Cement & Concrete Composites 34 (2012) 248–254

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Production of quasi-sulphoaluminate cementitious materials with electrolytic manganese residue

Peng-kun Hou, Jue-shi Qian *, Zhi Wang, Cheng Deng

College of Materials Science and Engineering, Chongqing University, Chongqing 400045, PR China

ARTICLE INFO

Article history:
Received 10 November 2010
Received in revised form 4 October 2011
Accepted 4 October 2011
Available online 12 October 2011

Keywords:
Electrolytic manganese residue (EMR)
Sulphoaluminate cement
Mechanical property
Energy-saving

ABSTRACT

Electrolytic manganese residue (EMR) is a harmful solid industrial waste that comes from the electrolytic manganese industry and has rarely been recycled in large quantities. To consume as much EMR as possible, quasi-sulfoaluminate cementitious material (Q-SAC) was prepared by firing high amounts of EMR together with limestone and kaolin at approximately 1200 °C (~50–100 °C lower than that of ordinary sulfoaluminate cement). The major crystalline phases of Q-SAC determined by XRD were calcium sulfoaluminate, dicalcium silicate and calcium sulfate. The final setting times of Q-SAC were less than half an hour. The early and long-term alkalinities of Q-SAC pastes were approximately 2 and 1 lower than those of OPC paste, respectively. The results also showed that Q-SAC prepared by mixing 10–40% of EMR can obtain compressive strength of 35–65 MPa at 56 days. When 5% of gypsum was added, the early and long-term strengths of Q-SAC were approximately 50% and 30% higher, respectively. The results showed that the use of EMR for Q-SAC production is a promising way to recycle EMR because of its low firing temperature and good mechanical performance.

1. Introduction

Sulphoaluminate cement (SAC) is a cementitious material with characteristics including low firing temperature [1], low CO_2 emission [2], low alkalinity, high early and long-term strengths, and slight expansion during hydration [3]. One type of research study concerning SAC is to use industrial solid wastes, especially sulfur-containing wastes such as chemical waste gypsum [4,5] and fluidized bed combustion wastes [6], to prepare SAC. By doing so, almost all of the main phases (mainly aluminosilicate and calcium sulfate) are fully utilized, which in the end turn into calcium silicates and calcium sulphoaluminate, the target mineral constituents of SAC. However, when using waste to make the ordinary SAC, due to the quality-instability of the waste, its amount should be small to avoid any great change to the raw materials [4,6,7]. Meanwhile, in order to adjust the proportions of the raw materials to fulfill the requirements of the ordinary SAC, many other raw materials must be used [4] accordingly. Thus, to recycle as much waste as possible, the strategy of making waste-involved SAC should be changed. In this work, a quasi-sulphoaluminate cement (Q-SAC), which was different from ordinary SAC in both mineral composition types and amount, was prepared by using 10–40% of a high sulfur-containing waste – electrolytic manganese residue (EMR). Although some properties of ordinary SAC, such as high early strength, were not obtained due to the alterations of the main mineral constituents in Q-SAC, its good long-term strength gain and, more importantly, high waste consuming capacity still make it suitable for EMR recycling.

EMR is discharged from the electrolytic manganese industry and it is a by-product of making electrolytic manganese powder, which is generally used as an additive for metal alloys to improve their wear and corrosion resistance. When making this powder, the commonly used manganese ore, manganese carbonate, is leached in sulfuric acid to obtain a solution containing Mn^{2+}. Then the solution is electrolyzed to produce electrolytic manganese powder. During this process, a great amount of impurities in the ore (nearly 80% by mass) turn into EMR. It is reported that in China (the major electrolytic manganese powder provider in the world, who supplied 95% electrolytic manganese powder of the world in 2007) about 10 million tons of EMR are discharged each year [8].

Currently, almost all EMRs are dumped into landfill sites and rarely used [9]. EMR is a hazardous waste as it contains Cr, Mn, NH_3–N and suspending substances, as shown in Table 1. The concentrations of some pollutants that percolate from EMR are significantly higher than the limits of Chinese standards. Disposal of EMR is an ongoing financial burden for electrolytic manganese powder manufacturers due to its long-term maintenance. Furthermore, finding new disposal sites is becoming increasingly difficult. Thus, techniques for the utilization of EMR are urgently needed.

Among all possible uses, the use of EMR to produce sulphoaluminate cementitious material shows great potential. When taking

* Corresponding author. Tel.: +86 23 65126109.
E-mail address: qianjueshi@126.com (J.-s. Qian).

0958-9465/$ - see front matter
doi:10.1016/j.cemconcomp.2011.10.003

Table 1
Concentration of pollutants from manganese industry.

Pollutants	Pollutant concentration [11]	Emission standard [12]
Sewage in pond site		
pH	4.88	6–9
Suspending substance (mg/L)	309	100
NH_3–N (mg/L)	402.5	15
COD-Cr (mg/L)	1900	100
Mn^{2+} (mg/L)	531	2
Manganese industrial wastewater		
Cr^{6+} (mg/L)	0.96	0.5
NH_3–N (mg/L)	52	15
Chromaticity (mg/L)	300	50

SiO_2, Al_2O_3 and CaO of Table 2 to make cementitious material with EMR, Fig. 1 schematically shows that if extra calcium is provided EMR will fall into the phase region of OPC. So it can be deduced that the preparation of the raw materials for making Q-SAC with EMR may be simple and less than that of OPC and ordinary SAC.

It is widely known that cement firing is an energy-intensive process. Therefore it is important to reduce the energy used during this process. Fortunately, making Q-SAC from EMR is less energy-intensive. This is not only due to the main mineral compositions of SAC, i.e., calcium sulfoaluminate and belite, are formed in a relative low temperature [10], but also because of the chemical composition characteristics of EMR. It is shown in Fig. 2 that the phase region of EMR is located in the lowest valley of the melting chart of SiO_2–Al_2O_3–CaO phase diagram, which makes it a suitable handling method of recycling EMR at high temperatures.

With the guideline of using as much waste as possible and obtaining a final product with acceptable properties, Q-SACs were prepared by adding different amount of EMR (10–45%). At the same time, the mineral and chemical compositions, alkalinity, setting time and compressive strength evolution characteristics were investigated.

2. Experimental protocols

2.1. Materials

The chemical and physical properties of common EMRs are shown in Table 2. It demonstrates that EMR is a kind of aluminosilicate material with a high content of sulfate. The fineness of EMR

Table 2
Chemical and physical properties of EMR.

Common EMRs		As-received EMR
Chemical (% by mass)		
SiO_2	25–40	26.51
Al_2O_3	8–20	8.37
SO_3	20–30	27.78
CaO	~10	12.13
Fe_2O_3	5–10	3.61
Mn^{2+} (eqv:MnO_2)	2–7	4.10
MgO	1–3	2.45
Physical		
Density (g/cm^3)	2–3	3.04
pH	4–6	4.88
Fineness[b] (cm^2/g)	~3000	3378
Water content (%)	20–30	18.6
LOI[a] (%)	~20	20.12

[a] LOI: Loss on ignition of EMR at 950 °C for 30 min.
[b] Fineness: Blaine fineness measured according to GB/T 8074-2008: Testing method for specific surface of cement-Blaine method.

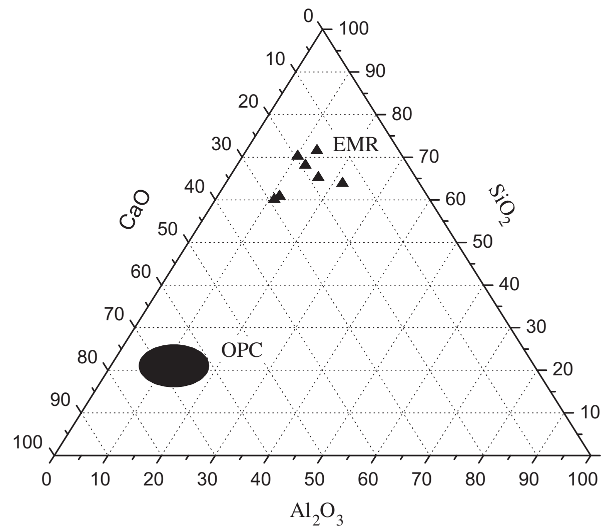

Fig. 1. The composition relationship between EMR and OPC.

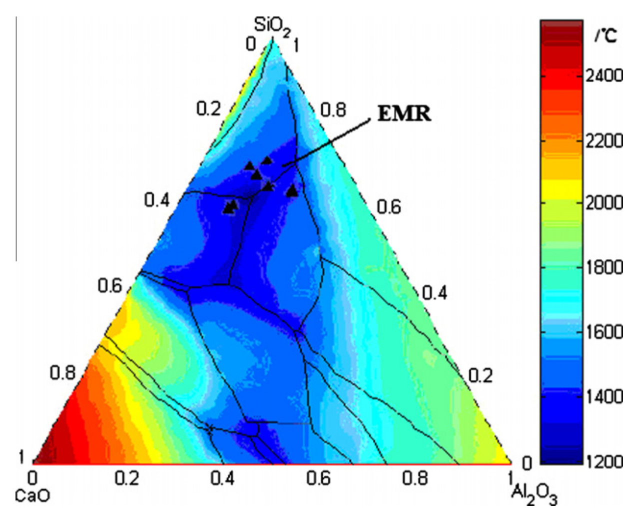

Fig. 2. The phase region of EMR in the melting graph of SiO_2–Al_2O_3–CaO system.

reaches as much as 3000 cm^2/g, which is a positive contributor for its firing. The as-received EMR was fresh and its properties are also listed in Table 2.

The mineral composition of EMR was determined by XRD and the result is presented in Fig. 3. It demonstrates that the main crystalline phases of EMR are finely crystallized dihydrate gypsum, quartz, mullite, hematite and pyrolusite. The diffusive background shows that there are some amorphous or semi-crystalline phases in it.

When preparing raw materials, limestone and kaolin were used as calcium and alumina providers, respectively, and their properties are presented in Table 3.

2.2. Mix proportion of raw materials

When producing OPC, Bogue equations are commonly used to establish relationships between the chemical compositions of raw materials and the mineral compositions of target clinker. When SAC is prepared, the modified-Bogue equations are used and three main moduli are carefully selected [3]: