



An investigation on the use of electrolytic manganese residue as filler in sulfur concrete



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HIGHLIGHTS

- Electrolytic manganese residue (EMR) was used as filler in sulfur concrete.
- Sulfur concrete with EMR showed good mechanical strength and corrosion resistance.
- This study establishes EMR as a suitable raw material for sulfur cement concrete.

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ABSTRACT

Utilization of sulfate-rich industrial residue building materials can reduce both the production cost and the environmental impact of the solid wastes. In this paper, the possibility of using electrolytic manganese residues filler for sulfur cement concrete has been investigated and compared with those of the relevant mortar samples. Mechanical properties, microstructure and durability of the sulfur concrete samples prepared with the above mentioned waste filler has been discussed. The microstructure results indicate that electrolytic manganese residue and aggregates were tightly wrapped by hydrophobic modified sulfur forming particle packing structure. The new sulfur concrete samples showed high mechanical strength and excellent environmental durability. Leaching test showed that the leaching concentrations of the heavy metal ions were far below the regulatory limits of National Integrated Waste water Discharge Standards in China (GB 8978-1996). Therefore, the results obtained in this study established a technical suitability of electrolytic manganese residue as raw material for sulfur cement concrete.

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1. Introduction

Electrolytic manganese residue (EMR) is solid waste produced in filters after sulfuric acid leaching of manganese carbonate ore, MnO₂ oxidative deferrization and ammonia neutralization. Approximately 6–7 tons of residues are discharged into the environment during the process of one ton of electrolytic manganese production [1]. In China, the accumulated amount of EMR during the past many years is huge amounting to more than 60 million tons. Random disposal of such large quantities of waste residue often led to waste management problems. More recent studies showed that there are certain amounts of soluble heavy metal ions

such as Cr³⁺, Cd²⁺, Zn²⁺, Ni³⁺, Co³⁺ in EMR [2–4], which could become potential sources of contamination if disposed of incorrectly. Furthermore, it is very difficult to dispose of the EMR due to its diversity of pollutants and its water content, fineness and viscosity. Currently, almost all EMRs were dumped in the open field. Thus, pollutants can seep into the soils in natural environment, migrate and transfer continuously and gradually pollute the surface and ground water [5]. Such a large amount of EMRs without pretreatment poses a potential threat to the environment, as well as the health of the people and the economy. Therefore, the development of the EMR disposal technologies is urgently needed.

Although there were some previous research studies about EMR disposal and its utilization, they did not solve this complex problem. Liu et al. used manganese slag as supplementary cementitious Materials [6], but the amounts of the added Mn-slag were too low (<5%) to make a dent in getting rid of these wastes. Usage of EMR for brick production [7] and metals extraction [8] was also

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investigated, but these applications could not be generalized in practice due to the low efficiency and immaturity of the technology. In recent years, stabilization/solidification technology is extensively applied to harmlessly dispose of the solid waste [9,10], due to its high efficiency, low cost, and simple procedure. As for EMR, the main chemical components are SiO_2 , Al_2O_3 and Fe_2O_3 including certain amounts of sulfate, MnO_2 and CaO . Like both gypsum and hydraulic industrial solid wastes, EMR can be used as a resource of building materials like brick, ceramic and concrete as has been suggested previously [11–13]. However, the primary drawback in terms of EMR's use as a building material is its high sulfate ammonium salt concentration and moisture content (20–30%) which could cause the corrosion/expansion and thereby decreasing the quality of building products [14,15]. That is why EMR cannot be used extensively for the manufacture of building materials in large scale unless it is pretreated to reduce its hydrophilicity and sulfate ammonium salt content [16].

Sulfur Concretes (SC) and mortars are high performance thermoplastic composite materials made of mineral aggregate, filler, and with sulfur as a binder, at temperature above the hardening point of sulfur (120 °C) [17]. Different from that of traditional Portland Cement Concrete (PCC), sulfur concrete has very low water permeability and exceptional resistance to acid and salt agents [18–20], due to the different binder system. It also has high strength and fatigue resistance and can be hardened to required characteristics in as quickly as 24 h. All these characteristics allow it to be used in extremely aggressive environment for years, regardless of weather conditions and it can be recycled. More importantly, high hydrophobicity of sulfur will make SC an excellent solidification agent for hazardous ions contained in solid waste [21].

Herein, we produced SC samples using EMR as filler, tested their microstructure, mechanical properties and leaching behavior. The purpose of this study was to investigate the feasibility of producing new SC cement concrete with EMR waste, and then to optimize the most appropriate preparation conditions. Additionally, microstructure, mechanical strength, and environment resistance were investigated as these are important characteristics which could provide a significant theoretical basis for future research and practical applications for manganese slag in sulfur cement concrete. Other properties, including leaching toxicity were also measured to examine the environmental safety of newly developed sulfur cement concrete.

2. Materials and methods

2.1. Raw materials

The initial components for obtaining technologically imposed sulfur concrete were: modified sulfur, river sand (aggregate) and electrolytic manganese residue (fillers).

Sublimed sulfur, as the basic component for a modified sulfur binder, was purchased from the Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China), and its purity is 99.9%. Styrene and dicyclopentadiene were purchased from the Tianli Chemical Reagent Co., Ltd., (Tianjin, China) and the Shenshi Chemical Reagent Co., Ltd., (Wuhan, China). Modified sulfur was prepared following the procedure described in an earlier US patent [22]. Typically, 16 g of styrene was mixed with 360 g of melted sulfur in the temperature range of 120–140 °C for 30 min, and then 24 g of dicyclopentadiene was added and mixed for 2–3 h at the same temperature. Finally, the obtained sulfur polymer was cooled at the rate of ~6 to 8 °C/min to room temperature and solidified. Microstructures of sublimed sulfur and modified sulfur were investigated by scanning electron microscope (SEM) (see Fig. 1), type JEOL JSM-5800 with EDX, and the results were analyzed based on previously reported research [18]. The structure of sublimed sulfur (Fig. 1a), obtained by Claus's procedure, is composed of regular orthorhombic crystals of alpha form of sulfur (S_2), while modified sulfur (Fig. 1b) consists of flat plate-shaped monoclinic crystals of beta form of sulfur (S_8), the latter partially polymerized in zigzag chains. The microstructure confirmed that dicyclopentadiene was uniformly dispersed in sulfur, as coverage of sulfur particles and plate joints. This anomalous microstructure helps to resist cracking and to tolerate thermal expansion.

EMR sample was collected from the Xibang Electrolytic Manganese Company, Hunan province, China. Each EMR sample of approximately 500 g was collected from different locations in a landfill. The samples were sealed for preservation and were desiccated at a temperature of 120 °C for a period of 2 h, and then crushed to pass through a 100-mesh sieve (0.154 mm). X-ray diffraction (XRD) pattern of EMR (Fig. 2) was obtained with a diffractometer (Rigaku D/max- β B) using $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15432$ nm). Sand with maximum grain size of 9.5 mm was used as an aggregate. It is obtained by sieving of river sand and gravel. Chemical analysis indicated that the aggregate mainly consisted of silica and alumina. Grain size distribution of EMR and sand, determined by sieving is given in Fig. 3.

2.2. Preparation and characterization of concrete samples

Preparation of sulfur concrete was done according to the manufacturing process described in the literature [23,24]. The preparation of sulfur concrete consisted of mixing modified sulfur into heated and homogenized dry mixture of aggregate and filler at the sulfur melting temperature of 135–140 °C. After homogenization and mixing that lasted for 30 min, concrete mixture was cast into molds preheated at 120 °C and vibrated for 1 min. After cooling at room temperature, the samples were removed from the mold and cured at ambient conditions (25 °C, 50% R.H.) prior to testing. Various sulfur concrete samples designated as S1 to S9 with different compositions are shown in Table 1.

The Portland cement concrete mixtures were made with the same aggregate as in the case of sulfur concrete. These were made by mixing Portland cement and water with a water to cement (w/c) ratio of 0.5, in a Hobart mixer. The aggregate was first charged into the mixer and mixed with some tap water. Then, the cement and the rest of the mixing water were added and homogenized. The overall mixing time was about 6 min. The concrete mixture was poured into molds and compacted by a vibration table. The specimens were demolded after 24 h casting and then cured in a moist room at a temperature of 20 ± 2 °C with 95–98% relative humidity for 27 additional days, before being subjected to the different tests.

The prism-shaped samples with dimensions (4 × 4 × 16) cm were prepared. Each reported value is the average of three measurements obtained from samples, to ensure the reliability of the test results.

Mechanical strength of the samples (both flexural S_f and compressive S_c) was conducted, using the "Amsler" press with a maximum load of 200 kN as per standardized method for testing the strength of concrete (SPRS EN 196-1: 2008). Three replicate samples were tested to obtain strength values. For sulfur concrete corrosion resistance and durability testing the standard testing method [17] was used. The prismatic samples were immersed in various aggressive environments: H_2SO_4 (98 wt%), HCl (36.5 wt%), HNO_3 (65 wt%), NaOH (10 wt%) or $\text{NH}_3 \cdot \text{H}_2\text{O}$ (34.7 wt%) solutions at room temperature. After 24 h of immersion in the above solutions, the samples were taken out from the solution and the surfaces were wiped with clean paper. Both mass change (ΔW_t) and compressive strength change (ΔS_c) were measured and recorded. At the same time, resistance of Portland cement concrete samples with identical dimensions in the same aggressive environments was examined for comparison.

A leaching test for heavy metal ions was carried out based on a reported procedure in the literature [25]. The samples were leached in deionized water with liquid/solid ratio of 10:1 at room temperature for 10–150 days. The concentration of various ions was measured with an emission spectrometer, ICP-AES "IRIS Intrepid II XSP" manufactured by Thermo Company.

3. Results and discussion

3.1. Characteristics of EMR

The XRD pattern of EMR is shown in Fig. 2. It can be clearly seen from Fig. 2 that the main minerals of EMR are finely crystallized quartz (SiO_2), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), plaster ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and muscovite ($\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$). Chemical analysis of the slag was carried out using X-ray fluorescence (XRF) and the result shows that the main constituents of slag are SiO_2 , Al_2O_3 , SO_3 and Fe_2O_3 amounting to ~83% of the total composition (Table 2). The slag also contained CaO , MnO and MgO in significant amounts. The contents of trace elements such as Cd, Cu, Ni, Zn, Cr, Pb, and Se are also shown in Table 3. The soluble sulfates in EMR would dissolve after rain, and the content of soluble sulfates will decrease with storage time in the pond [26]. Even though, there is the well-known risk of river and soil pollution from these sulfates, it is very likely that more of these sulfates will dissolve and cause pollution if improperly disposed. It was corroborated by previous studies, which showed that using sulfate-rich sludge (the sulfate content of EMR is about 10.62% in this research) as cement filler caused internal sulfate attack [27], due to the

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