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Sulfoaluminate-belite cement from low-calcium fly ash and sulfur-rich and other industrial by-products

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Abstract

The study describes the preparation and characterization of an environmentally friendly cement with performance characteristics similar to those of Portland cement, from a lime kiln bag house dust, a low-calcium fly ash, and a scrubber sludge. Promising preliminary results show the formation of relatively low-temperature phases calcium sulfoaluminate ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$) and dicalcium silicate ($2CaO{\cdot}SiO_2$) at ~1250°C if nodulized raw meal is used for clinker preparation and at 1175°C if powdered raw meal is used as compared to the ~1500°C sintering temperature required for Portland cement. Phases of the developed cements were predicted using modified Bogue calculations. Isothermal calorimetric measurements indicate the hydration properties of the cements are comparable to ordinary Portland cement. Mechanical properties and microstructural evaluations also were carried out.

Keywords: Hydration; Ca_2SiO_4; $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$; Sulfate; Waste management

1. Introduction

Socioeconomic conditions of many countries around the world are seriously threatened by energy shortage and spiraling fuel prices. Portland cement, the essential material for better quality of life, consumes a large amount of energy for its production. Portland cement mainly consists of four principal clinker minerals: $3CaO{\cdot}SiO_2$(C_3S), $2CaO{\cdot}SiO_2$(C_2S), $3CaO{\cdot}Al_2O_3$(C_3A), and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$($C_4AF$). The lime contents for these four compounds are 73.7%, 65.1%, 62.2%, and 46.2%, respectively. Apart from requiring a large amount of calcium-rich raw materials, these phases require high-temperature burning for their formation. Consequently, production of Portland cement poses two major problems: (1) consumption of a large amount of calcium-rich raw materials, and (2) consumption of a large amount of high-quality energy.

In recent times, much attention has been given to the development of some modified special cement clinkers, leading to energy saving [1]. One of such cements containing the main phases C_2S, $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$($C_4A_3S$*), C_4AF, and $CaO{\cdot}SO_3$(CS*) was developed and reported by many researchers [2–14]. This special cement contains C_2S and two sulfate phases C_4A_3S* and CS* instead of high-temperature C_3S and C_3A. Raw mixes for C_4A_3S* clinkers differ from those for Portland cement in that they contain significant amounts of sulfates; therefore, reactions and products are quite different from those normally found in Portland cement production. The total lime requirement to produce such a modified Portland cement is about 50 wt% as against about 65% for Portland cement, and can be synthesized at a lower temperature of 1200°C, rather than the 1400°C to 1500°C of Portland cement. These special cements are commonly referred to as calcium sulfoaluminate-belite (SAB) cements.

It is conceived that cement containing a calcium sulfoaluminate and a reactive C_4AF can derive its early strength and other physical properties from formation of calcium sulfoaluminate hydrates. The hydration of the C_4A_3S* phase follows a very rapid hydration reaction, leading to the formation of needle-like ettringite, which is responsible for the quick setting of the sulfoaluminate cements.

The available literature [2–14] indicates that calcium sulfoaluminate-belite cements were mainly prepared from reagent grade chemicals, minerals, and industrial waste materials like belitic waste, blast furnace slag, and phosphogypsum. The main objective of this study is the preparation and characterization of environmentally friendly cement from industrial wastes like bag house dust, low-calcium fly ash, and scrubber sludge, with performance characteristics similar to those of Portland cement. Computational model

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Table 1
Chemical analysis of raw materials on loss free basis

Oxide (wt%)	BHD Q-146 (A)	Class "F" B-97 (B)	Sludge Q-51 (C)
SiO_2	11.12	49.93	2.18
Al_2O_3	6.26	26.72	0.17
Fe_2O_3	4.89	16.60	0.21
TiO_2	Nil	1.35	0.01
CaO	69.82	1.78	73.56
MgO	0.85	0.77	2.16
Na_2O	0.13	0.25	0.055
K_2O	0.69	2.26	0.047
P_2O_5	Nil	Nil	Nil
SO_3	6.22	0.32	21.35
MnO	0.01	0.03	0.016
B_2O_3	0.02	Nil	0.087

[15] and modified Bogue calculations were used to select the appropriate raw composition from the aforementioned industrial raw materials.

2. Experimental

2.1. Raw materials

Three types of industrial waste materials [MRL code numbers, Q-146 (bag house dust), B-97 (Class F fly ash), and Q-51 (scrubber sludge)] were used for the experiments. The oxide compositions of these raw materials on loss free basis are given in Table 1. Computational model [15] was used to formulate the batch compositions of the raw clinker. Theoretical phase compositions were predicted from these batches using a modified Bogue calculation. Batch formulations and theoretical phase compositions are given in Table 2.

2.2. Mixing and firing

All the raw materials were dried in an oven at 100°C for 4 h and ground to pass 320 mesh sieve before batch compositions were made. The batch compositions were mixed thoroughly. After thorough homogenization, raw meals were either used as powders or nodulized to the size of approximately 10-mm diameter each. Nodules were dried in an oven at 100°C for 4 h before introducing into the furnace. The batch compositions were subjected to different firing temperatures between 1100°C and 1300°C. The sintering duration at the maximum temperature was varied between 30 and 60 min. The typical firing schedule is presented in Fig. 1. The fired clinkers were relatively soft and friable, and were easy to grind; consequently, the whole process results in considerable saving of energy.

2.3. Hydration calorimetry

Isothermal hydration calorimetry was performed for selected clinkers at 25°C. The w/s ratio was maintained at 0.40 for all the measurements. Heat evolution during the first few hours of hydration was measured. All the calorimetric measurements were performed with a Thermonetics model C12-45-2E calorimeter. A Haake A 82 bath was used to maintain isothermal conditions. The heat evolution was recorded using a Soltec Corporation model 3314 strip chart recorder. The chart speed was maintained at 1 cm/h for all the measurements.

2.4. X-ray powder diffraction

X-ray diffraction (XRD) for phase analysis was conducted on clinkers fired at different temperatures and duration times. The samples were sieved to pass 325 mesh and slurry mounted on a zero background quartz plate using ethanol. The powder patterns were gathered over the range of 5–60° 2θ at a scanning rate of 2° 2θ per minute. All the measurements were performed using a Scintag PAD-V diffractometer supplied. The data were processed using a Scintag Vax 3100 automated graphics workstation.

2.5. Compressive strength measurement

Compressive strengths were measured on 25 mm × 25 mm × 25 mm cubes. Paste samples were mixed using an API procedure and poured into the cubes. The w/s ratio was maintained at 0.40 for all the mixings except for the control mixture, which was maintained at 0.30. After 1 day of curing, the molds were removed. The specimens were cured in a 25°C curing chamber for 1 day and in a 38°C curing cham-

Table 2
Calculated phases of calcium sulfoaluminate-belite cement

Phase composition (wt%)	Composition 1 (wt%) (0.6 A + 0.2 B + 0.2 C)	Composition 2 (wt%) (0.6 A + 0.225 B + 0.175C)	Composition 3 (wt%) (0.6 A + 0.3 B + 0.1 C)	Composition 4 (wt%) (0.4 A + 0.25 B + 0.35 C)	Composition 5 (wt%) (0.4 A + 0.2 B + 0.4 C)
C_2S	49.07	52.49	62.77	50.79	43.94
C_4A_3S*	10.15	10.94	13.97	10.51	8.91
C_4AF	19.16	20.41	24.15	18.81	16.32
CS*	11.47	10.39	Nil	14.74	16.88
Free CaO	7.71	3.26	Nil	2.43	11.33

A, Q 146; B, B 97; C, Q 51.

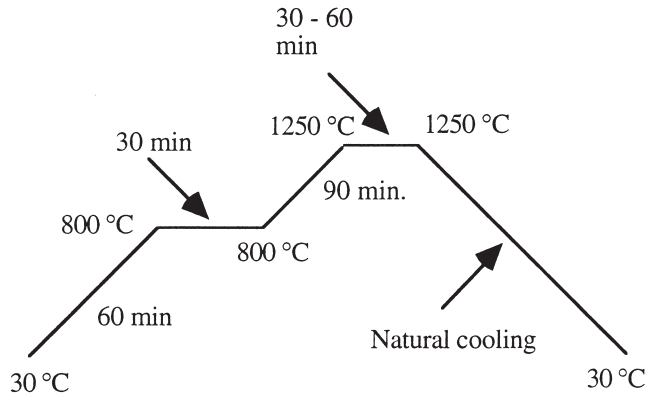

Fig. 1. Schematic diagram of firing profile used for the clinker preparation.

ber for 27 days. The compressive strengths of three samples each were measured after 1, 7, and 28 days of curing. The compressive strengths were measured using a Tinius Olsen instrument (Testing Machine Company, Willow grove, PA). The cross-head speed was maintained at 0.05 inch/min for all the measurements. The hardened pastes were freeze dried for 24 h and stored for further characterization.

2.6. Scanning electron microscopy

Microstructural features of clinkers and hardened pastes were examined. Specimens were fractured and small samples were affixed to the scanning electron microscope (SEM) specimen holder with epoxy resin. Specimens then were coated with a very thin layer of gold to promote electrical conductivity. A dual-stage model ISI-DS 130 SEM was used for the measurements.

3. Results and discussion

Most of the earlier studies on sulfoaluminate cement preparation reported the possibility of obtaining sulfoaluminate cements between 1200 and 1250°C. The first phase of the study was devoted to determining the suitable compositions that formed the required sulfoaluminate phase and other cementitious phases in this temperature range. All the batch compositions were initially fired at 1250°C for 30 min. Nodulized raw meals were used in this part of the study. The powder XRD patterns of these clinkers are given in Fig. 2. The JCPDS powder patterns for β-C_2S, C_4A_3S*, CS*, C_2AS, and C_4AF phases are given in Fig. 3. Batch compositions 2 to 5 do not form the main sulfoaluminate phase C_4A_3S* at this temperature. Composition 1 showed the formation of C_4A_3S* and β-C_2S phases, the major components of sulfoaluminate cement, in about equal proportions. Composition 1 was identified as the most promising one for further studies. Isothermal hydration calorimetric measurements were done for all the compositions. Compositions 2 to 5 do not show significant heat evolution peaks during the early stages of hydration.

In the second part of the study, composition 1 was fired at different temperatures starting from 1150°C to 1250°C for a 30-min soaking period. Nodulized raw meals were

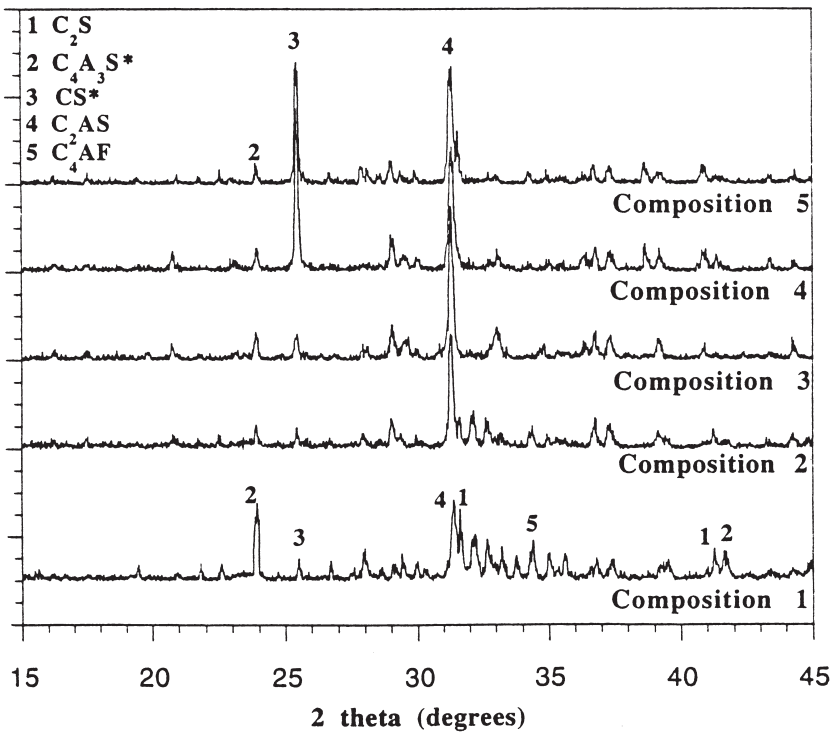

Fig. 2. XRD powder patterns for the different compositions shown in Table 2, fired at 1250°C for 30 min.

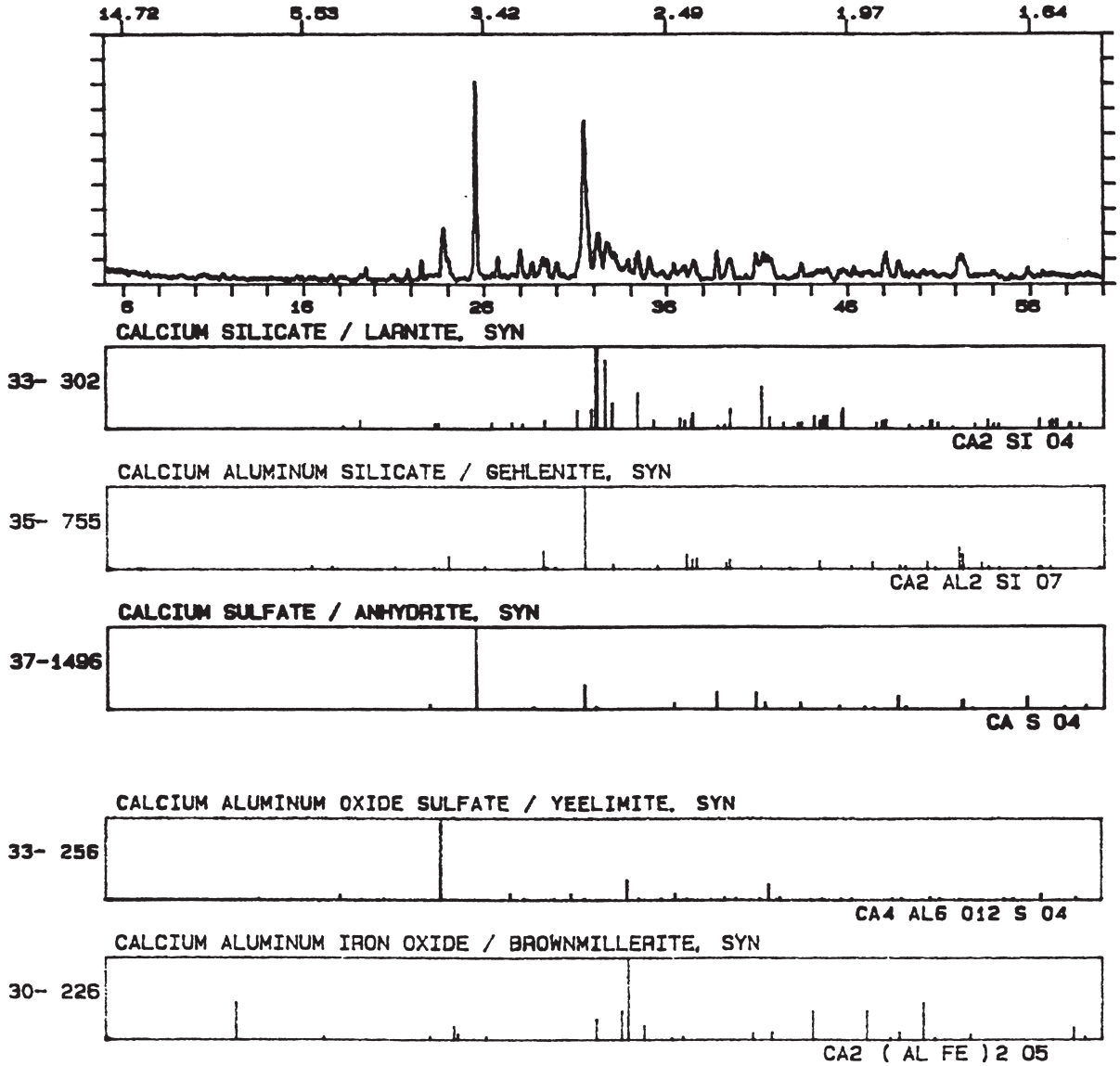

Fig. 3. Comparison of peaks using JCPDS powder patterns for the phases β-C_2S, C_4A_3S*, CS*, C_2AS, and C_4AF.

used for all experiments. The formation of the sulfoaluminate phase was not observed below 1250°C sintering. In the third part of the study, the sintering cycle were repeated with powdered raw meal. After a number of trial studies involving various sintering temperatures and duration of times, 1175°C was identified as the lowest temperature at the which sulfoalumiante phase formed. The sintering duration was varied between 30 and 60 min at 1175°C. The powder XRD patterns of powder samples fired at 1175°C for 45 and 60 min are given in Fig. 4. Gradual reduction in CS* was observed as the clinkering duration increased. Maximum C_4A_3S* intensity was observed at 60 min of firing.

The following conclusions may be drawn from the XRD patterns of the sintering studies (Figs. 2 and 3).

When nodulized raw meals were used for clinker preparation:

1. β-C_2S phase formation was reduced from composition 1 to composition 5 and none was apparent in composition 5.
2. C_4A_3S* phase formed only in composition 1, very little in compositions 2 to 5.
3. Formation of nonhydrating calcium aluminum silicate phase C_2AS (gehlenite) was responsible for the decrease in intensity of C_4A_3S* from composition 1 to 5. The intensity of C_2AS increased from composition 1 to 5.
4. Intensity of CS* also increased from composition 1 to 5.

When powdered raw meals were used for clinker preparation:

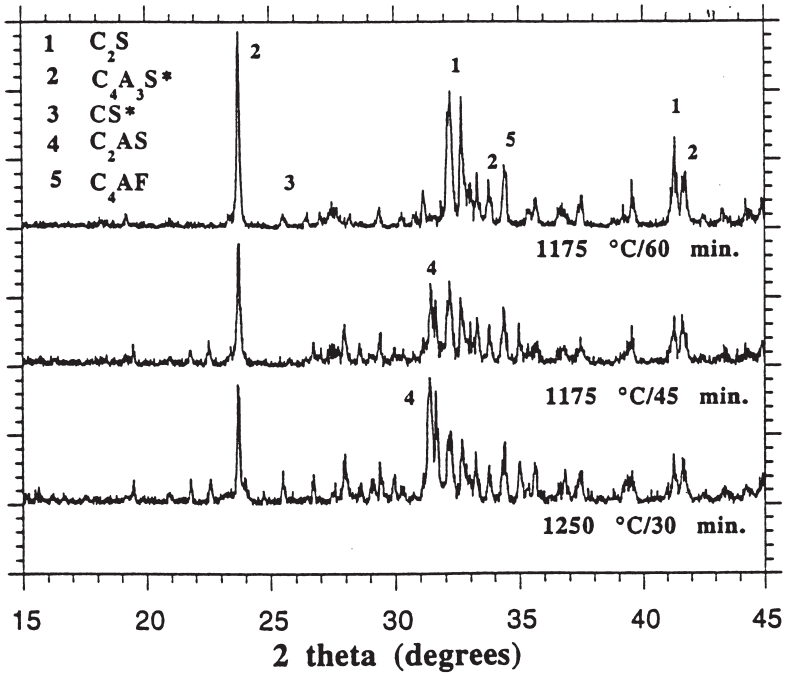

Fig. 4. XRD powder patterns of the composition 1 fired at 1250°C for 30 min, at 1175°C for 45 min, and at 1175°C for 60 min.

1. Intensity of β-C_2S in composition 1 increases in the following order: 1250°C/30 min to 1175°C/45 min to 1175°C/60 min.
2. Intensity of C_4AS^* increased at the expense of C_2AS as the sintering duration increased from 30 to 60 min.

3.1. Hydration calorimetry

Hydration behavior of the samples fired at 1175°C for 45 and 60 min was investigated using isothermal hydration calorimetry. The heat evolution patterns for these samples are shown in Fig. 5. The sample fired at 1175°C for 45 min

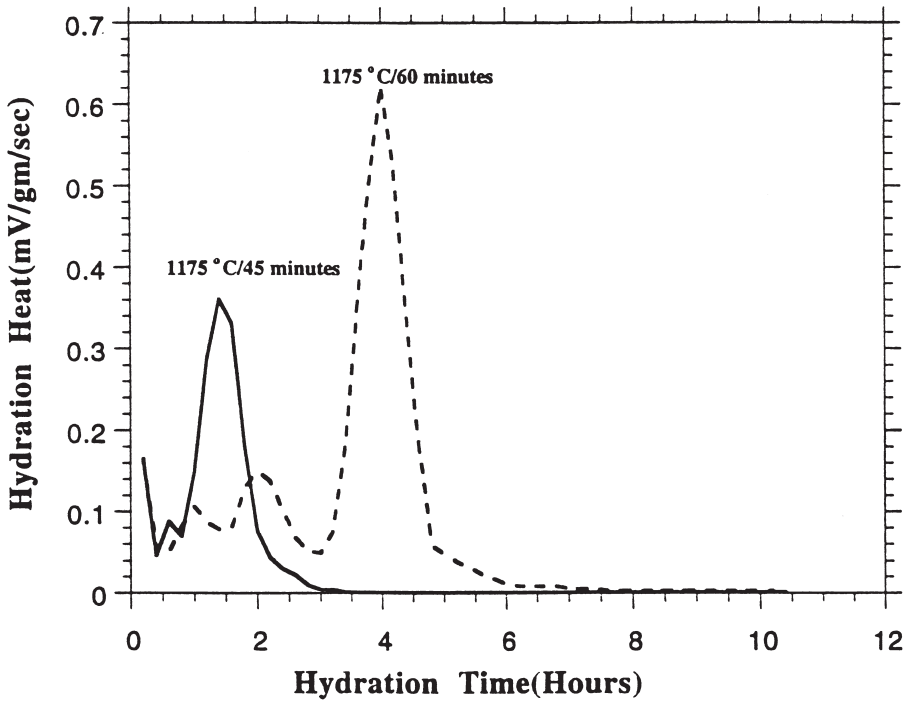

Fig. 5. Isothermal hydration heat evolution for composition 1 fired at 1175°C for 45 min and 60 min.

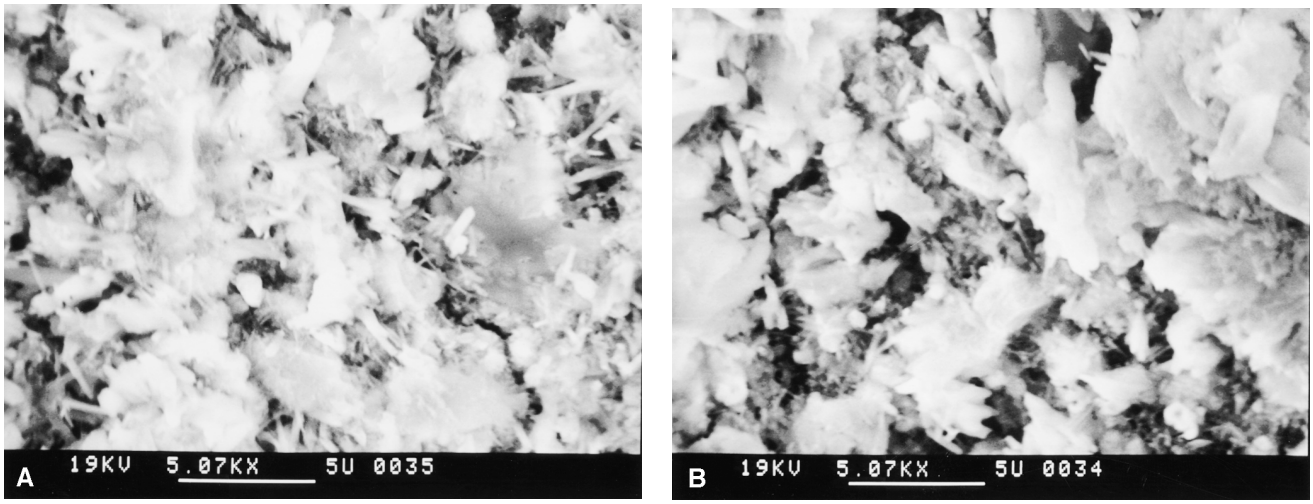

Fig. 6. SEM image of the 1-day hydrated paste (A) and 28-day hydrated paste (B), both of composition 1, fired at 1175°C for 60 min.

shows very little heat evolution at the early stages of hydration. The sample fired at 60 min shows much stronger hydration heat curves at the early stages of hydration.

3.2. Microstructure of the hydrated phases

SEM studies of the 1- and 28-day hydrated pastes were carried out for the composition sintered at 1175°C for 60 min. The SEM image (Fig. 6A) shows the presence of sponge-like sulfoaluminate phases in the whole matrix and needle-like ettringite phases in the voids after 1 day of hydration. The belite phase is observed to remain much less hydrated during this period. After 28 days of hydration (Fig. 6B), small amounts of calcium hydroxide and calcium silicate hydrate were observed, indicating β-C_2S hydration has taken place. It is expected that C_4A_3S* would be completely hydrated much before 28 days of hydration.

3.3. Compressive strength

Compressive strengths for 1-, 7-, and 28-day curing ages were measured for pastes made from composition sintered at 1175°C for 60 min (Fig. 7). These compressive strengths were compared with compressive strengths of ordinary Portland cement control mixture. In general, the strength of the new cement is lower than ordinary Portland cement at all stages of hydration. It should be noted, however, that the ordinary Portland cement had a w/c ratio of 0.30 compared with 0.40 for SAB. However the compressive strength of this new cement is in good agreement with similar studies

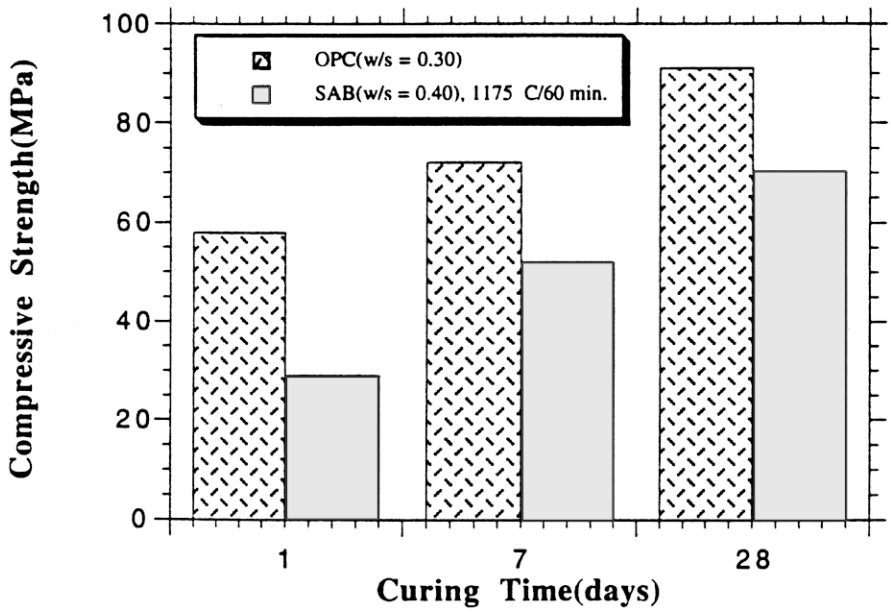

Fig. 7. The 1-, 7-, and 28-day compressive strengths of ordinary Portland cement control mix and composition 1 fired at 1175°C for 60 min.

reported in literature [7,16]. The formation of ettringite contributes to the strength development in samples containing sulfoaluminates mainly during the first early stages of hydration. In later ages, strength development depends mostly on C-S-H gel formation.

4. Conclusion

1. Industrial wastes like bag house dust, low-calcium fly ash, and scrubber sludge can be used for the preparation of environmentally friendly cement.
2. Low-temperature phases calcium sulfoaluminate ($4CaO \cdot 3Al_2O_3 \cdot SO_3$) and β-dicalcium silicate($2CaO \cdot SiO_2$) can be formed at around 1250°C if nodulized raw meal is used for clinker preparation, and at 1175°C if powdered raw meal is used.
3. Compressive strength and microstructural evaluations confirm the usefulness of this new cement.

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