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Simultaneous stabilization/solidification of Mn^{2+} and $NH_4{}^+$-N from electrolytic manganese residue using MgO and different phosphate resource

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ABSTRACT

This study examined simultaneous stabilization and solidification (S/S) of Mn^{2+} and $NH_4{}^+$-N from electrolytic manganese residue (EMR) using MgO and different phosphate resource. The characteristics of EMR $NH_4{}^+$-N and Mn^{2+} S/S behavior, S/S mechanisms, leaching test and economic analysis, were investigated. The results show that the S/S efficiency of Mn^{2+} and $NH_4{}^+$-N could reach 91.58% and 99.98%, respectively, and the pH value is 8.75 when the molar ratio of Mg:P is 3:1 and the dose of PM (MgO and $Na_3PO_4{\cdot}12H_2O$) is 8 wt%. In this process, Mn^{2+} could mainly be stabilized in the forms of $Mn(H_2PO_4)_2{\cdot}2H_2O$, $Mn_3(PO_4)_2{\cdot}3H_2O$, $Mn(OH)_2$, and MnOOH, and $NH_4{}^+$-N in the form of $NH_4MgPO_4{\cdot}6H_2O$. Economic evaluation indicates that using PM process has a lower cost than HPM and HOM process for the S/S of Mn^{2+} and $NH_4{}^+$-N from EMR at the same stabilization agent dose. Leaching test values of all the measured metals are within the permitted level for the GB8978-1996 test suggested when the dose of PM, HPM and HOM is 8 wt%.

1. Introduction

In 2016, electrolytic metal manganese output was 1.15 million tons in China, accounted for over 98.5% of global supply (Shu et al., 2016a; Xu et al., 2014). Electrolytic manganese residue (EMR) is a solid waste which derived from the pressure filters after sulphuric acid leaching of manganese ore (Wang et al., 2016). So far, almost all the EMR are directly piled into residue field without any pretreatment, which has seriously damaged the local ecological environment and hindered the development of global electrolytic metal manganese industry. Because $NH_4{}^+$-N and Mn^{2+}, the main contaminants in EMR, could infiltrate into the soils nearby, and then migrate into the ground water (Shu et al., 2016b). To produce 1 t of manganese, 10–12 t of EMR would be discharged (Chen et al., 2015). And the amount of accumulated EMR was more than 120 million tons in the past several decades and was increasing at an annual quantity of 10 million tons. Thus, harmless treatment of EMR is extremely urgent, and the stabilization/solidification of $NH_4{}^+$-N and Mn^{2+} is at the heart of the problem.

Many researches have been carried out on the resource utilization of EMR, such as chemical raw materials (Peng et al., 2010), cementing material (Wang et al., 2012), geopolymer (Rong Zhao, 2013), ground granulated blastfurnace slag cement (Wang et al., 2013), autoclaved bricks (Zhou et al., 2014), road beds (Yang et al., 2014), synthesis of zeolite (Li et al., 2015a, 2015b, 2015c), and leaching of Mn^{2+} from EMR (Xin et al., 2011). These methods had not been applied into actual production, because of their low additional value, time-consuming, energy-intensive consumption and low leaching efficiency. Therefore, much attention was focused on the harmless treatment of EMR before the resource utilization. The stabilization of Mn^{2+} and removal of $NH_4{}^+$-N from EMR have been studied. Inorganic chemicals were used for stabilizing Mn^{2+} and removing $NH_4{}^+$-N (Du et al., 2015, 2014). Calcium sulfide and modified sulfur was applied to immobilize Mn^{2+} (Li et al., 2014a; Yang et al., 2014). Quicklime was an effective additive used for solidifying heavy metals (Zhou et al., 2013). In our previous work, electrokinetic remediation technology was used to remove Mn^{2+} and $NH_4{}^+$-N from EMR (Shu et al., 2015).

Stabilization/solidification (S/S) is a simple, efficient and low-cost technology, which is applied to dispose solid waste (Li et al., 2014b; Montanes et al., 2014; Quina et al., 2014). Considerable research efforts have been devoted to apply low-grade MgO to immobilize heavy metals

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in highly contaminated soils (Garcia et al., 2004). Moreover, an approach in the use of reactive MgO for stabilizing lead and zinc was described by Jin and Al-Tabbaa (2014). Wang et al. (2015) have reported on combining ground granulated blastfurnace slag and MgO to stabilize heavy metals. MgO and KH_2PO_4 were used for the immobilization of mercury in waste ash (Cho et al., 2014a, 2014b). Meanwhile, NH_4^+-N in landfill leachate and wastewater were removed soluble phosphates and magnesium (Davis et al., 2015; Huang et al., 2015; Ishii and Boyer, 2015).

In our study, MgO and different phosphate were used for simultaneous S/S of Mn^{2+} and NH_4^+-N from EMR. The characteristics of EMR, S/S behavior of NH_4^+-N and Mn^{2+} and the mechanism of S/S were investigated. Meanwhile, leaching test and economic analysis were studied.

2. Materials and methods

2.1. Raw materials

To simultaneously S/S of Mn^{2+} and NH_4^+-N from EMR, MgO, $Na_3PO_4{\cdot}12H_2O$, $Na_2HPO_4{\cdot}12H_2O$, and $NaH_2PO_4{\cdot}2H_2O$ were purchased from Chongqing Boyi Chemical Reagent Co., Ltd., China (analytical grade) and used without further purification in this study. The EMR was collected from Jiayuan Mining Co. Ltd. (Chongqing, China), and was dried to a consistent weight at 80 °C. EMR and broken until it could pass through a 80 mesh sieves. Deionized water was provided by the Water Purification System (HMC-WS10).

2.2. Experiment process

In this study, the EMR was treated with single and two stabilization agent. First, the EMR was stabilized by the MO (MgO), PO ($Na_3PO_4{\cdot}12H_2O$), HP ($Na_2HPO_4{\cdot}12H_2O$), and HO ($NaH_2PO_4{\cdot}2H_2O$), respectively, and the effects of four different dose of stabilization agents (2.0, 5.0, 8.0, and 10.0 wt% of the EMR) on S/S sample were evaluated. Second, the EMR solidified with the PM (MgO and $Na_3PO_4{\cdot}12H_2O$), HPM (MgO and $Na_2HPO_4{\cdot}12H_2O$), and HOM (MgO and $NaH_2PO_4{\cdot}2H_2O$), respectively. The effects of different Mg:P ratio (3:1, 4:1, 5:1, 6:1, and 7:1) and dose of stabilization agents (2.0, 5.0, 8.0, and 10.0 wt% of the EMR) on S/S efficiency were examined. The experimental conditions are shown in (Supplementary material). In the S/S process, EMR and MgO were mixed with different phosphate ($Na_3PO_4{\cdot}12H_2O$, $Na_2HPO_4{\cdot}12H_2O$, $NaH_2PO_4{\cdot}2H_2O$) for 10–15 min; then an appropriate amount of distilled water (weight of water to EMR was 1:2) was added to the mixture of the EMR sample and mixed at a high speed for 20 min; and the S/S of EMR was placed in a ventilated cabin to react for 48 h at room temperature. Finally, pH value of EMR, S/S efficiency of NH_4^+ and Mn^{2+}, and leaching test were measured. Leaching test details were described by our previous study (Shu et al., 2016a).

Ammonia S/S efficiency ($S/S_{NH_4^+-N}$) and manganese S/S efficiency ($S/S_{Mn^{2+}}$) are separately defined by Eqs. (1 and 2) as follows:

$$S/S_{NH_4^+-N} = \frac{C_{NH_4^+-N,0} - C_{NH_4^+-N,t}}{C_{NH_4^+-N,0}} \times 100\% \qquad (1)$$

$$S/S_{Mn^{2+}} = \frac{C_{Mn^{2+}-,0} - C_{Mn^{2+}-,t}}{C_{Mn^{2+}-,0}} \times 100\% \qquad (2)$$

where C_{NH_3-N} ($mg\,L^{-1}$) is the ammonia concentration and C_{Mn} ($mg\,L^{-1}$) is the manganese concentration. Subscripts 0 and t indicate the initial and sampling times, respectively.

2.3. Analysis methods

Atomic absorption spectrophotometry in flame (AAS; HITACHI 180/80, Japan) was used for determining the concentration of metal ions. NH_4^+-N was measured via Nessler's reagent spectrophotometry method. FT-IR spectra were obtained using a Magna 550II FT-IR spectrometer (Nicolet, USA) via the KBr pellet method. The S/S samples were analyzed by X-ray diffractometer (XRD, SHIMADZU-6000, Japan), Energy-dispersive X-ray spectroscopy system (EDS; ΣIGMA + X-Max20, Zeiss, Germany) and Scanning Electron Microscopy (SEM; S4800; HITACHI, Japan).

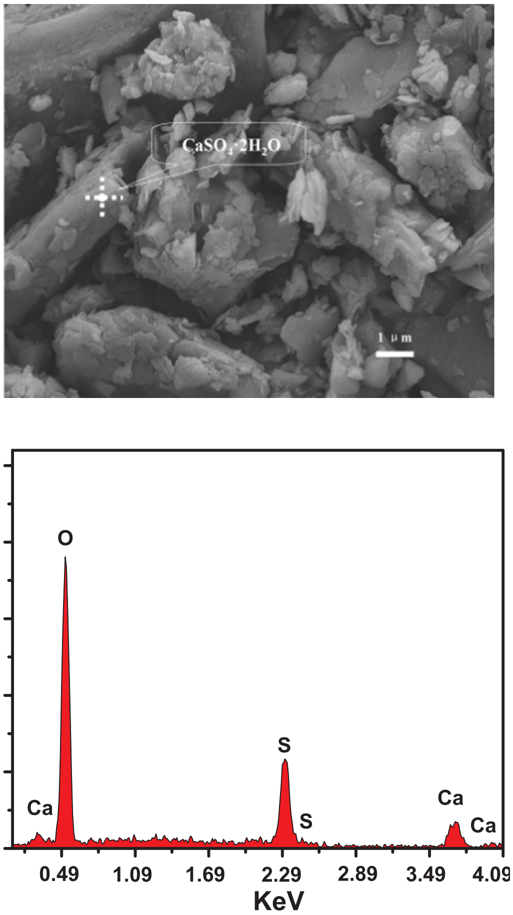

Fig. 1. SEM images of EMR and matching EDX data for point analysis.

3. Results and discussions

3.1. Characteristics of EMR

SEM shows that some columnar structure granules and irregular particles randomly overlap each other (Fig. 1). EDX analysis indicates that the columnar structure granules are $CaSO_4{\cdot}2H_2O$. X-ray fluorescence of EMR are shown in Table 1. The main chemical compositions of EMR are SiO_2, SO_3, CaO, Al_2O_3, Fe_2O_3, MnO, K_2O, MgO, amounting to 98.0% of the total composition, as shown in Table 2. In Fig. 2, the mineralogical components of EMR mainly contain gypsum ($CaSO_4{\cdot}2H_2O$), quartz (SiO_2), $(Na,Ca)Al(Si,Al)_3O_8$, $KAl_2Si_3AlO_{10}(OH)_2$, $MnSO_4{\cdot}H_2O$, $Al_2Si_2O_5(OH)_4$, and $(NH_4)_2(Mg,Mn,Fe)(SO_4)_2{\cdot}6H_2O$ (Wu et al., 2013). EMR leaching test values before the S/S are presented in Table 2. The results showed that Mn^{2+} (2057.00 mg/L) and NH_4^+-N (185.50 mg/L) were the main contaminants in the EMR, and trace amounts of Cr, Pb, Ni, Cu, Se, Cd and Zn are also existed (Hou et al., 2012).

3.2. Mn^{2+} and NH_4^+-N S/S behavior

3.2.1. Single stabilization agent treatment

In this work, the effect of single stabilization agent on S/S efficiency