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Preparation and strength property of autoclaved bricks from electrolytic manganese residue

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ABSTRACT

To reduce the Electrolytic manganese residue (EMR) hazard to environment and invent new construction materials, an autoclaved process was employed to prepare non-fired bricks with EMR, gelling agent (lime or cement) and aggregate (sand and stone clips) as raw materials. Based on analysis of EMR characteristics, lime was added. The influence of mix proportion of gelling agent including lime and ordinary Portland cement (OPC), and the forming pressure on strength of the autoclaved bricks was investigated. The results showed the optimal mix is 30% EMR, 10.5% OPC and 59.5% aggregate, and the optimal forming pressure and steaming condition are 25 MPa and 1.2 MPa for 8 h, respectively. The bricks from the pilot-scale experiment were well conformed to autoclaved lime-sand bricks GB 11945-1999 for MU 25 grade. Leaching tests undertaken on the autoclaved bricks showed that the concentrations of heavy metals in the leachates were largely inside the regulatory limits so bricks from EMR can be regarded as non-hazardous material.

1. Introduction

China is the world's largest country of production, consumption and export of the electrolytic metal manganese (EMM) (Duan et al., 2011). With rhodochrosite (manganese ore) as its main raw material, China's EMM industry still uses hydrometallurgical technology developed by the Bureau of Mines U.S. (Brantley and Rampacek, 1968). Accordingly, the EMM industry discharges the electrolytic manganese residue (EMR), which contains mainly soluble manganese and ammonia and other toxic and hazardous substances (Zn, Cu, Pb, Cd, Cr). It is reported that with the grade of manganese ore decreasing the EMM industry discharges 10–12 metric tons of EMR per ton manganese product. About 10 Mt of EMR are discharged each year and the amount will reach about 50 Mt over coming years (Duan et al., 2011, 2010; Xin et al., 2011). Currently, almost all EMRs without any treatment are open-dumped into uncontrolled waste pits and open fields. Hence, with the long-term weathering and effects of interaction with transport by rain, pollutants in EMRs can seep in the natural environment, migrate and transfer continuously, and seriously pollute the surface and ground water (Qian et al., 2012). Such a large amount of EMRs without pretreatment and management pose a serious threat to the environment, human health and have consequential negative social and economic impacts. The development of EMR disposal and utilization technologies is urgent.

There is some existing research into EMR disposal and utilization. Feng et al. (2006) used manganese slag as cement setting retarder. Li et al. (2007) used burned EMR and fly ash as a complex additive for cement. The amounts of the Mn-slag added were too low (<15%) and was not applied at large scale. Usage of EMR for crops (Lan, 2005, 2006; Lan and Wang, 2006) and application of Mn-slag to roadbed backfill (Xu, 2001) were investigated, but could not be applied in practice due to the low efficiency and immaturity of the technology.

The building bricks industry is a large consumer of conventional clay building material in China (Yang et al., 2009). In the last 50 years the production of fired clay bricks has destroyed considerable cultivated area, and consumed millions of tons of coal with the emission of significant SO_2 and CO_2. For environmental protection and sustainable development, the utilization of waste materials to produce bricks is increasingly emphasized. A wide variety of waste materials have been studied, including fly ash, mine tailings, slags, construction and demolition (C&D) waste and wood sawdust. Zhang (2013) recently provided a detailed research review of the various wastes and methods. However, there has been little investigation on the production of bricks from EMR. Manganese Metal Company in South Africa tried to prepare fired bricks with

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EMR, and the result showed, with appropriate addition of EMR, the prepared bricks (230 mm × 113 mm × 65 mm) satisfied the relevant building material standards. However, due to the presence of soluble substances (such as manganese ion) in the EMR, tawny stains on the wall from this bricks degraded the building aesthetics (Zhou et al., 2010). Wang (2010) used EMR with cement and sand to make autoclaved bricks and they analyzed the properties of the bricks but did not investigate the strength mechanism.

In this paper, bricks were prepared without firing by combining EMR, lime, cement, and aggregate (sand and stone chips) as raw materials using autoclaving technology. The effects of mix proportion of materials and forming pressure on the strength of bricks were investigated. The mechanism impacting strength to the bricks was investigated by XRD and SEM/EDX. Furthermore, the performance of bricks from pilot-scale experiments in a EMM factory (Huifeng EMM factory in Guizhou province) and their extraction toxicity were evaluated. The knowledge derived would be instrumental to promoting the process and utilization of the bricks from EMR.

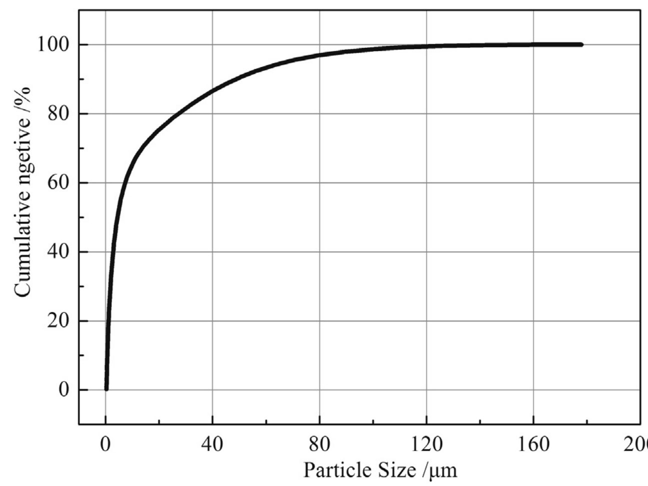

Fig. 2. Particle size distribution of EMR.

2. Experimental

2.1. Materials

The EMR was supplied by Tianxiong Electrolytic Manganese factory in Chongqing City. The X-ray diffractometer (XRD) pattern of the EMR was shown in Fig. 1. The main mineral phases were gypsum ($CaSO_4 \cdot 2H_2O$), quartz (SiO_2), albite ($KAl_2Si_3AlO_{10}(OH)_2$), respectively. The particle size distribution of the EMR, with medium particle size of 17 μm, was shown in Fig. 2. Lime was obtained from the local lime kiln near the Manganese factory, demolded and ground to pass through a 180 mesh sieve for use. Sand and stone chips (average particle size of 0.15 mm and 0.42 mm respectively, as aggregate for bricks), and ordinary Portland cement (OPC, 42.5) were obtained from the local construction materials market. The chemical composition of raw materials was shown in Table 1.

2.2. Pretreatment of EMR with lime

According to our previous research, the EMR was pretreated by lime additive to stabilize manganese and remove ammonia. The dried EMR and lime were mixed thoroughly at a mass ratio of 8:1 and then mixed with 30% water (based on the total mass of all solid raw materials) to a homogeneous paste. The paste was place under ventilated conditions to react for 4 h.

2.3. Preparation of brick specimens

The process of no-fired bricks is shown in Fig. 3. The pretreated EMR, lime, OPC, and aggregate were blended in a mechanical mixer uniformly. A suitable amount of water was added in the blending procedure. The mix proportions of EMR, CaO, aggregate and OPC are given in Table 2. After digesting for a certain period of time, the mixture was rolled and remixed with a suitable amount of water. The mixture was then poured into a steel mould of internal dimension (240 mm × 115 mm × 53 mm) equivalent to a standard burnt clay brick in China. Brick bases were formed by pressing in a hydraulic machine at a pressure of 25–35 MPa. After standing for 2 h, the formed brick base was wet-cured in a steaming autoclave at the pressure of 1.2 MPa for 8 h. The prepared bricks were tested for compressive strength and bending strength after air drying for over 24 h according to the Chinese standard for autoclaved lime-sand bricks (GB 11945-1999). The leach toxicity of the bricks was tested according to the Chinese government standard of Identification standards for hazardous wastes – Identification for extraction toxicity (GB 5085.3-2007).

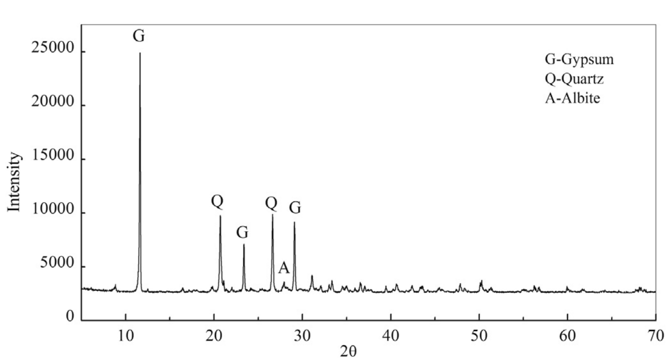

Fig. 1. XRD pattern of EMR.

Brick specimen was broken into 20–30 mm small chips, immersed in ethanol for 24 h, and dried at 40 °C for 48 h. Then a small section of the dried sample was prepared for SEM analysis after coating with gold on a JSM-6301F Scanning Electron Microscope; and the crystalline phase was investigated by XRD on a MXPAHF X-ray diffractometer from 5° to 70° with a Cu Kα of 1.54056 Å.

3. Results and discussion

In our study, the influence of gelling agent including lime and ordinary Portland cement (OPC), mix proportion, and forming pressure on strength of the autoclaved bricks was investigated to develop a feasible technology for making autoclaved bricks for building materials. We used the single factor experimental design.

3.1. Effect of the content of lime on the strength of bricks

The samples T1–T3 were used to determine the optimal content of lime and the result is shown in Fig. 4. It can be seen that strength peaks at 9% lime addition. This is attributed to the fact that a suitable of Ca/Si ratio (Chindaprasirt and Pimraksa, 2008; Fang et al., 2011). At low Ca:Si, less calcium silicate hydrates are formed by CaO and SiO_2 with water resulting in lower strength. At the high Ca:Si, the excess hydrate lime can inhibit the formation of low-alkali calcium silicate hydrates (such as tobermorite and xonotlite) which have much higher strength than high-alkali calcium silicate hydrates (Millogo et al., 2008).

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