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Production of quasi-sulphoaluminate cementitious materials with electrolytic manganese residue

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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

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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 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.

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.

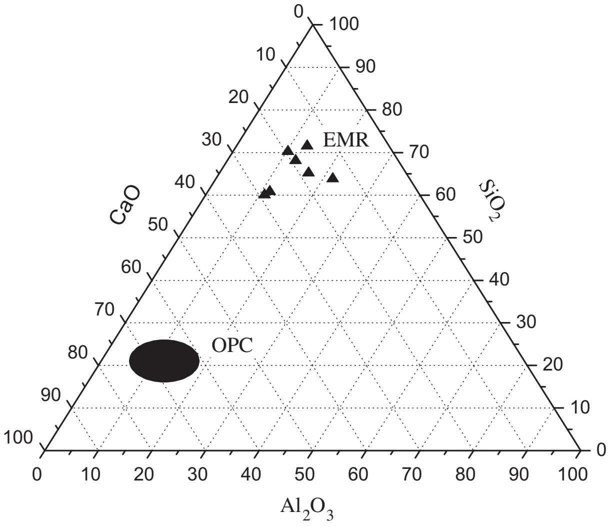


Fig. 1. The composition relationship between EMR and OPC.

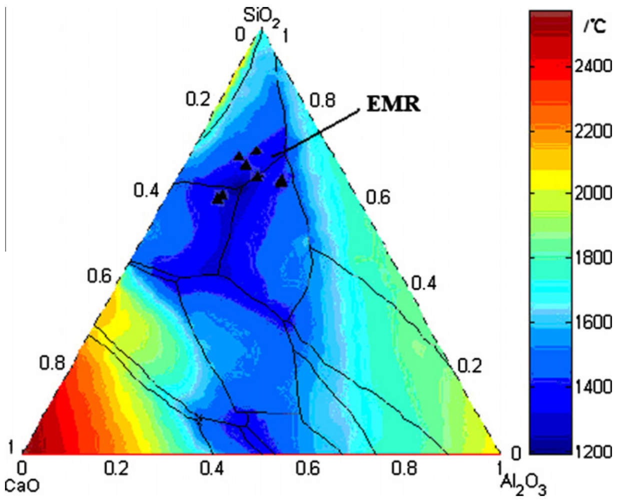


Fig. 2. The phase region of EMR in the melting graph of SiO_2–Al_2O_3–CaO system.

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]:

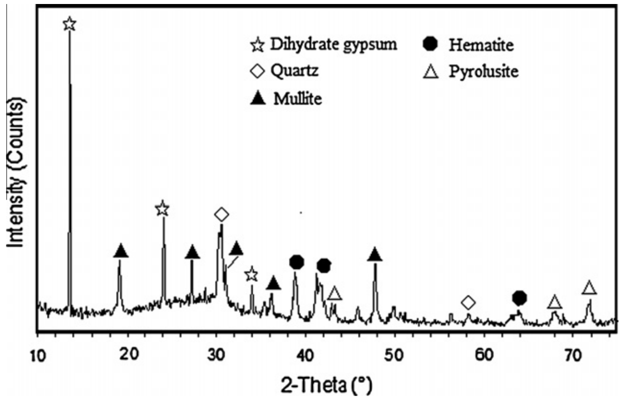


Fig. 3. XRD pattern of EMR.

(1) alkalinity modulus (Cm, Cm = 0.95–0.98), indicating the satisfactory degree of CaO that meets the demand of taking up all the acidic oxides of the raw materials;
(2) alumina–sulfur modulus (P, P < 3.82), indicating the satisfactory degree of Al_2O_3 that meets the need of gypsum, after reacting with ferrite, which eventually forms calcium sulphoaluminate ($3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$) and,
(3) aluminate to silicate ratio (N), indicating the proportion of calcium sulphoaluminate to that of calcium silicate.

In this study, the mix proportions of Q-SAC were chosen under the guidelines of ordinary SAC. Meanwhile, the composition of EMR and the strategy of utilizing EMR were fully considered. The final mix proportions were selected by means of trial mixing [3] and are listed in Table 4.

2.3. Mixing and firing

Before mixing, all the raw materials were dried at 105 °C and ground to pass a 100 mesh (150 μm) sieve. Then the batch constituents were mixed thoroughly by adding 10% of tap-water. The raw materials were hammered into biscuits of Φ50 mm × 8 mm and then subjected to different firing temperatures from room temperature to a peak between 1100 °C and 1270 °C in porcelain crucibles. The time duration at the temperature peak was 30 min. After firing, the clinkers were sharply cooled to room temperature and were ground to the fineness of about 3500 cm^2/g (Blaine).

2.4. Mineralogy

X-ray diffraction (XRD, D/MAX-IIIC, Japan) was used to determine the mineral phases of EMR and Q-SAC at room temperature. In all cases, samples were ground to less than 80 μm in size. The detector scanned over a range of 2θ angles from 20° to 70° at a step size of 0.02°. The operating voltage was 40 kV with 30 mA of current using a Co Kα radiation (λ = 1.5406 nm). All XRD data were identified by comparing the peak intensities and positions with those in the Joint Committee on Powder Diffraction Standards (JCPDS) data files.

Table 3
Chemical compositions of limestone and kaolin (by mass/%).

	Limestone	Kaolin
CaO	50.74	0.20
MgO	1.27	/
SiO_2	4.44	45.00
Al_2O_3	/	38.00
Fe_2O_3	/	0.20
LOI	42.54	16.40

Table 4
The proportions of raw materials (by mass%).

Mixture	Limestone	Kaolin	EMR	Cm	P	N
A	55	0	45	0.77	0.48	0.28
B	60	0	40	0.90	0.48	0.27
C	60	15	25	0.77	1.42	0.46
D	70	20	10	1.00	3.62	0.56

Note: Cm: alkalinity modulus; P: alumina–sulfur modulus; N: aluminate to silicate ratio.

2.5. pH value

Q-SAC pastes were prepared with a w/b of 0.3. When determining the alkalinity, the core of the paste was sampled to avoid the errors in measurement due to the carbonization of the pastes. Five grams of each sample were obtained and ground to a fineness of less than 150 μm. All the powder was mixed with 50 g of distilled water. After a constantly stirred leaching duration of 15 min, the solution was filtered and its alkalinity was determined by a pH meter (PHS-3C, with an accuracy of 0.01).

2.6. Compressive strength

Compressive strengths were measured on 20 mm × 20 mm × 20 mm cube samples. All paste samples had a w/b ratio of 0.3. After 1 day of mold-curing at room temperature of 21–23 °C, the samples were demolded. Then samples were cured in air at 21–23 °C. Compressive strengths were measured after 7, 14, 28 and 56 days of curing. Six samples were tested for each curing time, the average of which was taken to be the representative strength value.

3. Results and discussions

3.1. Chemical composition

The chemical compositions of clinker A were analyzed and compared with its theoretical values from Bogue equations. The result in Fig. 4 shows that the clinker composition agrees well with its theoretical value. There is a significant difference between the sulfur content: the measured sulfur content is just half of its theoretical value. The theoretical value of sulfur content was obtained by assuming that no sulfur composites in raw materials will decompose during firing and they will entirely turn into SAC clinker. However, due to the decomposing of sulfates in EMR, the final sulfur content is lower than its theoretical value.

3.2. Mineralogy determination

3.2.1. Mix proportions vs. phase compositions

Fig. 5 shows the XRD results of samples listed in Table 4. The samples were clinkered at a peak firing temperature of 1270 °C for 30 min.

It can be seen in Fig. 5 that the major mineral phases of the clinkers varies regularly and widely. Two obvious characteristics of the variation can be drawn:

(1) With the increase of kaolin, as well as the decrease of EMR (from A to D), the characteristic peaks of SAC, calcium sulphoaluminate, are strongly strengthened while the calcium sulfate peaks are gradually weakened and then disappear in sample D. From A to B (Cm goes from 0.77 to 0.90), the

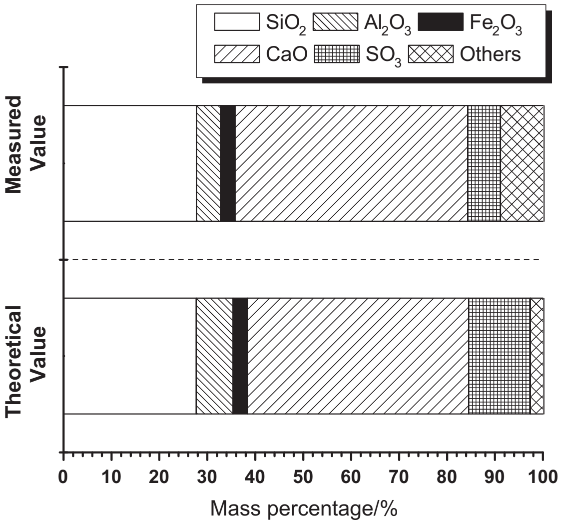


Fig. 4. The compositions of Q-SAC (measured value vs. theoretical value), 1200 °C, 30 min, Sample A.

peak intensity of calcium sulphoaluminate at $d = 0.37$ nm grows from 25 to 52 and the calcium sulfate peak intensity at $d = 0.348$ nm decreases from 300 to 170. All this indicates that the induction of alumina source and an ideal alkalinity factor are two important factors in controlling the formation of the characteristic phases of SAC.

(2) From sample B to D, XRD patterns show that there is slight difference between the dicalcium silicate phase peaks, which demonstrates that the solid reaction occurred predominantly during their sintering processes. The existence of a tricalcium silicate phase in samples A and D shows that liquid reactions happened during their sintering processes. This may due to two different reasons. For sample A, a high content of EMR means a high content of calcium sulfate, which acts as a fluxing agent at a high sintering temperature, and it contributes to the formation liquid phase where tricalcium silicate phase is formed. For sample D, a high alkalinity factor benefits the formation of tricalcium silicate phase, which is also indicated by its free lime peaks.

The comparison of mineral compositions of ordinary SAC and Q-SAC in Fig. 5 clearly shows the difference of mineral phase types of Q-SAC to those of ordinary SAC.

3.2.2. Sintering temperature vs. phase composition

To investigate the effects of sintering temperature on the phase compositions of Q-SACs, proportions A and C were fired at different peak temperatures. All the samples were clinkered for 30 min and the XRD results were demonstrated in Fig. 6.

It is shown in Fig. 6 that for sample A the characteristic mineral phase of SAC, calcium sulphoaluminate, does not exist but the peaks of dicalcium silicate (C_2S) is significantly strong. When the sintering temperature went up to 1270 °C, C_2S turned to tricalcium silicate by absorbing free lime. The results show that the transition of C_2S to C_3S can be achieved at a lower temperature than that of

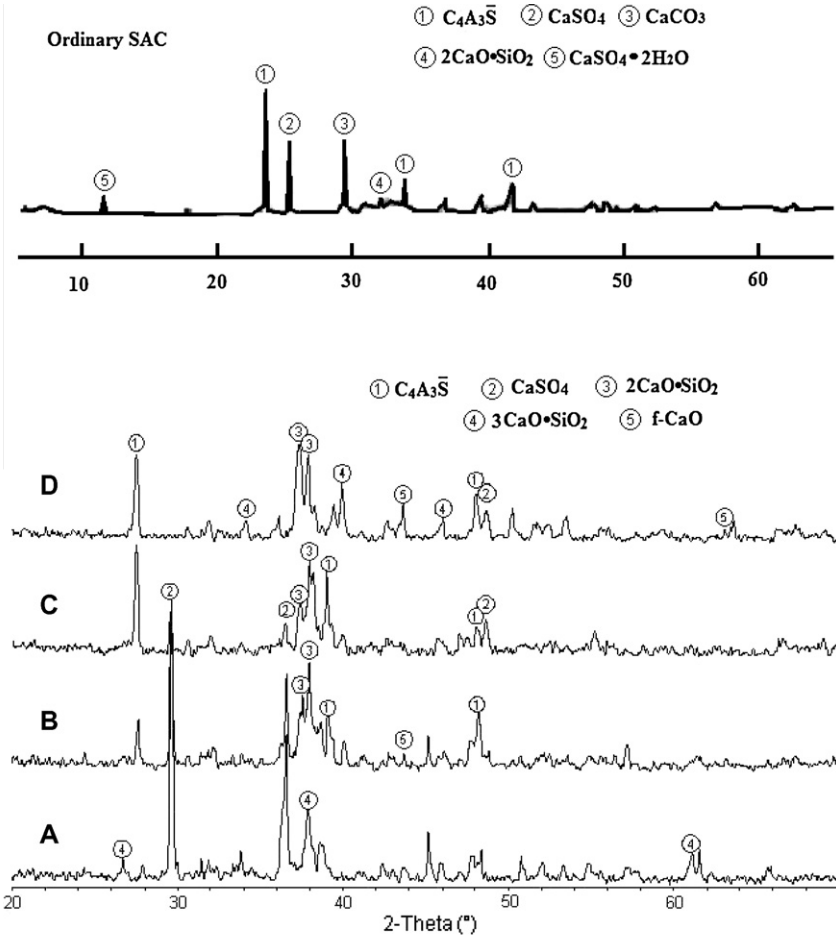


Fig. 5. XRD patterns of ordinary SAC [13] and Q-SAC clinkers.

OPC (as much as 1400–1450 °C). Fig. 6 also demonstrates that the transient phase of gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) disappeared when the sintering temperature was higher than 1200 °C.

When alumina source (kaolin) was provided, the calcium sulphoaluminate phase intensity increased when the sintering temperature became higher. Meanwhile, the calcium sulfate peak intensity gradually weakened. In the same way, it shows that another transient phase, sulphospurite ($4CaO{\cdot}2SiO_2{\cdot}CaSO_4$), disappeared at 1200 °C, which is as much as 50–100 °C lower than the case of firing ordinary SAC [3]. The comparison of the peak intensities of C_2S indicate that its transient was less sensitive and stayed constant during these temperature domains.

Compared to SAC, the final clinker composition and the transient phase transition characteristics of Q-SAC by firing EMR were different. All the XRD results imply that making Q-SAC with EMR is an energy-saving process.

3.3. pH value

As stated above, SAC is a kind of low alkalinity cementitious material. The low alkalinity of pore solution can be beneficial in certain situations [14]. The pH value of clinker pastes of OPC and Q-SACs were examined. All the Q-SAC samples were sintered at 1270 °C for 30 min.

It is demonstrated in Fig. 7 that the early age pH value of OPC was as high as 12.5 and grew steadily at later ages. The pH value of OPC stabilized at approx. 13 after about 7 days (168 h) of hydration. However, pH values of Q-SAC developed in a different way. Their final alkalinities were approx. 1 less than that of OPC. The early age pH of sample B was as low as 10, and grew sharply to 11 in 24 h. Its later age pH growth was slow, reaching 12 (288 h) after 28 days (672 h). A relatively high pH value of sample D may be due to its high calcium content. In addition, the existence of free lime would be another reason for its pH development characteristic.

3.4. Setting time

The setting times of the Q-SAC samples are listed in Table 5. All the Q-SAC samples were sintered at 1270 °C for 30 min. It is shown that the setting time of Q-SACs is short, which is shorter than the initial setting time threshold of 25 min by Chinese standard. All final setting times are within half an hour. This may due to the high content of quick-hardening constituents, i.e., calcium sulphoaluminate, free lime and calcium sulfate. By adding some organic retarding agents, the setting time can be controlled, which will make it possible for practical use [15].

3.5. Mechanical property

3.5.1. Strength development of Q-SAC clinker

The strength development of the four samples clinkered at different temperatures were studied and the results are shown in Fig. 8. During these measurements, no calcium sulfate was incorporated. The selected clinkering peak temperatures were determined by the XRD results and the sintering time was 30 min.

It is shown in Fig. 8 that the strength development of the Q-SAC samples were closely connected to the proportions and sintering temperatures of the raw materials. XRD results show that the main mineral phase of samples A and B is C_2S. This is also demonstrated by their strength development histories: a relatively low early strength and a constant strength gain in later ages. The early strengths of samples C and D developed quickly, which may be due to the existence of their quick-hardening constituents (see in Figs. 5 and 6) illustrated by the modulus of P and N listed in Table 4. It is shown that, for sample B, clinker sintered at 1200 °C demonstrated the highest strength, which could be as high as 67 MPa at 56 days. The result implies that a proper mix proportion and a reasonable clinkering temperature are the most important factors of obtaining a good strength development of Q-SAC.

By comparing the strength development history of ordinary SAC [3], the early strength development of Q-SAC is slow, which is also due to the difference in mineral compositions.

3.5.2. Strength development of Q-SAC with $CaSO_4$

During the hydration process of SAC, calcium sulfate plays an important role [16]. Its effects were shown in the following equations:

$$3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + CaSO_4 \cdot 2H_2O + Ca(OH)_2 + 22H_2O \rightarrow 2(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O) + Al_2O_3 \cdot 3H_2O \tag{1}$$

$$3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + 2(CaSO_4 \cdot 2H_2O) + 34H_2O \rightarrow 2(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O) + 2(Al_2O3 \cdot 3H_2O) \tag{2}$$

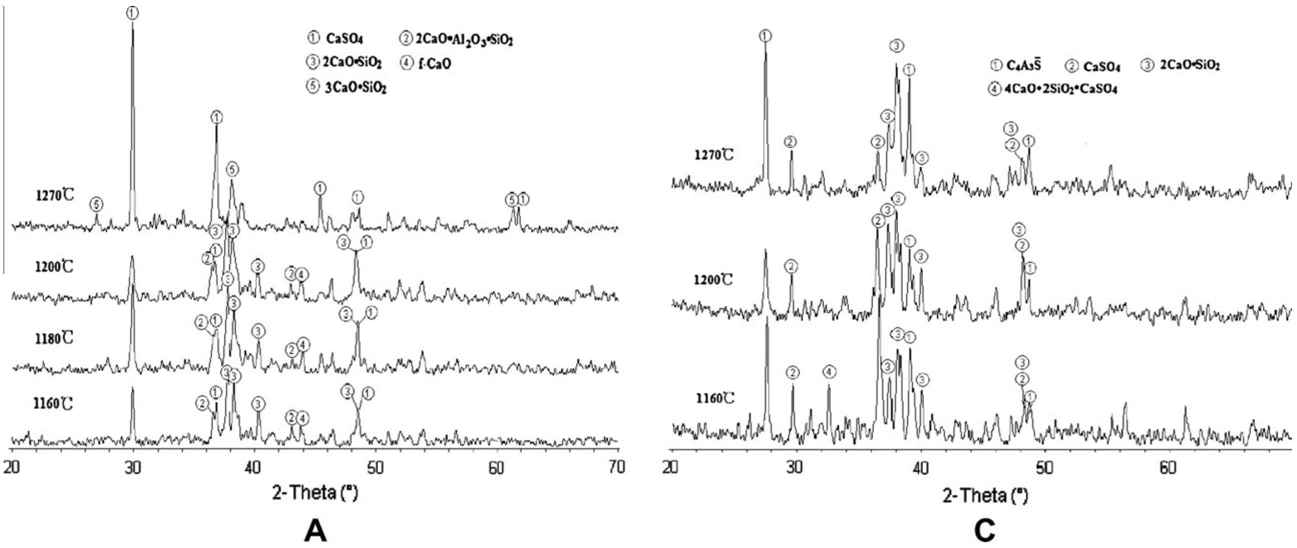


Fig. 6. Effect of firing temperature on mineral compositions of A and C.

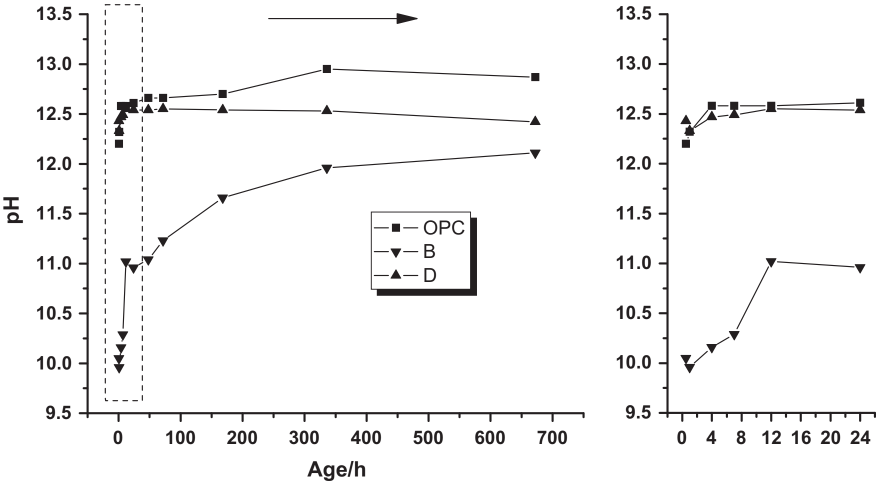


Fig. 7. pH value of Q-SAC pastes.

Table 5
Setting time of clinker.

Mixture	Initial setting time (min)	Final setting time (min)
A	16	26
B	19	26
D	16	23

Based on the XRD results in Figs. 5 and 6, 5% and 10% of gypsum were provided during the hydration process of samples C and D, which were sintered for 30 min at 1200 °C and 1250 °C respectively. As shown in Fig. 5, the anhydrate gypsum peak is strong in clinker A and B, so no extra gypsum was added in these two clinkers.

It is shown in Fig. 9 that the incorporation of gypsum greatly enhances the early and long-term strength of each sample. Proper gypsum incorporation can increase the early strength by more than 50%. All the long-term strength data show that 5% of gypsum is most favorable for the strength development. The long-term strength development is accounted for the hydration of C_2S.

4. Conclusions

Electrolytic manganese residue (EMR), a high sulfur-containing solid waste discharged from the electrolytic manganese industry, is suitable for producing quasi-sulphoaluminate cementitious mate-

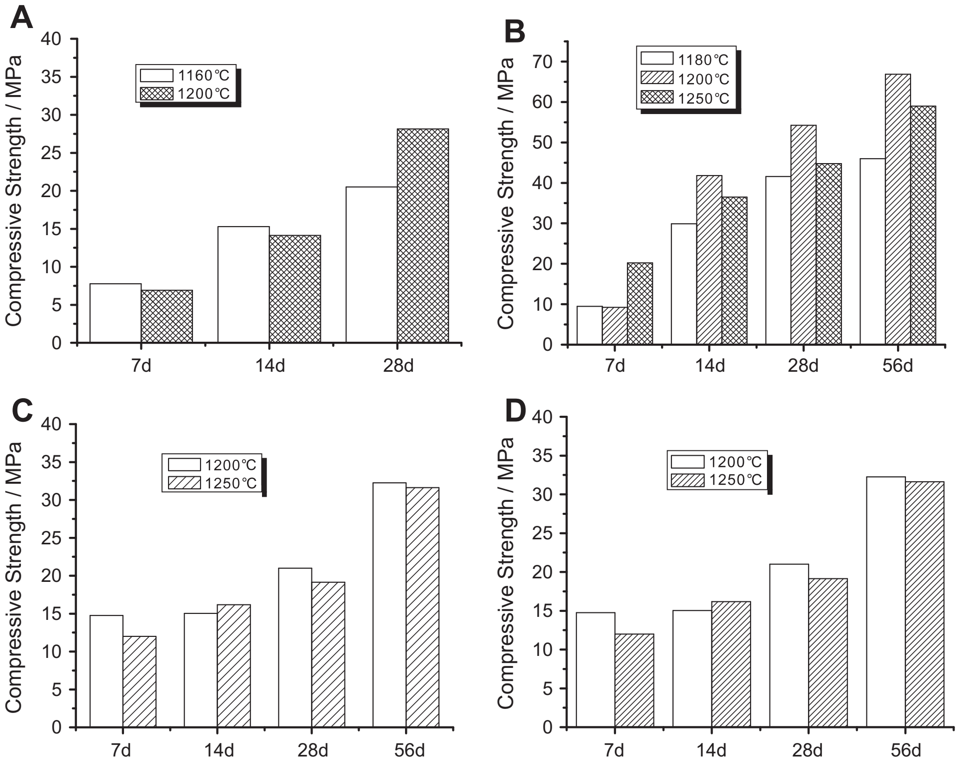
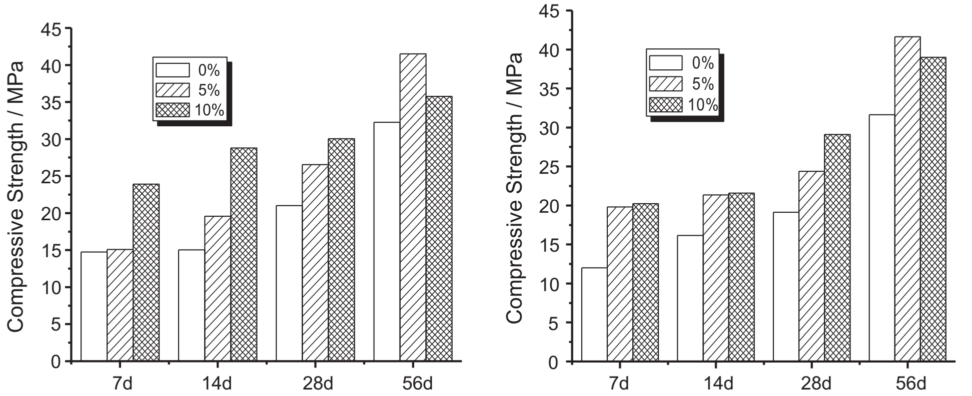
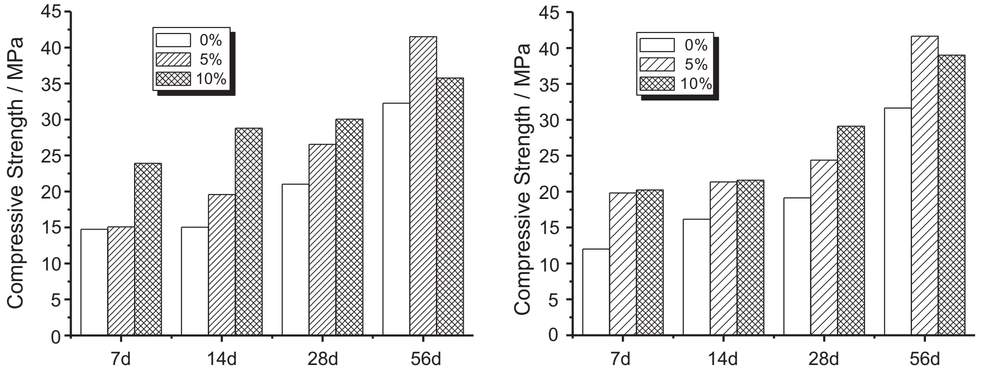


Fig. 8. Mechanical properties of Q-SAC for different clinkering temperatures.



C, clinkered at 1200°C

C, clinkered at 1250°C



D, clinkered at 1200°C

D, clinkered at 1250°C

Fig. 9. Strength development of Q-SAC with gypsum.

rial. Not only will great amounts of EMR be used but the clinker performance will also be acceptable. Meanwhile, the chemical compositions of the waste facilitate the preparation of the raw materials. Results show that:

(1) The major crystalline phases of Q-SAC are calcium sulphoaluminate, dicalcium silicate and anhydrate. The introduction of alumina source and the selection of a proper alkalinity factor are important for the formation of calcium sulphoaluminate and transition of transient phases into clinkers. The Q-SAC manufacturing process happens at 50–100 °C lower than that of ordinary sulphoaluminate cement, which makes it energy-saving.

(2) The final setting of Q-SAC is within half an hour, yet it is possible to use Q-SAC in actual construction projects when retarding agents are used. The pH value of Q-SAC is 2 and 1 lower in the early and long-term, respectively, than those of OPC. Q-SAC prepared by mixing 10–40% of EMR can obtain compressive strength of about 35–65 MPa at 56 days. Through incorporation of 5% gypsum the early and long-term strengths increased by 50% and 30%, respectively.

Acknowledgments

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