Pergamon

Cement and Concrete Research 31 (2001) 1257–1261

CEMENT AND CONCRETE RESEARCH

Microwave sintering of sulphoaluminate cement with utility wastes

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Received 23 June 1999; accepted 19 June 2001

Abstract

Class C flyash, baghouse dust and scrubber sludge have been successfully used for sulphoaluminate belite (SAB) cement preparation by microwave sintering. For proper raw mix proportioning, the modulus of gehlenite (C_2AS)[1] formation (MG) and modulus of calcium sulphosilicate ($2C_2S{\cdot}C\bar{S}$) formation (MS) were put forward. The results indicated that, when MG and MS were 0.90–1.10, C_2AS and $2C_2S{\cdot}C\bar{S}$ could be chemically eliminated when microwave-sintered at low temperature; with the 1150°C/10 min sintering condition, microwave-prepared sample had developed into SAB cement clinker with the main phases of C_4A_3S and β-C_2S, while a conventionally fired one had not; with proper gypsum addition, microwave-prepared SAB cement developed strength similar to Type-I cement in 28-day hydration.

Keywords: Microwave sintering; Sulphoaluminate belite cement; Industrial by-products; X-ray diffraction; Hydration

1. Introduction

Sulphoaluminate belite (SAB) cement has drawn much attention due to its lower energy consumption and environmental benefits. Generally, limestone, bauxite, industrial by-products phosphogypsum and/or flyash are used for its manufacture [1–5]. Phase compatibility within the SAB system has also been investigated with regards to the use of industrial wastes [6,7] in its manufacture.

Furthermore, in place of the above-mentioned raw materials, utilization of class F flyash, baghouse dust and scrubber sludge have been successfully used for the conventional preparation of SAB cement [8].

On the other hand, since Quéméneuer et al. first reported the feasibility of microwave clinkering [9], microwave process has shown its advantages in cement preparation as being a highly effective sintering method and resulting in more active reactants. Some cementitous and related materials have been prepared successfully [10–12] by microwave heating, indicating that chemical components in portland cement clinker can absorb microwave energy well and thus be sintered effectively in microwave field. Though having a different mineral composition compared with portland cement, SAB cement clinker contains the same basic oxides as portland cement does. This implies that SAB cement may also be sintered well in microwave field. As a part of a study series on microwave process of materials, we have conducted microwave sintering of SAB cement clinker manufactured from by-product materials.

2. Materials and experiments

2.1. Raw materials and proportioning

Class C flyash, baghouse dust and scrubber sludge were used as starting materials for microwave clinkering of SAB cement. Table 1 shows their chemical compositions. Tables 2 and 3 show the experimented proportioning and their chemical compositions.

2.2. Sample preparation

The by-products (passed sieve No. 200, opening 74 μm) in desired proportions were mixed by hand in a ceramic mortar for about 10 min, the mixture then mixed with water in W/C ≈ 0.5 for another 20 min by hand in a plastic beaker.

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[1] Conventional cement notation is used here, i.e. C = CaO, S = SiO_2, etc.

0008-8846/01/$ – see front matter
PII: S0008-8846(01)00579-8

Table 1
Chemical compositions of industrial wastes (%)

Type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Class C flyash	39.5	16.9	6.4	24.8	6.3	1.99
Baghouse dust[a]	11.12	6.26	4.89	69.82	0.85	6.22
Scrubber sludge[b]	2.18	0.17	0.21	73.56	2.16	21.35

[a] Center lime.
[b] Allegheny power.

The paste was transferred to a petri dish and dried at about 100°C until totally dry. The sample pie was cut into desired dimensions when it was in plastic state during drying.

2.3. Microwave sintering setup

Microwave sintering packet setup was as reported elsewhere [12]. A multimode microwave oven with maximum output of 1100 W in 2.45 GHz was used as microwave sintering equipment. The average heating rate was controlled at about 60°C/min. The holding time for all sintering experiments was 10 min. Special cautions were taken to minimize microwave energy discharge [13] during sintering.

2.4. Sample testing

Phase composition was determined by powder X-ray diffraction (Scintag PAD R). Mechanical properties were determined using β-point bend tests on small ($\approx 0.6 \times 0.6 \times 2.5$ cm) bars.

3. Results and discussion

3.1. Proportioning control

We had experience that gehlenite (C_2AS) and calcium sulphosilicate ($2C_2S{\cdot}C\bar{S}$) were likely to be present in microwave-prepared SAB cement sintered at low temperature if the raw mix proportioning was not controlled well. The existence of C_2AS reduces $C_4A_3\bar{S}$ content and $2C_2S{\cdot}C\bar{S}$ reduces β-C_2S amount in SAB cement, and both degrade the cement hydraulic property. In our research, two moduli had been successfully put forward to monitor the raw mix chemical compositions. Selection of these moduli were based on previous studies [7,8].

Table 2
Sample proportioning (%)

	Comp-1	Comp-2	Comp-3	Comp-4
Flyash	45.0	46.25	47.50	48.75
Baghouse dust	45.0	46.25	47.50	48.75
Sludge	10.0	7.50	5.0	2.50

Table 3
Chemical composition of sample (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Comp-1	23.04	10.45	5.10	49.94	3.44	5.84
Comp-2	23.57	10.73	5.24	49.82	3.46	5.40
Comp-3	24.19	11.01	5.37	48.62	3.50	4.97
Comp-4	24.74	11.30	5.51	47.97	3.53	4.53

3.1.1. Modulus of C_2AS formation (MG)

$$MG = [CaO + 1.40MgO - 0.70Fe_2O_3 - 0.732Al_2O_3 - 0.70(SO_3 - 0.40Al_2O_3)] / (1.87SiO_2) \quad (1)$$

where: 1.40 — 1 wt.% MgO contributes to CaO%; 0.704 — CaO wt.% absorbed by 1% Fe_2O_3 to form C_2F; 0.732 — CaO wt.% absorbed by 1% Al_2O_3 to form $C_4A_3\bar{S}$; $0.70(SO_3 - 0.40Al_2O_3)$ — CaO wt.% absorbed by extra SO_3 to form $CaSO_4$ after $C_4A_3\bar{S}$ formation; 1.87 — CaO wt.% absorbed by 1% SiO_2 to form C_2S.

C_2AS is a transitional mineral, which will be decomposed to form β-C_2S when sintering temperature increases beyond 1100°C. However, if CaO concentration is not sufficient to convert all SiO_2 into C_2S, C_2AS may still be formed and exist in final clinker. Thus, MG is a parameter indicating the SiO_2 saturation degree in respect to CaO to form C_2S (Eq. (1)). Theoretically, $MG < 1.00$, it means that the CaO present is not sufficient, and C_2AS is liable to form and exist in clinker.

3.1.2. Modulus of $2C_2S{\cdot}CaSO_4$ formation (MS)

$$MS = \frac{SO_3}{0.022SiO_2 + 0.40Al_2O_3} \quad (2)$$

where: 0.022 — SO_3 wt.% incorporated into 1 wt.% SiO_2; 0.40 — SO_3 wt.% absorbed by 1% Al_2O_3 to form $C_4A_3\bar{S}$.

Theoretically, if $MS > 1.00$, it means that SO_3 is more than enough to form $C_4A_3\bar{S}$, the extra SO_3 will form $CaSO_4$, which is liable to combine C_2S into $2C_2S{\cdot}C\bar{S}$ (Eq. (2)).

In practice, it was noticed that the suitable ranges for both MG and MS was from 0.9 to 1.1, within these ranges, C_2AS and $2C_2S{\cdot}C\bar{S}$ may be chemically prevented from formation. According to calculations, the proportioning range with right MG and MS in baghouse dust–class C flyash–scrubber sludge system is shown in Fig. 1. Table 4 shows the MG and MS of experimental formulations.

3.2. SAB cement sintering

3.2.1. Comparison between microwave and conventional sintering

Samples of comp-1 were prepared by both microwave and conventional sintering, the XRD results are shown in Fig. 2.

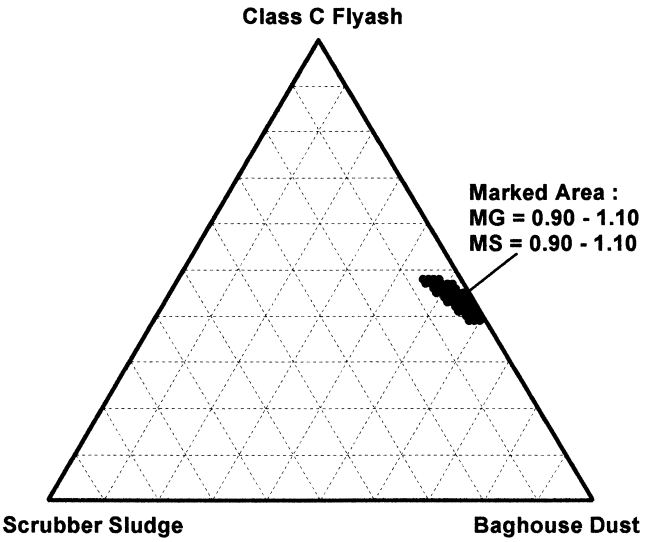

Fig. 1. Suitable formulation area with right MG and MS values in by-product raw material system.

In the case of microwave sintering, the main phases were predicted $C_4A_3\bar{S}$ and β-C_2S. Since the MS of comp-1 was 1.25, SO_3 was more than required to form $C_4A_3\bar{S}$, thus, a small amount of $CaSO_4$ existed in the clinker. The gypsum remaining in the microwave sample is likely the result of an incomplete reaction of the scrubber sludge. On the other hand, the phase composition from conventional sintering was not as developed well, a lot of unexpected $2C_2S{\cdot}C\bar{S}$ and even $C_{12}A_7$ existed in the clinker. Apparently, the formation of SAB cement was not completed yet and the condition of 1150°C/10 min in conventional sintering was not enough for SAB cement formation. From this comparison, it can be seen that microwave sintering was more effective than conventional process.

3.2.2. Microwave sintering of SAB cement with different chemical compositions

Fig. 3 shows the phase composition development in samples prepared by microwave sintering (gypsum had been added into samples). Generally, the phase composition development was rather well with predicted main phases of $C_4A_3\bar{S}$ and β-C_2S in SAB clinkers though there were slight differences among samples. When MS>1.00, as in comp-1 and comp-2, SO_3 concentration was more than required for $C_4A_3\bar{S}$ formation, therefore, there was a small amount of $CaSO_4$ existing in samples. With proper MG and

Table 4
MG and MS of proportions

	MG	MS
Comp-1	0.98	1.25
Comp-2	0.96	1.12
Comp-3	0.91	1.00
Comp-4	0.88	0.89

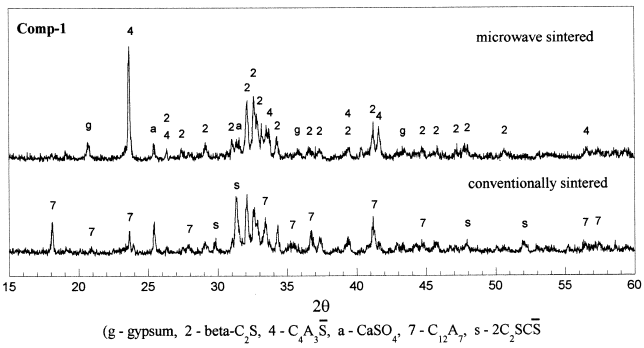

Fig. 2. XRDs of samples prepared by conventional and microwave sintering at 1150°C/10 min.

MS, the formation of the nonhydraulic C_2AS and $2C_2S{\cdot}C\bar{S}$ were completely prevented in comp-3. As MG was too low (=0.88) in comp-4, there was a trace of C_2AS existence.

3.3. Hydration characteristics

Fig. 4 shows the hydration phase development of microwave-sintered comp-3 sample. When hydrated for 1 day, $C_4A_3\bar{S}$ and the added gypsum had hydrated completely, indicating highly hydraulic reactivity of $C_4A_3\bar{S}$ compared to the conventionally prepared one where anhydrous $CaSO_4$ persilled beyond 90 days of curing [5]. Before 7 days of hydration, ettringite peaks were rather weak, suggesting that ettringite was formed as a very fine crystal. After 7 days, the ettringite peaks were apparently increased and continually enhanced through 28 days. This ettringite formation characteristic was much related with β-C_2S hydration. Without CaO in hydration environment, ettringite was formed according to the following reaction [5] (Eq. (3)):

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_3A(C\bar{S})_3H_{32} + 2AH_3 \qquad (3)$$

It was also reported that without CaO ettringite was difficult to grow into large crystal [14]. As later develop-

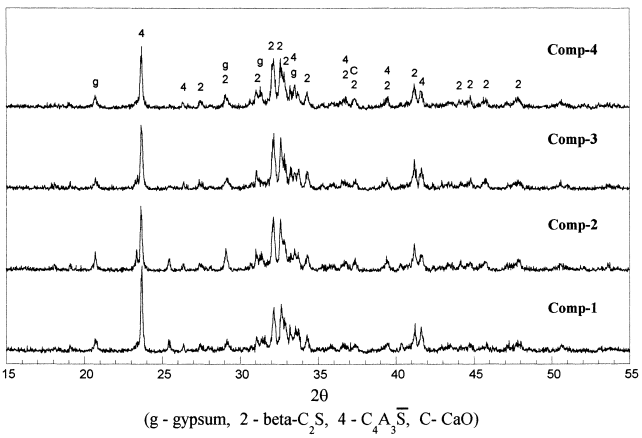

Fig. 3. XRDs of samples prepared by microwave sintering at 1150° C/10 min.

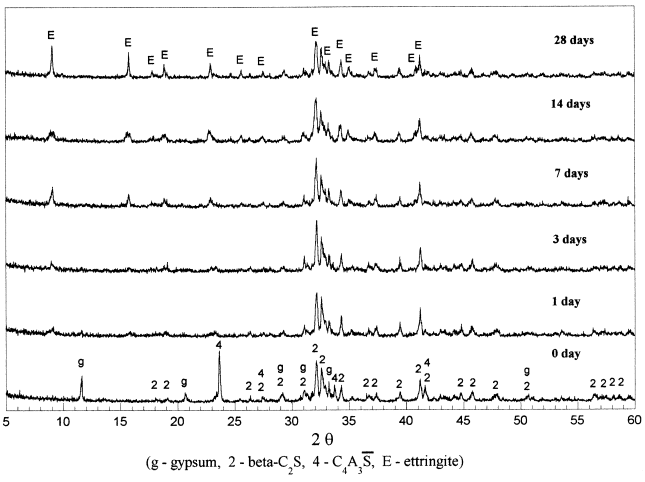

Fig. 4. Comp-3 hydration phase development (W/C = 0.50, 20°C, 10% gypsum addition).

ment, ettringite formation was accelerated greatly according to the following reaction [5] (Eq. (4)):

$$C_4A_3\bar{S} + 6CH + 8C\bar{S}H_2 + 74H \rightarrow 3C_3A(C\bar{S})_3H_{32} \qquad (4)$$

In our experiment, the clinker main phases were $C_4A_3\bar{S}$ and β-C_2S, before β-C_2S hydration, there was no $Ca(OH)_2$ produced and $C_4A_3\bar{S}$ had to hydrate without excess $Ca(OH)_2$.

3.4. Strength development characteristics

Three-point bending strength measurements were used since tensile properties are often the limiting factor in the use of cement.

3.4.1. Effect of SO_3 on strength development

Fig. 5 shows the effect of gypsum addition on strength development of comp-3 samples. As had discussed previously, gypsum and $C_4A_3\bar{S}$ had completely hydrated within 1 day, the strength increase rate in 1 day was the maximum for all samples. For higher gypsum addition, the strength was degraded between 1 and 7 days as in curves 4 and 5. In the experiment, it was noticed that these samples had developed deformation in 3 days of hydration, illustrating some expansion existing inside samples. The following regaining of strength increase was contributed to β-C_2S hydration. For proper gypsum addition (8%) in curve 3, the strength development was the best, its quick increase between 3 and 7 days also implied the earlier beginning of β-C_2S hydration. Less gypsum addition as in curve 2, or no gypsum addition as in curve 1, would not lead to strength degradation, but their strength development was slower. It is clear here that SO_3 concentration in SAB cement was a governing factor for strength development. Too much SO_3 leads to early expansion though the ettringite was less crystallized in early hydration as indicated in Fig. 4.

3.4.2. Strength development of SAB cement with different compositions

The strength development trends of comp-1, -2, -3 and -4 samples are shown in Fig. 6. In these microwave-prepared SAB cements, no fast-setting phenomenon was found due to the lack of CaO participation in hydration, but higher early strength was observed, generally, 1-day strength reached almost half of the 28-day strength.

For comp-1 and -2, the strength development was slower, especially in comp-1 the strength degradation was observed. In our experiments, we have found that the higher MS was (when >1.0), the more sample deformation was seen and thus the lower strength was measured even when less or no gypsum was added. Therefore, $CaSO_4$ existing in microwave-prepared SAB cement clinker seemed to have a reverse effect on its strength development, this was also observed in conventional preparation [2]. It seemed that comp-3 yielded the best result as its MG (= 0.91) and MS (= 1.00) were appropriate, with suitable gypsum addition its strength could be that as Type-I cement in the age of 28 days

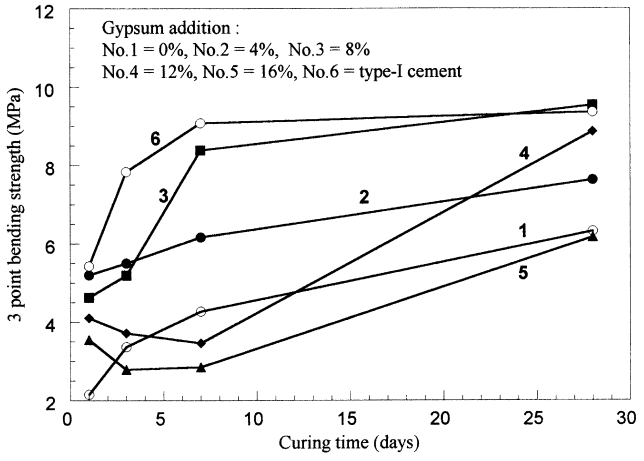

Fig. 5. Effect of gypsum addition on strength of comp-3 sample (W/C = 0.50, 20°C, paste).

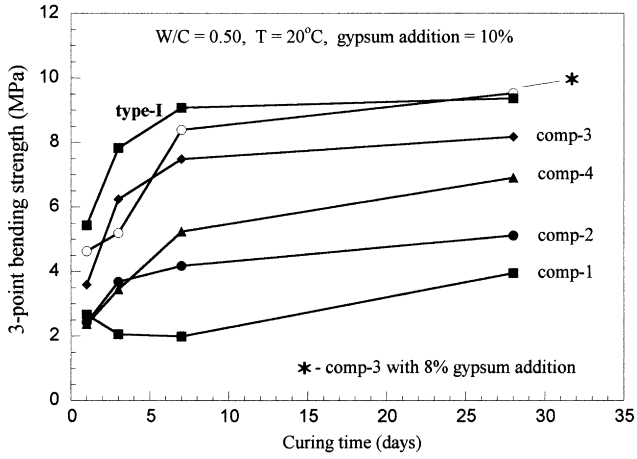

Fig. 6. SAB cement strength development.

of hydration. In the case of comp-4, the strength was reduced due to its lower MG (=0.89) and MS (=0.88).

From the above discussion, it has been shown that the strength of microwave-sintered SAB cement was governed by MG, MS and gypsum addition, proper control of these factors could improve the strength development.

4. Conclusion

(1) MG and MS were useful for raw mix proportioning control in SAB cement preparation with industrial wastes baghouse dust, scrubber sludge and class C flyash. The appropriate MG and MS values were 0.90–1.10, with which C_2AS and $2C_2S{\cdot}C\bar{S}$ could be chemically eliminated in clinker when microwave sintered at low temperature. However, more complete studies are needed to completely define the appropriate range.

(2) Microwave sintering had shown its advantages on SAB cement preparation. Condition of 1150°C/10 min was sufficient to microwave clinkering SAB cement.

(3) $C_4A_3\bar{S}$ and β-C_2S in SAB cement prepared by microwave sintering had highly hydraulic reactivity. $C_4A_3\bar{S}$ hydrated completely within 1 day and, β-C_2S had started its hydration before 7 days of hydration.

(4) With appropriate raw mix proportioning, the microwave-sintered SAB cement from utility wastes could yield satisfied strength as Type-I cement in 28 days of hydration. Studies using larger-size samples and compressive strength measurements are required.

Acknowledgments

This research was partly supported by a research grant from Electric Power Research Institute, which is gratefully acknowledged.

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