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Activation of silicon in the electrolytic manganese residue by mechanical grinding-roasting

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ABSTRACT

Electrolytic manganese residue (EMR) is a solid waste containing several potentially harmful substances, which could pose severe environmental problems. The EMR also contains a large amount of silicon in the form of quartz that cannot be really absorbed by plants. Plants can only absorb effective silicon, hence, an increase in the content of the effective silicon is of great importance from the viewpoint of EMR utilization. In this study, silicon activation in EMR was systematically carried out by coupling mechanical grinding and roasting. The effects of particle size, Na_2CO_3/SiO_2 mass ratio, roasting temperature, and time on the recovery rate of the active silicon were analyzed. The experimental results of mechanical activation show that the content of the effective silicon gradually increased with the ball milling time. After grinding, the samples was then roasted with Na_2CO_3 and the content of the effective silicon increased from 0.19% in the raw EMR to 12.59% in the activated RMR as the mass ratio of Na_2CO_3 to SiO_2 was 1:0.5, roasting temperature is 900 °C, and the roasting time is 120 min. Mechanical activation can cause lattice distortion, while roasting with additives leads to the breakage of Si–O bonds; consequently, the silicate minerals become disordered and amorphous and can be easily absorbed by vegetation. Results of toxicity leaching tests revealed that the coupling method not only resulted in activation of silicon, but also facilitated the solidification of heavy metals, both promote the safe utilization of EMR.

1. Introduction

Electrolytic manganese residue (EMR) is a solid waste produced from filtering the sulfuric acid leaching solution of manganese carbonate ore (Yang et al., 2014). For every ton of the electrolytic manganese product, approximately 6–7 tons of residues are formed. Recent studies showed that EMR contains several soluble heavy metals, such as Cr, Cd, Zn, and Ni, which could become potential sources of contamination if disposed improperly. Furthermore, large amounts of EMR generated have long been considered to be a heavy burden on both the environment and the industry because of the high costs associated with post-treatment, storage and disposal (Li et al., 2015a,b). Therefore, effective solutions for treating EMR are urgently needed (Wang et al., 2013).

Based on its chemical composition, mainly of SiO_2 and small amounts of Al_2O_3 and Fe_2O_3, EMR is considered to be a type of silicate mining and metallurgy waste. Several researchers attempted to recycle manganese and ammonium from EMR by electrolytic processes (Shu et al., 2016a,b), wet processes, and biological methods (Xin et al., 2011). EMR is also used in preparation of building materials, such as concrete (Shu et al., 2016c) and brick (Kovács et al., 2017). However, these methods focused only on extracting some beneficial elements or simple filling. The abundant silicate minerals in EMR are not fully utilized.

Silicon is one of the plant nutrients (Imtiaz et al., 2016). However, most forms of silicon cannot be directly absorbed by plants, although it is widely present in soil. Plants can only absorb silicon in the form of mono-silicic acid or those can be readily transformed into mono-silicic acid. Effective silicon (i.e., absorbable silicon) can not only strengthen the cell wall, contribute to harvests, and adjust pH, but also reduce the activities of heavy metals, to minimize their spreading. In addition, effective silicon can prevent the absorption of heavy metals, such as Cr, Cd, Hg, Pb, Mn, Fe, and Al by plants (Collin et al., 2014; Adrees et al., 2015; Anwaar et al., 2015). Liu et al. (2015) studied the effect of effective silicon on rice growth in soils containing lead. They found that effective silicon not only resulted

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in an increased output, but also reduced the lead content in rice. Keller et al. (2015) reported that the effective silicon could solidify heavy metals, such as Cd and Cu, in plants. Gu et al. (2011) proved that silicon could co-precipitate with Cd in rice plant stems, which reduces the Cd content in the rice. EMR is a type of solid waste containing a large amount of silicon, which exists in the form of quartz and therefore cannot be effectively absorbed by plants. Hence, an increase in the content of effective silicon is of great importance from the viewpoint of EMR utilization. It can be achieved by decreasing the crystallinity of silicon in EMR to generate soluble silicates. Using this strategy, EMR can be reused safely and the heavy metals also can be fixed simultaneously. However, the activation of silicon in EMR has rarely been studied.

Mechanical activation is a widely used technique to treat minerals to destroy their inherent structure, generating lattice distortion and lattice defects, and increasing the specific surface area of the particles. It has been reported that mechanical activation could significantly decrease the apparent activation energy and reduce the apparent reaction order (Hou et al., 2012), thus contributing to the activation of silicon. Kumar et al. (2013) activated EMR by ball milling and found that the particle size and crystallinity decreased. However, the activation rate was not high enough. Recently, our research group found that ball milling with additives could promote the activation of silicon. By using the additives, the roasting temperature significantly reduced, and the content of effective silicon also increased.

Therefore, mechanical agitation and roasting play an important role in the activation process for effective silicon. No reports on the process and mechanism of activation for the effective silicon were found in our literature review. In this study, we investigated the effects of mechanical grinding and an activation method coupling roasting by studying several parameters i.e., (balling time, ratio of EMR to Na_2CO_3, roasting temperature and time) on the morphology of samples, changes in the silicate mineral phase and structure, and the toxicity of the activated EMR. The main objectives of this study were to increase the activation rate of silicon to make full use of silicon and to solidify the heavy metals in EMR.

2. Experimental

2.1. Materials

The EMR used in this study was obtained from an electrolytic manganese factory in Guangxi, China, and its chemical composition is tabulated in Table 1. The EMR was crushed after drying and then passed through a 100-mesh sieve (particle size < 150 μm) before subsequent treatment.

Table 1 shows that the contents of silicon, iron, and calcium are relatively high in the EMR. Although the content of SiO_2 is as high as 23.41%, the content of effective silicon is only 0.19%. From Fig. 1, the main phases of EMR could be deduced to quartz (SiO_2), muscovite ($KAl_2Si_3AlO_{10}(OH)_2$), gypsum ($CaSO_4 \cdot 2H_2O$), and soluble anhydrite (γ-$CaSO_4$).

A MLA-650 Mineralogical Parameters Automatic Analyzer (consisting of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX), and the JKTech mineral logical parameters analysis software was used to analyze the distribution of silicon in the EMR and the results are shown in Fig. 2. Silicon mainly exists in the forms of quartz (SiO_2, black), rhodonite ((Mn, Fe, Mg, Ca)SiO_3, red), ferrosilite ((Fe, Mg)SiO_3, cyan), orthoclase ($KAlSi_3O_8$, blue), sanidine ((K, Na)$AlSi_3O_8$, green), and muscovite ($KAl_3Si_3O_{10}(OH)_{1.9}F_{0.1}$, purple). Quartz accounts for 49.61% of the total silicon, while rhodonite accounts for 30.55%. Quartz usually appears as a single mineral with various shapes and particle sizes. The liberation degree of quartz is the highest followed by that of rhodonite.

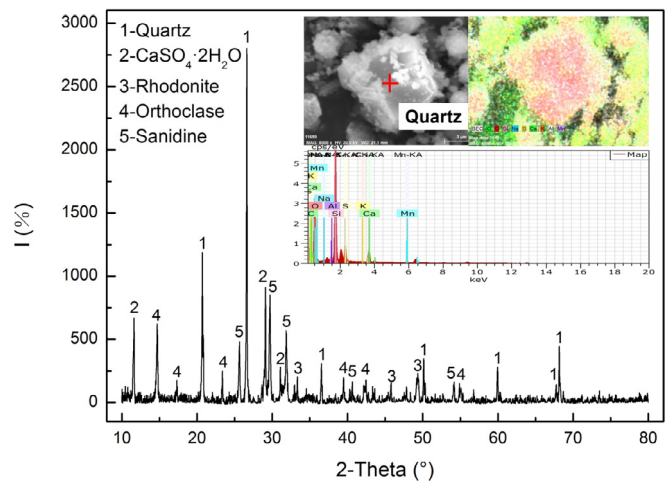

Fig. 1. XRD pattern of EMR.

2.2. Activation methods

After drying and ball milling, EMR (50.0 g) was mixed with a

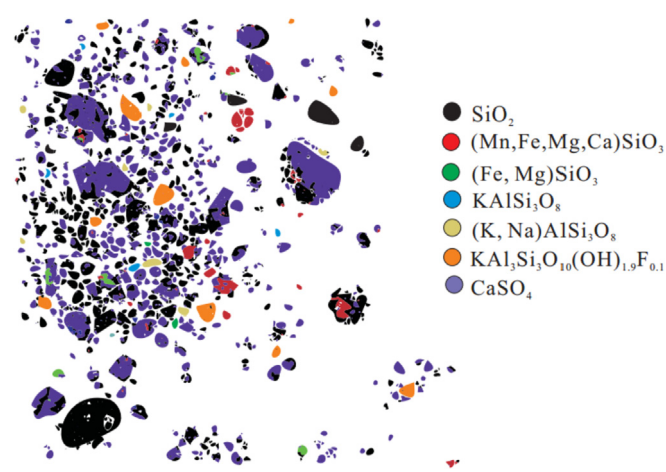

Fig. 2. The distribution characteristics of Si in EMR.

Table 1
Chemical composition of the EMR (mass fraction, %).

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO
0.053	1.235	2.461	23.41	0.320	27.578	0.601	14.962	0.148	4.804
Fe_2O_3	NiO	CuO	ZnO	PbO	Rb_2O	SrO	ZrO_2	BaO	effective silicon
8.572	0.037	0.008	0.008	0.017	0.005	0.005	0.003	0.172	0.191