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New applications of calcium sulfoaluminate cement

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Abstract

This paper presents four innovative utilizations of calcium sulfoaluminate (CSA) cement:

- development of concrete with high early strength: 40 MPa, 6 h after its preparation, and higher than 55 MPa after 24 h,
- design of self-leveling screed with limited curling, when unbonded to its support,
- design of self-leveling topping mortar presenting the following properties: time of workability higher than 30 min, set within 75 min, and low drying shrinkage (< 250μm/m).
- glass-fiber-reinforced cement (GFRC) composites that can be demolded 4 h after casting and present high ductility and durability after aging in different weathering conditions.

Keywords: Calcium sulfoaluminate cement; Mechanical properties; Shrinkage; Fiber reinforcement; Workability

1. Introduction

Calcium sulfoaluminate (CSA) cements have essentially been developed in China in the 1970s. Designed by the China Building Materials Academy (CBMA), they were intended to the manufacturing of self-stress concrete pipes due to their swelling properties. Sulfoaluminate cements contain the phases belite (C_2S), yeelimite or tetracalcium trialuminate sulfate ($C_4A_3\bar{S}$), and gypsum ($C\bar{S}H_2$) as their main constituents. They also contain other phases like C_4AF, $C_{12}A_7$, C_3A, and C_6AF_2 [1–3].

When CSA cement hydrates, ettringite ($C_6A\bar{S}_3H_{32}$) is formed according to the following reactions [4]:

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 36H \Rightarrow C_6A\bar{S}_3H_{32} + 2AH_3,$$

in absence of calcium hydroxide, (1)

$$C_4A_3\bar{S} + 8C\bar{S}H_2 + 6CH + 74H \Rightarrow 3C_6A\bar{S}_3H_{32},$$

in presence of calcium hydroxide. (2)

The microstructure of ettringite is strongly dependent on the presence of lime [5]. Ettringite produced by the reaction in Eq. (2) is expansive and this property is exploited in special applications such as shrinkage-resistant and self-stressing cements [6]. Ettringite formed in the absence of lime by the reaction in Eq. (1) is nonexpansive and generates high early strength in cementitious systems [7].

This last property was exploited to develop a concrete with high early strength (40 MPa after 6 h of age) and workability maintained for 60 min.

The property of limited shrinkage due to the production of expansive ettringite was used to develop self-leveling screed with limited curling and self-leveling repair mortar.

Glass-fiber-reinforced cement (GFRC) is an interesting construction material of considerable potential. But its development has been lower than expected due to the high alkalinity or Portland cement matrices. Borosilicate E-glass is chemically destroyed in Portland cement, and even alkali-resistant glass fiber is subjected to physical attack by calcium hydroxide crystals. Pozzolanic additions like metakaolin or microsilica are used to decrease the calcium hydroxide content and therefore guarantee the durability of GFRC composites [8,9]. Less alkaline non-Portland cement matrices have been developed for reinforcement by glass fibers: high-alumina cement, supersulfated cement, and CSA cement [10,11]. This paper presents the prelimi-

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Table 1
Composition of CSA and OPC clinkers (wt.%)

Clinker	$C_4A_3\bar{S}$	C_3S	C_2S	C_3A	C_4AF	Perovskite
CSA	53.5		21.2		16.3	9.0
OPC		61.6	21.5	7.6	8.4	

nary results obtained on white sulfoaluminate cement reinforced b AR glass fibers.

2. Concrete with high early-age strength

The following materials were used in the study:

- CSA cement produced by Carrières du Boulonnais, containing 80% CSA clinker and 20% phosphogypsum. The composition of CSA clinker, assessed by X-ray diffraction and chemical analysis is given in Table 1.
- ordinary Portland cement (OPC), class CEM I 52.5, according to the European Standard EN 197-1. Its Bogue composition is given in Table 1.
- limestone powder (98% $CaCO_3$),
- liquid-based polycarboxylate with a dry matter content of 30%,
- lithium carbonate (Li_2CO_3), which acts as an accelerator of OPC and calcium aluminate cement [12]. It was a pure PROLABO powdered product.
- silicocalcareous river sand (0/5 mm) and coarse aggregate (5/14 mm).

In concrete, the cementitious material (CM) was a mixture of 80% CSA and 20% OPC. The introduction of OPC in the blend prevents the loss of strength at later ages [13]. Three CM contents were investigated: 400, 500, and 600 kg/m^3. Powdered limestone was introduced in the mixture to enhance workability. Its content was 7.5% of the CM content. The W/CM was 0.37 and the superplasticizer dosage was 2.5%. The Li_2CO_3 dosage was 0.05%. Table 2 shows the composition and workability of the different mixtures.

Table 2
Mixture proportions of concrete

Content (kg/m^3)	Mixture		
	1	2	3
CM	400	500	600
Powdered limestone	30	37.5	45
Sand (0/5 mm)	940	840	740
Gravel (5/14 mm)	940	840	740
Water (W/CM = 0.37)	150	185	220
Superplasticizer	10	12.5	15
Li_2CO_3	0.020	0.025	0.030
Time of workability (minutes)	50	100	65

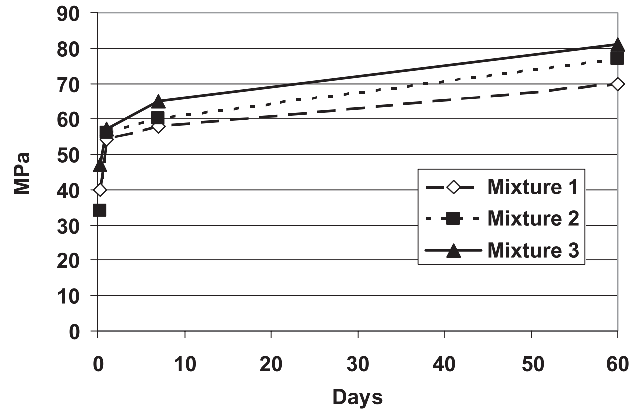

Fig. 1. Strength development of concrete.

Good workability was maintained for 50 min at least. As illustrated in Fig. 1, the 6-h strength, measured on cylinders ($\phi = 110$ mm, $h = 220$ mm), was higher than 40 MPa, except for mixture 2. This is certainly due to an extended time of workability (100 min instead of 50 or 65 min). After 7 days of hydration, high-strength concrete was obtained regardless of the CM content. As shown in Fig. 1, the long-term strength development is not blocked and the strength increase between 1 day and 60 days is higher than 30%.

3. Self-leveling screed

The development of cement-based screeds unbound to their support is still limited because of the curling that occurs at the corners and perimeter of the screed (Fig. 2). This phenomenon is mainly due to the moisture gradient that appears within the thickness of the screed. Curling is caused by differential shrinkage between the top and the bottom of a slab or a screed, mainly drying shrinkage. The top surface dries and shrinks, while the bottom stays wet and undergoes little change in dimensions [14].

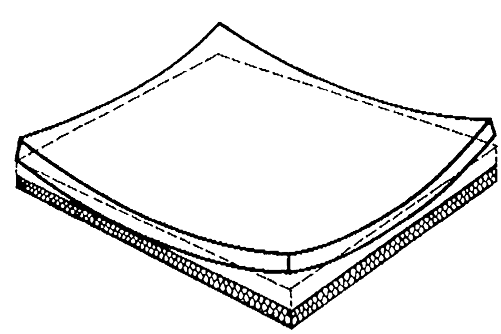

Fig. 2. Curling of screed.

Table 3
Values of vertical displacement

η (%)	D (mm)	y (mm)
70	25	2.7
70	4	6.8
30	4	24.0

This phenomenon increases as the thickness of the slab and the maximal size of the coarse aggregate decrease [15,16]. When OPC is used, the vertical displacement at corners can be assessed using the Soum formula:

$$y = 2,6\left[\frac{(1-\eta)^3}{D}\right]^{1/2}$$

where:

- y is the vertical displacement (cm),
- η is the relative humidity (%),
- D is the maximum diameter of the aggregates (cm).

Table 3 shows the values that are obtained for vertical displacement in different conditions.

In the present study, the same CSA cement as that used for high-early age strength concrete was utilized to cast the screed. The mixture proportions are given in Table 4. To prevent segregation, a viscosity-modifying agent (VMA) was introduced in the mixture. The VMA powder was composed of guar gum, polyvinyl alcohol, and antifoaming agent in the proportions 1:1:1. A water-retaining agent (polyol) was also present in the mixture.

The workability of the mortar was measured by means of the static spread of a truncated cone (ϕ_{inf} = 95 mm, ϕ_{sup} = 55 mm, h = 70 mm). The values obtained at different times are presented in Fig. 3. The loss of workability within 3 h was very low (13%).

The compressive strength and drying shrinkage (20 °C, 50% RH) were measured during the first 28 days on prismatic samples (40 × 40 × 160 mm). Their values are shown in Figs. 4 and 5.

A square screed (4 × 4 × 0.05 m) was cast and the displacement of each corner was recorded. The average

Table 4
Mixture proportions of the screed

Materials	Content (kg/m^3)
CSA cement	350
OPC	50
Powdered limestone	50
Sand (0/5 mm)	1250
VMA	3
Water retaining agent	5
Superplasticizer (polycarboxylate)	6
Water	280

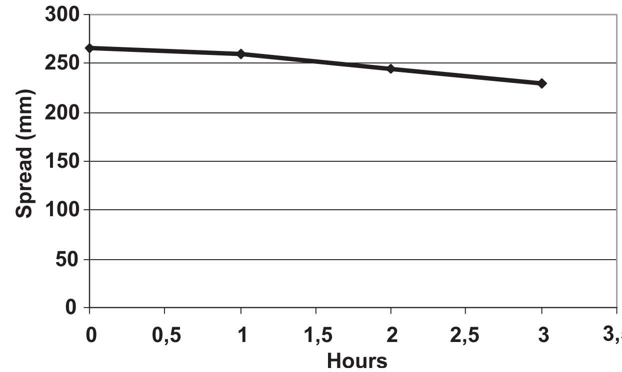

Fig. 3. Spread versus time.

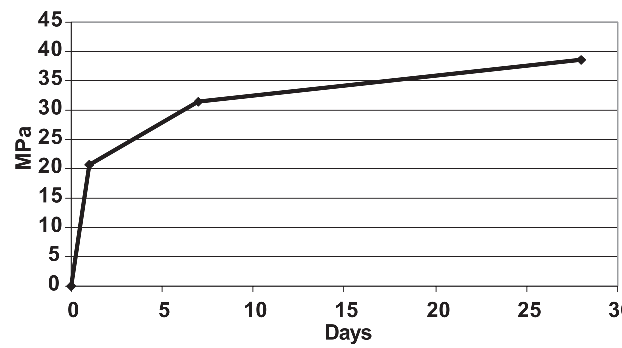

Fig. 4. Compressive strength versus time.

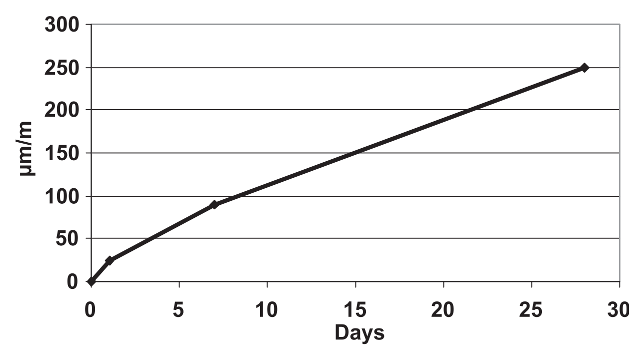

Fig. 5. Drying shrinkage versus time.

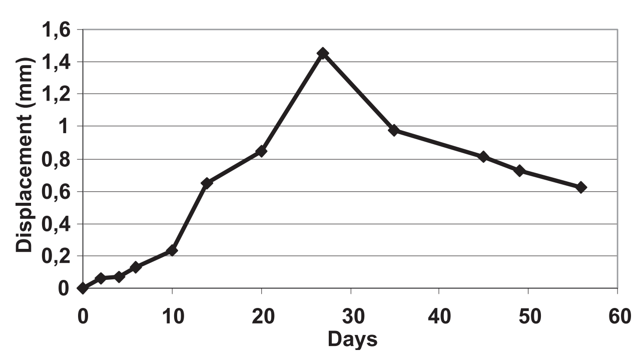

Fig. 6. Average vertical displacement of the corners.

Table 5
Mixture proportions of topping mortars

Content (kg/m^3)	Mixture				
	1	2	3	4	5
Sulfoaluminate clinker	810	765	720	675	630
Phosphogypsum	90	135	180	225	270
OPC	32	32	32	32	32
Sand (0/2 mm)	900	900	900	900	900
Admixtures	65	65	65	65	65
Water	390	390	390	390	390
Specific gravity	2.01	2.01	1.99	1.97	1.96

value of the displacement is shown in Fig. 6. The maximum value was reached after 28 days and was limited at 1.45 mm, which is low compared to the values obtained with OPC.

4. Self-leveling topping mortar

Another sulfoaluminate clinker was used in this study, presenting the following composition:

- $C_4A_3\bar{S} = 66\%$,
- $C_2S = 17\%$,
- Perovskite = 9.9%,
- $C_{12}A_7 = 7.1\%$.

The topping mortar was designed to fulfil the following requirements

- self-leveling,
- time of workability: 30 min,
- final setting within 75 min,
- no curling and limited shrinkage,
- thickness: 2–30 mm,
- 24-h strength: >35 MPa (measured on 40 × 40 × 160 mm prisms).

Five different mixtures were studied and are shown in Table 5. Different proportions of phosphogypsum were introduced in the mixtures to study the influence of the gypsum content on the engineering properties of the topping

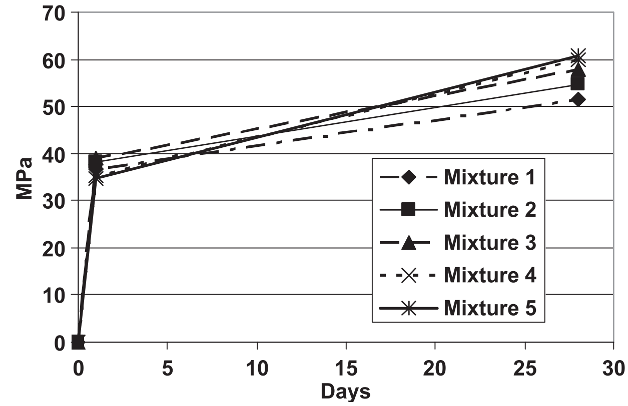

Fig. 8. Compressive strength of topping mortar.

mortar. The phosphogypsum/sulfoaluminate clinker ratio varied from 10:90 to 30:70. In this study, other parameters were kept constant. The water to total CM ratio was 0.42.

The five mixtures presented the required time of workability (30 min) and were self-leveling, as pointed out in Fig. 7.

As shown in Fig. 8, the gypsum content has a slight effect on the compressive strength of mortar. The five mixtures presented a 24-h strength very close to 35 MPa. After 28 days of age, a higher amount of gypsum led to higher strength.

The influence of gypsum content is more effective on length variations of specimens, as shown in Fig. 9. Those length changes were measured on mortars cured at 20 °C and 50% RH. Mixtures 1 to 3 started shrinking after 1 day of curing and reached unacceptable values at 28 days of age (>250 μm/m). The best compromise between a good strength and a limited shrinkage was obtained by mixture 4, which contained 75% sulfoaluminate clinker and 25% gypsum.

5. Development of glass-fiber-reinforced composites using white sulfoaluminate cement

As the hydration of CSA cement does not yield any calcium hydroxide, it should be interesting to use such

Fig. 7. Flowing properties of topping mortar.

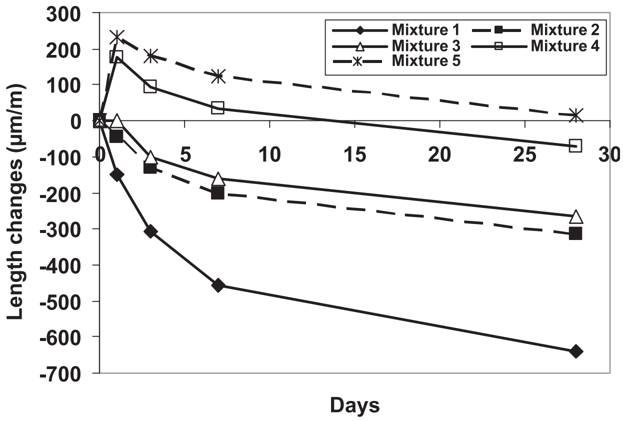

Fig. 9. Length changes of mortars cured at 20 °C and 50% RH.

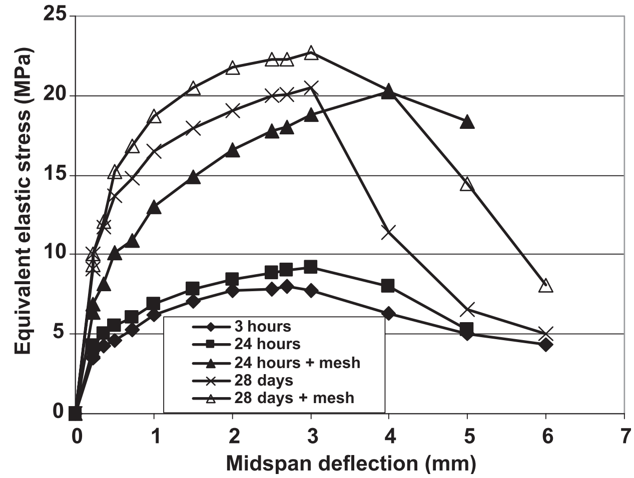

Fig. 10. Flexural behavior of GFRC composites at different ages.

cement in the production of glass fiber-reinforced composites. Moreover, in such matrix efflorescences due to the carbonation of calcium hydroxide cannot appear.

A white CSA clinker was prepared in a rotary kiln, from a mixture of residual aluminium hydroxide and phosphogypsum. The phase composition of this clinker was as follows:

- belite (C_2S): 11%,
- yeelimite ($C_4A_3\bar{S}$): 84%,
- ferrite (C_4AF): 4%,
- perovskite (C_3FT_2): 1%.

CSA cement was obtained by intergrinding 70% of that clinker and 30% phosphogypsum.

The mixture proportions of the matrix are shown in Table 6.

The sand was a very fine siliceous sand (< 500 μm). All chemical admixtures were powdered products:

- superplasticizer: polycarboxylate,
- accelerator: lithium chloride,

Table 6
Mixture proportions of the matrix

Cement/sand	1.00
Water/cement	0.37
Superplasticizer (% cement)	1.0
Accelerator (% cement)	0.05
Retarder (% cement)	0.27
Water-retaining agent (% cement)	0.06

Table 7
Properties of short fibers

Filament diameter	14 μm
Strand tensile strength	1700 Mpa
Elastic modulus	72 Gpa
Density	2.68 g/cm^3
Strand	38 tex (102 filaments)

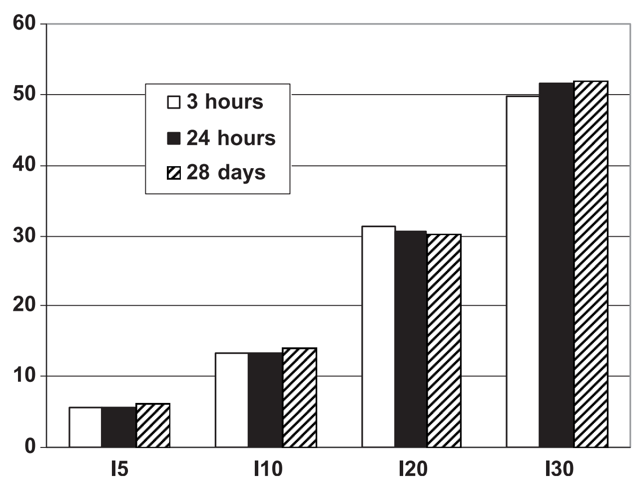

Fig. 11. Indices of toughness at different ages for composites reinforced by short fibers.

- retarder: sodium tetraborate,
- water-retaining agent: polyethylene-glycol.

Short fibers (l = 11 mm) and mesh were derived from the same AR-glass (Vetrotex, Cem-Fil). The properties of fibers are presented in Table 7.

Cem-Fil 120/1 had a nominal weight of 120 g/m^2 and was produced using 320 and 640 tex Cem-Fil direct rovings. The mesh density was 8 × 8 strands per 10 cm. The short fiber content was 2.83% of total weight (cement + sand).

Table 8
MOR values recorded at different ages

Age	MOR (MPa)
3 h	8.0
24 h	9.3
24 h with mesh	20.2
28 days	20.5
28 days with mesh	22.8

The mesh was placed at 5 mm from the extreme tensile fiber of the composite.

Thin plates (350 × 350 × 14 mm) were cast and cured at ambient temperature. They were demolded 90 min after casting. Specimens of 70 mm in width were cut in each plate and subjected to a three-point loading on a span of 200 mm at a cross-head speed of 1 mm/min. The load deflection was recorded during the test and allowed the calculation of the following parameters:

- limit of proportionality (LOP): stress corresponding to the first crack of the matrix,
- modulus of rupture (MOR): maximum stress recorded,
- several toughness indices.

These indices were those described by the ASTM C 1018 85 [17]: I_5, I_{10}, I_{20}, and I_{30}. The residual strength factors, $R_{20,10} = 10\ (I_{20} - I_{10})$ and $R_{10-5} = 20\ (I_{10} - I_5)$ were also calculated. Tests were performed at different ages: 3 h, 24 h, 7 days, and 28 days. Specimens tested after 3 h of age were sealed in plastic bags at 20 °C until the date of tests.

From the load-deflection curves recorded, equivalent elastic bending stress versus deflection curves were derived. Typical stress-deflection curves are shown in Fig. 10. All composites developed ductile behavior as shown in Fig. 11: all indices were higher than required values and remained constant with time.

As shown in Fig. 10, the presence of mesh increased the performances of composites and especially at 24 h of age. The MOR values obtained at different ages are summarized in Table 8. The main remarkable result was the performance obtained after 3 h of hydration: MOR = 8 MPa, ductile behavior. This is very important for the precast industry: such performance allows quick demolding and rapid rotation of molds.

At 28 days of age, the performances of the composite are similar to those obtained for a white OPC composite, reinforced by 3% fibers and mesh, containing metakaolin and a polymer. To get such result, the composite had to be cured at 40 °C for 3 days before being stored at 20 °C in sealed plastic bags.

6. Conclusion

From this limited research work, it can be concluded that a wide range of innovative building materials can be developed, using sulfoaluminate cement: high early strength concrete, self-leveling screed, self-leveling topping mortar, and high performance glass-fiber-reinforced composites. Those materials are based on three main properties exhibited by CSA cement: rapid formation of ettringite, expansive property of ettringite, and low alkalinity of the pore solution of the cementitious matrix. Other materials are under development: fire-resistant materials, materials including large amounts of industrial by-products.

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