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Preparation of the saving-energy sulphoaluminate cement using MSWI fly ash

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ABSTRACT

MSWI fly ash was used as a major cement raw material in sintering sulphoaluminate cement clinker successfully in the laboratory. Sintering system, mechanical performance, hydration process and microstructure of the clinker was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence spectrometry (XRF), etc. The result shows that the clinker can be sintered properly under the temperature of 1200–1300 °C and sintered time of 120 min. Cl^- content in the clinker made with MSWI fly ash is about 1.08%. However most Cl^- cannot leach out in water solution from the hardened cement paste during curing age between 1 d and 28 d because of the Cl^- being combined in clinker minerals and its hydrates. The compressive strength of the sulphoaluminate cement was high in early age while that developed smoothly in later age.

1. Introduction

In China, it is estimated that 200 million tons of municipal solid waste (MSW) is generated annually, accounting for 29% of the total world MSW production. The strategy for disposing of MSW becomes increasingly important. Since municipal solid waste incineration (MSWI) has unique advantage in reduction and resource utilization in comparison with landfill disposal and compost, it has become a most popular MSW treatment in China now. However, the amount of MSWI fly ash increases greatly with more MSW and MSWI factories, which leads to serious environmental problems.

Various methods have been used to treat MSWI fly ash such as melting, solidification/stabilization (S/S), acid extraction, vitrification and sintering. Recently the researches of fly ash are focused on its resource utilization, especially in preparation of cement-based material. There are three major application of MSWI fly ash in cement-based material: raw material in production of cement clinker [1–3], cement or concrete admixture [4,5] and concrete aggregate [6–8]. Among them, the first application is regarded as the most effective way to eliminate the toxicity of MSWI fly ash since the high temperature (above 1450 °C) in the kiln can capture most of heavy metals in Portland cement clinker.

In this study, the feasibility of reusing the MSWI fly ash as raw materials in saving-energy sulphoaluminate cement clinker was evaluated. The sintering temperature in the kiln could be controlled under the temperature of 1200–1300 °C which is 200 °C lower than that of Portland cement clinker. The cement quality was investigated to evaluate the reuse feasibility of MSWI fly ash in cement production.

2. Raw materials and methods

2.1. Experimental materials and preparation

The MSWI fly ash was originated from Suzhou Wastes Incineration Plant in China. The chemical compositions of MSWI fly ash and commercial sulphoaluminate cement with the fitness of 400 m^2/kg (Blaine) as parallel are given in Tables 1 and 2 separately. Pure analytical reagents $CaCO_3$, $CaSO_4$, $CaSO_4{\cdot}2H_2O$ and Al_2O_3 are used as raw materials. All the materials were ground and sieved through a 200-mesh sieve.

2.2. Experimental methods

Cement raw materials were blended in proportions following the Cement Modulus commonly used by cement industry [9,10]: alkalinity coefficient (Cm) = 1.05, alumina–sulfur ratio (P) = 2.5 and alumina–silica ratio (N) = 5. The replacement of MSWI fly ash was 30% as raw material.

Each material was weighed accurately in proportion and mixed. The samples were pressed and moulded into cylindrical samples of 30 mm in diameter × 5 mm in height for sintering. Then these dried cylinders were calcined in a Nabertherm furnace. The temperature was raised to different temperatures at the rate of 30 °C/min. After the sintering, the sample was removed from the furnace and cooled to room temperature rapidly.

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Table 1
Chemical composition of MSWI fly ash (wt.% by weight).

Composition	CaO	SiO_2	Cl^-	SO_3	Al_2O_3	K_2O	Na_2O	Fe_2O_3
Content	39.1	15.9	11.9	7.24	4.35	3.68	3.43	1.91
Composition	MgO	P_2O_5	TiO_2	ZnO	PbO	BaO	CuO	MnO
Content	1.64	1.08	0.61	0.54	0.23	0.14	0.13	0.10
Composition	SrO	NiO	ZrO_2	–	–	–	–	–
Content	0.04	0.02	0.01	–	–	–	–	–

Table 2
Chemical composition of commercial sulphoaluminate cement (wt.% by weight).

CaO	20.0
SiO_2	15.4
Al_2O_3	20.71
SO_3	31.80
MgO	0.81
Fe_2O_3	2.95
Loss	1.07

The phase of the clinker and the hydrates was determined by XRD. Chemical composition of clinker was determined by XRF. The morphology of the clinker was performed by SEM.

The selected clinker with $CaSO_4{\cdot}2H_2O$ or $CaCO_3$ as cement admixture was ground to making sulphoaluminate cement. The samples of the cement were mixed with water with the W/C ratio of 0.3, and the paste was put into the 1 cm × 1 cm × 1 cm cube moulds with vibration. These paste specimens were demoulded after being cured in moist air at 20 °C for 1 d; then the specimens were cured in water to 1 d, 3 d, 7 d and 28 d for the measurement of the compressive strength. The setting times of the cement samples were determined according to Chinese National Standard GB/T 1346-2001 (test methods for water requirement of normal consistency, setting time and soundness of the Portland cement).

The test method of leaching Cl^- was prepared in accordance with Chinese Ministry of Transport Standard JTJ 270-98 (testing code of concrete for port and waterwog engineering). The method might be summarized as follow: 30 g sample of cement harden paste is ground and sieved through a 24-mesh sieve, then It is placed to the oven in (105 ± 5) °C for 2 h. After that it is removed the loft drier and cooled to the room temperature. 20 g sample is measured accurately (0.01 g) and put into the conical flask with 200 ml distilled water. Then the conical flask should be corked tightly and shaken greatly for several minutes. After soaking for 24 h, the concentration of free Cl^- could be measured by the volumetric solution of $AgNO_3$.

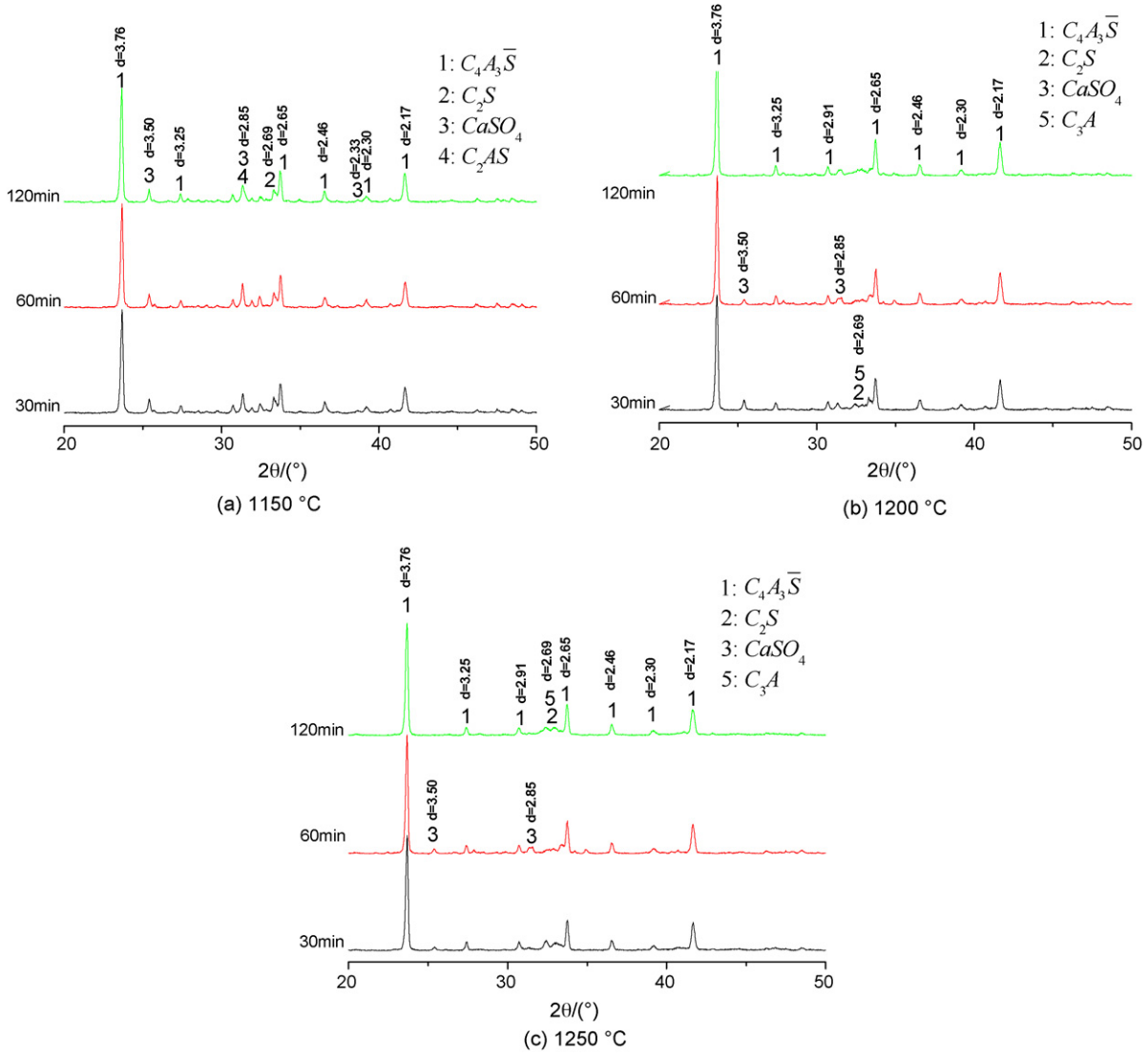

Fig. 1. XRD patterns of clinker SA in different temperatures and different soaking times.

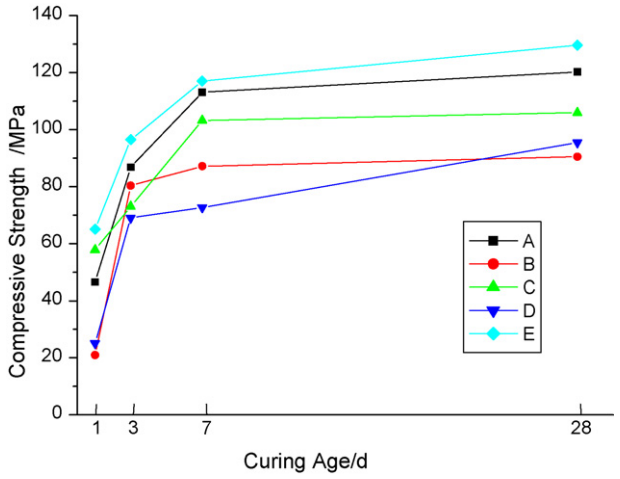

Fig. 2. Compressive strength of samples in different curing ages at 1200 and 1300. (A) 95% clinker in 1200 °C with 5% $CaSO_4{\cdot}2H_2O$; (B): 95% clinker in 1300 °C with 5% $CaSO_4{\cdot}2H_2O$; (C) 75% clinker in 1200 °C with 5% $CaSO_4{\cdot}2H_2O$ and 20% limestone; (D) 75% clinker in 1300 °C with 5% $CaSO_4{\cdot}2H_2O$ and 20% limestone; (E) commercial sulphoaluminate cement.

3. Results and discussions

3.1. The XRD analysis of the clinker

The sintering temperatures were selected at 1150 °C, 1200 °C and 1250 °C, while the soaking time was selected to be 30 min, 60 min and 120 min. The XRD patterns of clinker SA in different temperatures and different soaking times were shown as Fig. 1.

Fig. 1(a) showed that $C_4A_3\bar{S}$ was the major phase with C_2S, unreacted $CaSO_4$ and C_2AS as minor phases in clinker under 1150 °C. The existence of C_2AS revealed that the temperature of 1150 °C was lower since C_2AS was one of transient phases. C_2AS disappeared when the temperature increasing to 1200 °C (Fig. 1(b)) and 1250 °C (Fig. 1(c)). And the unreacted $CaSO_4$ was involved in the reaction with the prolonged soaking time in 1200 °C and 1250 °C so that it disappeared in 120 min.

From the above experiments, it was shown that the sulphoaluminate clinker could be synthesized between 1200 °C and 1250 °C. The test results showed that the soaking time has little effect on the major phase while the longer soaking time could eliminate unreacted $CaSO_4$. Thus 120 min was selected as the proper soaking time.

Table 3
Setting times of cement samples.

Type of samples	Setting time(h:min)	
	Initial	Final
A	0:45	1:25
B	0:55	1:35
C	0:30	1:05
D	0:50	1:25
E	0:35	1:05

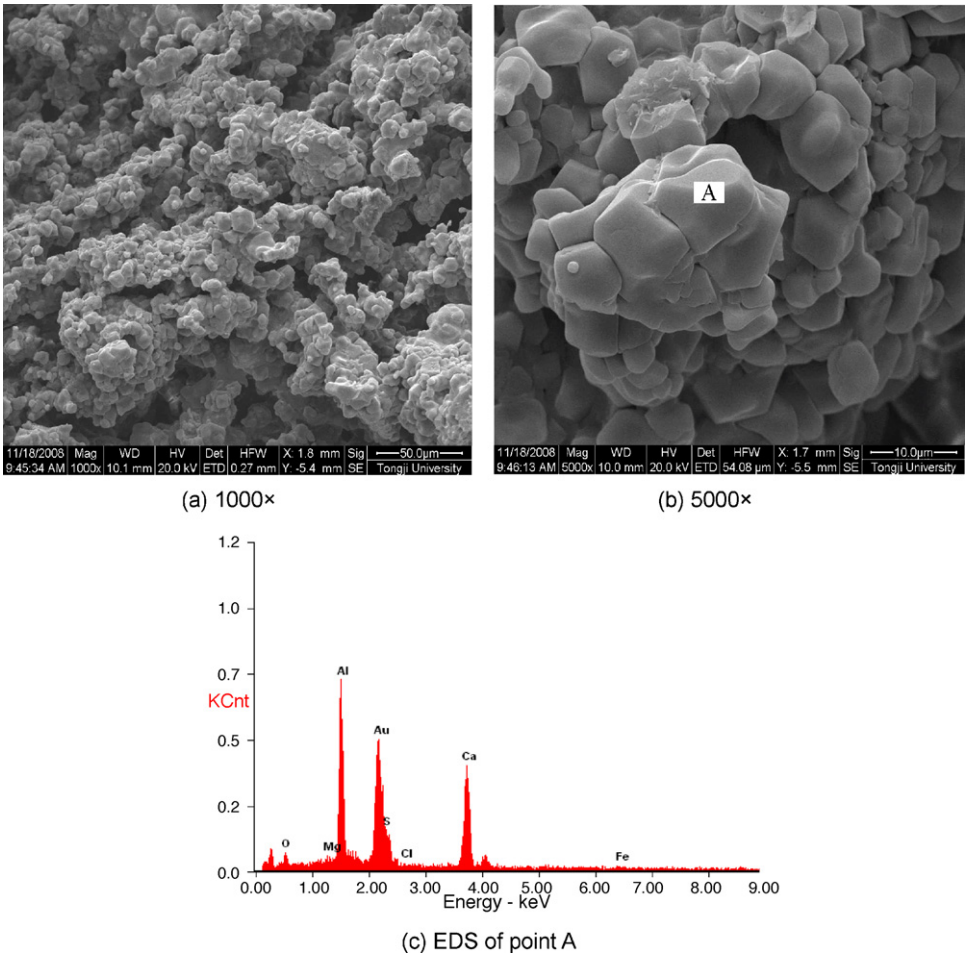

Fig. 3. SEM photos and EDS pattern of clinker SA.

Table 4
Atomic proportion of point A in Fig.3(b) (at./%).

Element	Ca	Al	S	Mg	Fe	Total
EDS value of point A	36.33	50.14	10.22	1.29	2.02	100.00
Theoretic value	36.36	54.54	9.09	–	–	99.99

3.2. The compressive strength of the clinker in different sintered temperatures

Two kinds of clinker were sintered at 1200 °C and 1300 °C with soaking time of 120 min so as to select a more proper temperature between 1200 °C and 1300 °C. Two kinds of sulphoaluminate cement were prepared by grinding the clinkers with 5% $CaSO_4{\cdot}2H_2O$, 5% $CaSO_4{\cdot}2H_2O$ and 20% limestone separately to a fineness of 400 m^2/kg (Blaine). The compressive strength of cements in different curing ages was tested. The results were illustrated in Fig. 2.

As displayed in Fig. 2, sample E has the highest compressive strength in all curing ages. The 1 d compressive strength development of all samples increased in the following sequence E > C > A > D > B. The sequence corresponds to that of limestone powder with filling effect in samples B and D, leading to appearance of higher early strength. However, the compressive strength of samples B and D developed very slowly between 3 d and 28 d. Thus compressive strength development of all samples increased in the following sequence E > A > C > B > D. The results indicated that all samples had good early strength in early stages but increasing slowly at later ages, which was one of characteristics for sulphoaluminate cement [9]. The compressive strengths of the cements combined with clinker sintered in 1200 °C were greater than that in 1300 °C almost in all ages. Considering the composite of phase, energy consumption and mechanical performance, the best sintering temperature was 1200 °C and the soaking time was 120 min in this temperature. The clinker mentioned in following experiments was sintered in that system.

3.3. The setting times of cement samples

The setting times of cement samples A and E were given in Table 3. It can be seen that the initial setting times of samples are not more than 60 min while the final setting times are within 100 min. All the samples has short setting times compared with Portland cement, which is a significant characteristic of sulphoaluminate cement. However, the observed delayed in the setting times of samples B and D may be primarily attributed to the content of low-activity limestone.

Table 5
Chemical composition of clinker SA (wt.% by weight).

CaO	43.40
SiO_2	9.08
Al_2O_3	28.80
Cl^-	1.08
SO_3	12.80
MgO	2.12
Na_2O	0.64
K_2O	0.49
Fe_2O_3	1.02
TiO_2	0.24

3.4. The SEM analysis of the clinker

The SEM photos of the clinker SA sintered at 1200 °C were shown in Fig. 3. The clinker appeared as irregular and high porous so that the clinker may have better grindability. Since $C_4A_3\bar{S}$ was the major phase in clinker SA, $C_4A_3\bar{S}$ could be observed identified by Energy Disperse Spectroscopy (EDS) in Fig. 3(c).

From Fig. 3(c) and Table 4, it was seen that the real value of composition of $C_4A_3\bar{S}$ was very close to the theoretic value. Mg was found most possibly as taking place of Ca while Fe was substituted with Al in phase of $C_4A_3\bar{S}$.

3.5. The XRD analysis of hydrated sample A

Fig. 4 showed the XRD patterns of hydrated sample A in 1 d and 28 d. From Fig. 4, it was seen that AFt ($C_3A{\cdot}3CaSO_4{\cdot}32H_2O$) was the main hydration product of sulphoaluminate cement in two different ages. The diffraction peaks of $C_4A_3\bar{S}$ also appeared in all ages for it was surrounded by hydration product of $Al(OH)_3$ gel or C–S–H gel which could not be shown in XRD. The main peak (d = 3.76) values of $C_4A_3\bar{S}$ in 28 d is much lower than that in 1 d implying most $C_4A_3\bar{S}$ reacted during 28 d.

3.6. Leaching tests of Cl^- in sulphoaluminate cement paste

Chemical composition of clinker SA was analyzed by XRF. The results were given in Table 5. Cl^- content in clinker SA was over 1% by weight, which was likely to lead to the corrosion of steel bar in concrete. However, Cl^- in concrete mainly exists in three different

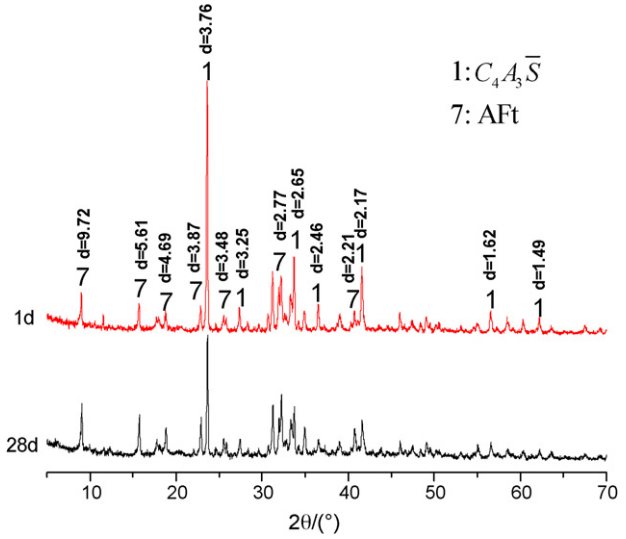

Fig. 4. XRD patterns of hydrated sample A in 1 d and 28 d.

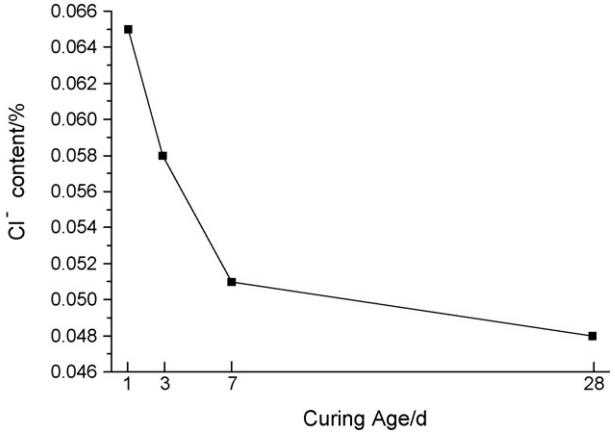

Fig. 5. Cl^- content of sample A in different curing ages.

conditions: chemically bounded with the clinker mineral; physically bound on the surface of the gel pores; free in the pore solution. It is only the concentration of free chlorides that is responsible for corrosion.

The free Cl^- content of sample A was determined in different curing ages shown in Fig. 5. The free Cl^- content of cement paste was in the range of 0.048–0.065% in different curing ages, which implied that most Cl^- in cement existing in condition of bounded with clinker minerals or hydration products. With curing age prolonging, the free Cl^- content decreased gradually for part of free Cl^- was bounded in the new hydrates.

4. Conclusions

MSWI fly ash was used as a major cement raw material in sintering sulphoaluminate cement clinker successfully in the laboratory at under the temperature of 1200–1300 °C and sintered time of 30–120 min.

Considering the composite of phase, energy consumption and mechanical performance, the best sintering system was 1200 °C with the soaking time was 120 min.

The sulphoaluminate cement has good compressive strength property. The hydration products of sulphoaluminate cement mainly include Ettringite, $Al(OH)_3$ gel and C–S–H gel. Most Cl^- in cement exists in condition of bounded with clinker minerals and its hydrates.

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