrast, the PS agents demonstrated a faster release of Mg^{2+} from $MgSO_4 \cdot 7H_2O$ compared to the PO agents. This is the reason why the 1 h reaction time gave the maximum efficiency of immobilization using PS agents. The Mg^{2+} from the PO agents came from a slow hydrolysis reaction of MgO, which resulted in the requirement for more MgO.
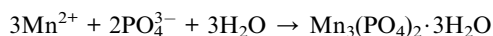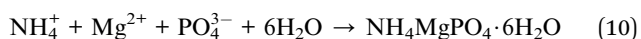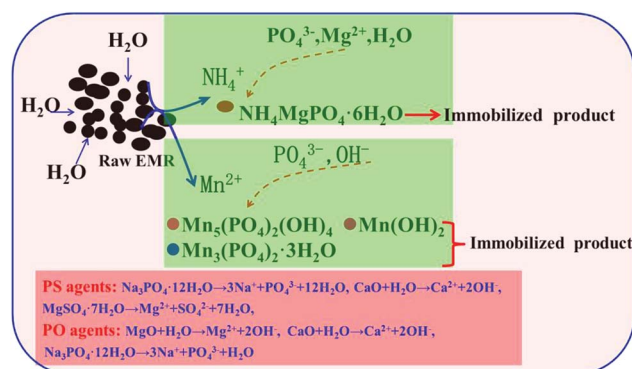

Fig. 9 Schematic illustrations of the immobilization of contaminants.

Table 3 Market prices of the chemicals used

Chemical	Market price ($ per kg)	PS agents		PS agents	
		kg t^{-1} EMR	$ per t EMR	kg t^{-1} EMR	$ per t EMR
CaO	0.06	30	1.8	10	0.6
MgSO$_4 \cdot$7H$_2$O	0.12	113	13.6	—	—
MgO	0.55	—	—	37	20.4
Na$_3$PO$_4 \cdot$12H$_2$O	0.38	175	66.5	175	66.5
Total	—	—	81.9	—	87.5

Table 4 Comparison of the relevant studies on the treatment of EMR to form a harmless product

Reagent	Experiment objective	Leached toxic substance concentrations of the treated EMR	Note	Ref.
MgSO$_4 \cdot$7H$_2$O, Na$_3$PO$_4 \cdot$12H$_2$O and CaO	Immobilization of NH$_4^+$ and Mn^{2+}	98 mg L^{-1} NH$_4^+$, 1.3 mg L^{-1} Mn^{2+}	NH$_4^+$ and Mn^{2+} were immobilized simultaneously and a modest pH was obtained in the EMR	This paper
Inorganic chemicals	Immobilization of heavy metal ions	The leached amount of Mn^{2+} was reduced to 100 mg per kilogram of EMR	NH$_4^+$–N was not studied	15
CaO	Stabilization of Mn^{2+} and removal of NH$_4^+$	0.5 mg L^{-1} Mn^{2+}	NH$_4^+$ was transformed into NH$_3$ and released into the air	16
Calcium sulfide	Immobilization of Mn^{2+}	0.05 mg L^{-1} Mn^{2+}	NH$_4^+$ was not studied	26
Modified sulfur and sand	EMR used as filler in sulfur concrete	0.05 mg L^{-1} Mn^{2+}	NH$_4^+$–N was not studied	2

3.5 Leaching test and economic analysis

After the immobilization of NH$_4^+$ and Mn^{2+} under the optimum conditions, the concentrations of NH$_4^+$ and Mn^{2+} in the leach liquor decreased respectively from 1264 to 98 mg L^{-1} and from 3518 to 1.3 mg L^{-1} using the PS agents. The concentration of NH$_4^+$ and Mn^{2+} in the leach liquor was reduced to 207 and 0.7 mg L^{-1} respectively using PO agents. The concentration of other heavy metal ions in the leach liquor were relatively small and were harmless to the environment. The concentration of heavy metal ions met the Integrated Wastewater Discharge Standard of China (GB8978-1996). This method can be used to immobilize NH$_4^+$ and Mn^{2+} simultaneously in the EMR slurry, in comparison with other EMR studies (shown in Table 4).

An economic evaluation of the immobilization of contaminants from EMR was performed. In the evaluation, the market prices of the used chemicals were obtained from the trading platform of Alibaba and the results are shown in Table 3. The cost of the chemicals used for NH$_4^+$ and Mn^{2+} immobilization using PS agents and PO agents were calculated as being $81.9 per t and $87.5 per t, respectively. Obviously, the use of PS agents has a lower associated cost. In addition, the optimal reaction time for using PS agents is 1 h, which was less than that required when using PO agents (shown in Fig. 5a and 6a). By comparison, the optimal method for NH$_4^+$ and Mn^{2+} immobilization from EMR was using PS agents and the optimum mass ratio of MgSO$_4 \cdot$7H$_2$O : Na$_3$PO$_4 \cdot$12H$_2$O : EMR was 0.113 : 0.175 : 1.

4. Conclusions

It was found that NH$_4^+$ and Mn^{2+} were the main contaminants from EMR by performing a leaching experiment. Simultaneous immobilization of NH$_4^+$ and Mn^{2+} was conducted using the chemicals; CaO, MgSO$_4 \cdot$7H$_2$O, MgO and Na$_3$PO$_4 \cdot$12H$_2$O. Higher immobilization efficiencies of contaminants were found when using PS agents compared to using PO agents. The optimum conditions for immobilizing NH$_4^+$ and Mn^{2+} using PS agents were determined to be as follows: a MgSO$_4 \cdot$7H$_2$O : Na$_3$PO$_4 \cdot$12H$_2$O : EMR mass ratio of 0.113 : 0.175 : 1, a CaO : EMR mass ratio of 0.03 : 1, and a 1 h reaction time. Under these conditions, the immobilization efficiencies of NH$_4^+$ and Mn^{2+} were 92.4% and 99.9%, respectively. The concentration of heavy metal ions decreased sharply in the leach liquor after immobilization and met the Integrated Wastewater Discharge Standard of China (GB8978-1996). The economic evaluation showed that using PS agents had lower associated costs compared to using PO agents.

In the process of contaminant immobilization, NH$_4^+$ was immobilized to form NH$_4$MgPO$_4 \cdot$6H$_2$O (struvite). Mn^{2+} was immobilized to form Mn$_5$(PO$_4$)$_2$(OH)$_4$, Mn$_3$(PO$_4$)$_2 \cdot$3H$_2$O and Mn(OH)$_2$. These newly formed phases were stable and insoluble, which was conducive to the stacking and reuse of EMR.

Conflicts of interest

The authors declare no conflicts of interest.

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