Acceleration of Slag Cement Hydration by Calcium Sulfoaluminate Cement

J. Pera[1], J. Ambroise[1], A. Bouamrane[1], M. Boulet[1]
[1]*Institut National des Sciences Appliquées de Lyon, Villeurbanne, France*

Abstract :

Two slag cements (S1 and S2) were investigated. S1 contained 48% slag and 52% portland cement; S2 was composed of 97% slag and 3% anhydrite. Each of them was accelerated by means of calcium sulfo-aluminate cement (CSA, C for calcium and SA for sulfoaluminate). CSA was composed of sulfoaluminate clinker and gypsum in the following proportions: 100/0, 85/15, 70/30, 60/40, 50/50, and 40/60. The compressive strength of standard mortars was measured at different ages and the microstructure of plain pastes was investigated. The results obtained show that CSA is a powerful accelerator of slag cement. The results depend upon the composition of slag cement. For S1, the 1-d strength is multiplied by 4 when 40% CSA containing 50% clinker and 50% gypsum is introduced in the mixture. For S2, the presence of CSA containing 85% clinker and 15% gypsum increases the 1-d strength by 300%. These results are very interesting for the precast industry: the use of CSA allows rapid demolding without any heating of concrete.

1. Introduction

The goal of the research work presented in this paper was to replace white portland cement by slag cement in the production of precast colored concrete blocks. The Libera's company in New England (USA) has used a blended portland-blast furnace slag cement in such application for about three years. Some of the properties that slag cement can impart are:

- an architecturally appealing lighter color,
- a finer, tighter surface texture or more swipe,
- reduced efflorescence,
- decreased permeability,
- increased compressive strengths.

Concrete containing GGBFS (ground granulated blast furnace slag) develops strength at a somewhat slower rate than concrete containing only portland cement, but ultimately can develop equivalent strength. This can be a concern where early strength development is important, as in the precast industry. Therefore, it is necessary to accelerate slag cement hydration using calcium salts, alkaline solutions or heat curing.

In the present study, calcium sulfoaluminate cement (CSA) was used to accelerate slag cement in order to avoid heat curing in the production of concrete blocks. Two slag cements (S1 and S2) were investigated. S1 contained 48% slag and 52% Portland cement; S2 was composed of 97% slag and 3% anhydrite. Both cements were proposed to the precast industry to replace white Portland cement. The aim of the study was to choose one type of slag cement and it is the reason why there were both investigated. CSA was composed of sulfoaluminate clinker and gypsum in the following proportions: 100/0, 85/15, 70/30, 60/40, 50/50, and 40/60. As reported in the literature, CSA is often used to accelerate Portland cement [1-7].

2. Composition of CSA

Calcium sulfoaluminate cements (CSA) were obtained by mixing different amounts of calcium sulfoaluminate clinker and calcium sulfate. The phase composition of calcium sulfoaluminate clinker is given in Table 1. Six calcium sulfoaluminate cements (CSA) were prepared (Table 2).

Table 1 — Composition of calcium sulfoaluminate clinker (w_t %).

Compound	Chemistry	%
Yeelimite	$Ca_4Al_6O_{12}SO_4$	73.5
Belite	β-Ca_2SiO_4	16.1
Perovskite	$Ca_3Fe_2TiO_8$	6.9
Mayenite	$Ca_{12}Al_{14}O_{33}$	0.6
Periclase	MgO	1.7
Anhydrite	$CaSO_4$	1.0
Quartz	SiO_2	0.2

Table 2 — Composition of calcium sulfoaluminate cements (CSA) (w_t %).

Reference	CSA0	CSA15	CSA30	CSA40	CSA50	CSA60
Clinker	100	85	70	60	50	40
Gypsum	0	15	30	40	50	60

The average diameter of the particule size distribution of gypsum and calcium sulfoaluminate clinker was nearly the same: 24 µm and 26 µm, respectively. The chemical composition of all the materials used in the present study is shown in Table 3.

Table 3 — Chemical composition of materials (w_t %).

Oxides	CSA clinker	Gypsum	S1	S2	CEM II-A
SiO_2	4.7	0.3	27.0	28.0	21.5
Al_2O_3	37.4	0.3	7.8	9.5	2.3
Fe_2O_3	1.9	0.1	1.6	0.7	0.3
MnO	< 0.1	< 0.1	0.1	0.2	< 0.1
MgO	1.7	< 0.1	4.1	6.8	0.6
CaO	39.2	30.4	49.3	38.9	65.1
Na_2O	n.d.	0.2	0.3	0.3	0.1
K_2O	0.2	n.d.	0.7	0.7	0.5
TiO_2	1.6	< 0.1	0.3	0.5	< 0.1
P_2O_5	0.2	0.3	0.2	< 0.1	< 0.1
SO_3	8.8	42.6	3.6	9.1	2.2
LOI	0.9	20.3	1.0	3.7	4.7

3. Acceleration of slag cement S1

S1 contained 48% slag and 52% portland cement. According to the European standard EN 197-1, S1 is a CEM III-A cement. The average diameter of the particle size distribution was 26 µm. S1 phase composition is presented in Fig. 1.

Four CSA cements were used in this first series of tests: CSA30, CSA40, CSA50, and CSA60. Standard mortars containing slag cement S1 and CSA were prepared. The S1/CSA ratio was 60/40. The sand to cement ratio was 3/1, and the water to cement ratio was 0.5. Prismatic bars (40 mm x 40 mm X 160 mm) were cast and kept in molds for 24 hours. Then, they were immersed in water. The compressive strength of these mortars was measured at 24 hours, 48 hours, and 7 days. It was compared to that obtained on mortars containing either plain S1 cement or CEM II-A white cement, usually utilized in concrete blocks.

The presence of portland cement in S1 reduced the time of workability of mortars prepared with S1 + CSA, as shown in Table 4. It was necessary to add a retarder (potassium tartrate) to get a good time of workability. The amount of retarder was 1% of the CSA weight.

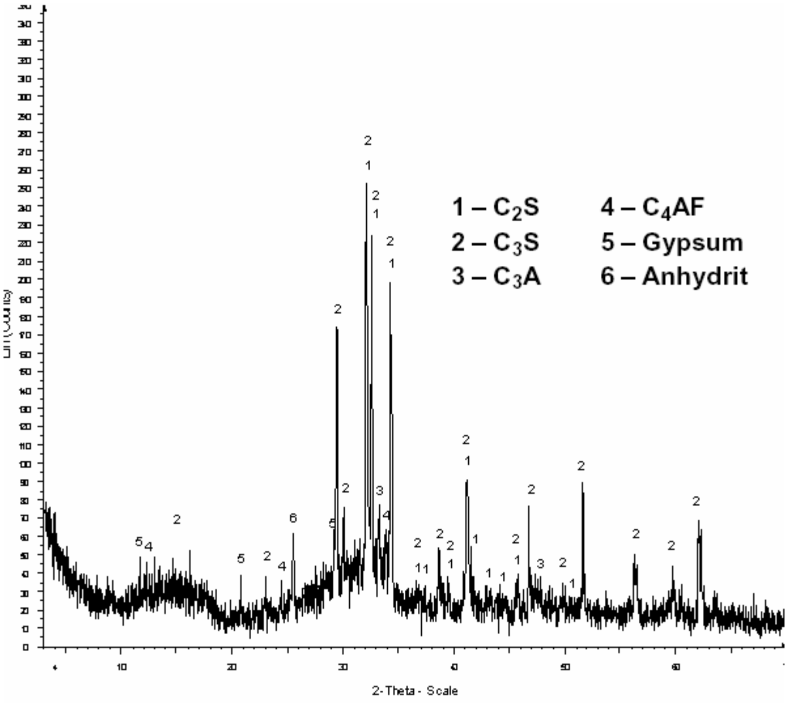


Figure 1 — Phase composition of S1.

Table 4 — Influence of a retarder on the time of workability of mortars.

Cement: S1 +		CSA 30	CSA 40	CSA 50	CSA 60
Time of workability (min.)	Without retarder	< 5	< 10	10	< 15
	With retarder	30	40	60	60

The 24-hr compressive strength of mortars is presented in Fig.2. The highest accelerating effect was obtained when using CSA50: the compressive strength reached 29.3 MPa, only 7.1 MPa for mortar prepared with plain S1, and 11.8 MPa for mortar cast with white portland cement.

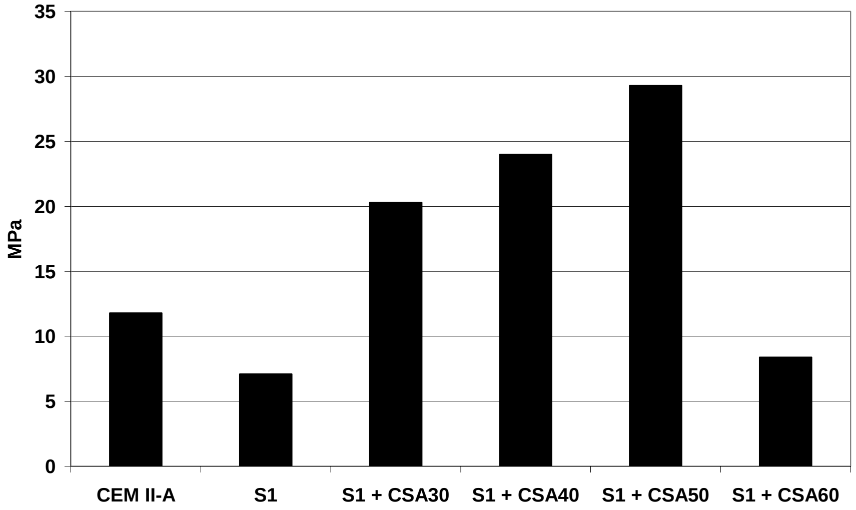


Figure 2 — 24-hr compressive strength of mortars prepared with S1.

The evolution of compressive strength versus time is reported in Fig. 3. After 7 days, the strength of mortars prepared with CEM II-A, S1, and S1 + CSA 50 was about the same. Other combinations of S1 and CSA led to lower strength.

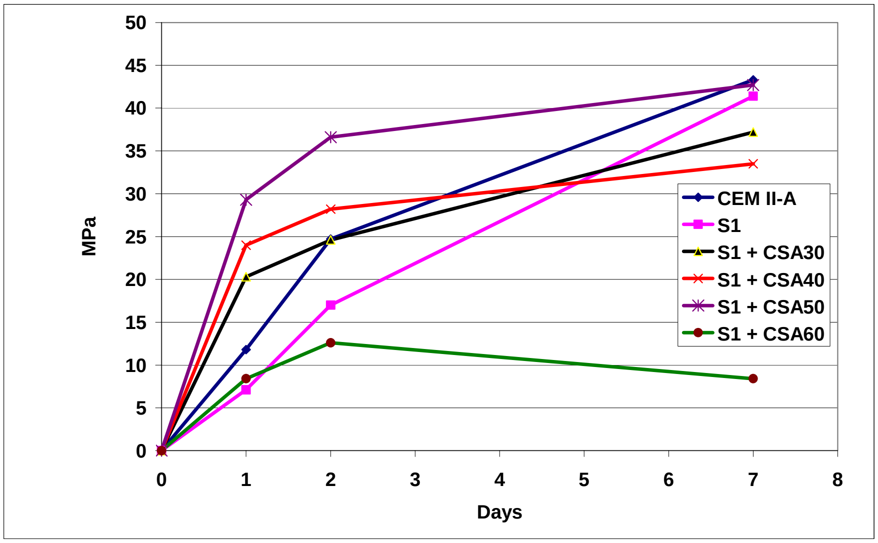


Figure 3 — Evolution of compressive strength versus time.

4. Acceleration of slag cement S2.

S2 was composed of 85% slag and 15% anhydrite. The average diameter of the particle size distribution was 23 µm. S2 phase composition is presented in Fig. 4.

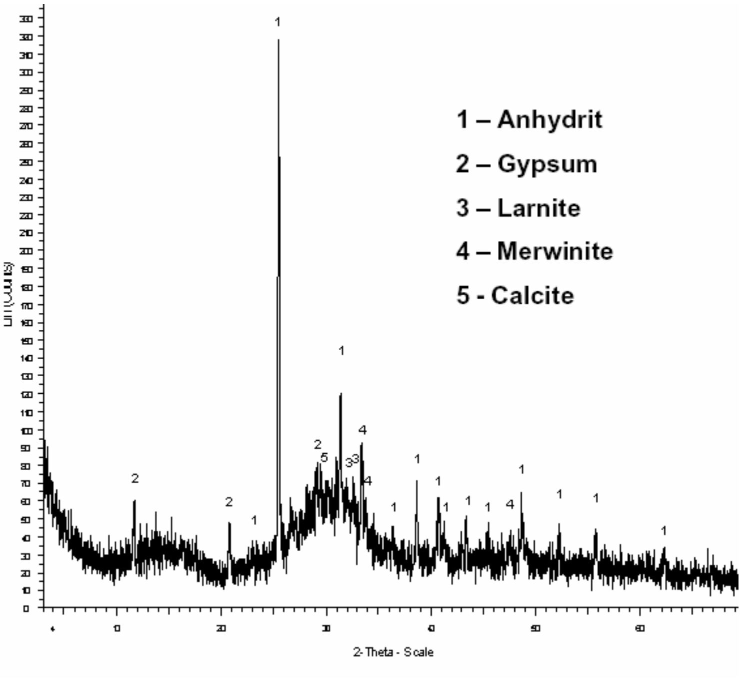


Figure 4 — Phase composition of S2.

Six CSA cements were used in this first series of tests: CSA0, CSA15, CSA30, CSA40, CSA50, and CSA60. Standard mortars containing slag cement S2 and CSA were prepared. The S2/CSA ratio was 60/40. The sand to cement ratio was 3/1, and the water to cement ratio was 0.5. Prismatic bars (40 mm x 40 mm X 160 mm) were cast and kept in molds for 24 hours. Then, they were immersed in water. The compressive strength of these mortars was measured at 24 hours, 48 hours, and 7 days. It was compared to that obtained on mortars containing either plain S2 cement or CEM II-A white cement, usually utilized in concrete blocks.

In this case, it was not necessary to add any retarder to get a good time of workability. This value was higher than 60 minutes for each mortar. The absence of calcium hydroxide yielded by Portland cement can explain this behaviour: when calcium sulfoaluminate cement reacts with calcium hydroxide, a drastic reduction of workability appears due to the quick precipitation of ettringite. The 24-hr compressive strength of mortars is presented in Fig.5. The highest accelerating effect was obtained when using CSA0 or CSA15: the compressive strength reached 20.1 or 18.9 MPa, while it was only 6.4 MPa for mortar prepared with plain S2, and 11.8 MPa for mortar cast with white portland cement.

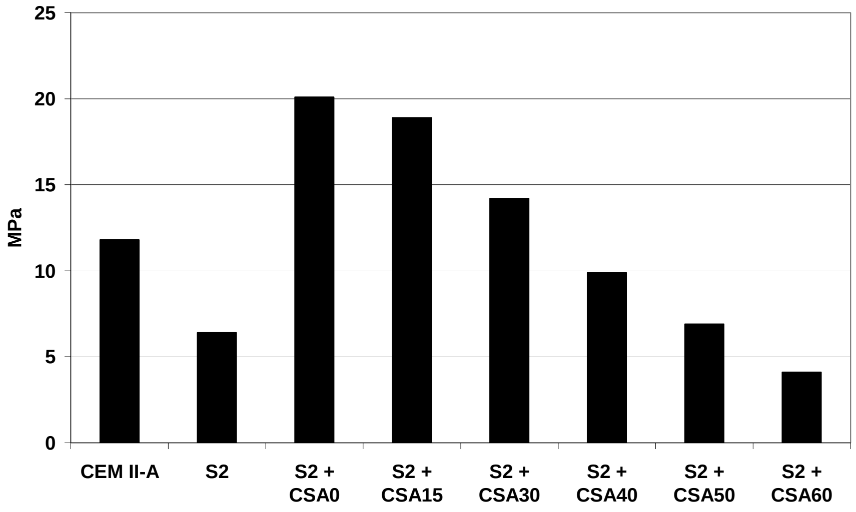


Figure 5 — 24-hr compressive strength of mortars prepared with S2.

The evolution of compressive strength versus time is reported in Fig. 6. The mechanism of acceleration of S2 is totally different of that observed for S1. For S1, the best acceleration was obtained with CSA50, while it is obtained with either CSA0 or CSA15 for S2. The samples containing CSA30, CSA40, and CSA50 cracked after 2 days of hydration. For S2, the performances were lower than for S1 after 7 days of hydration.

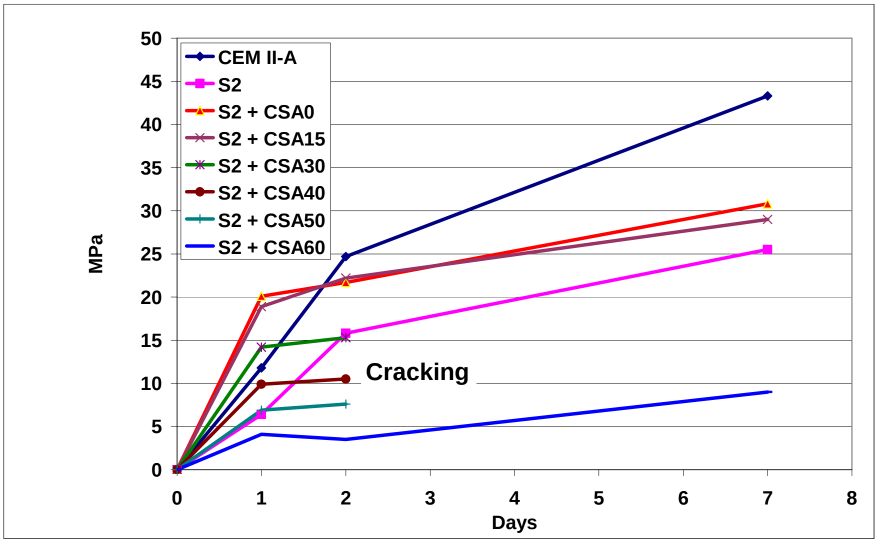
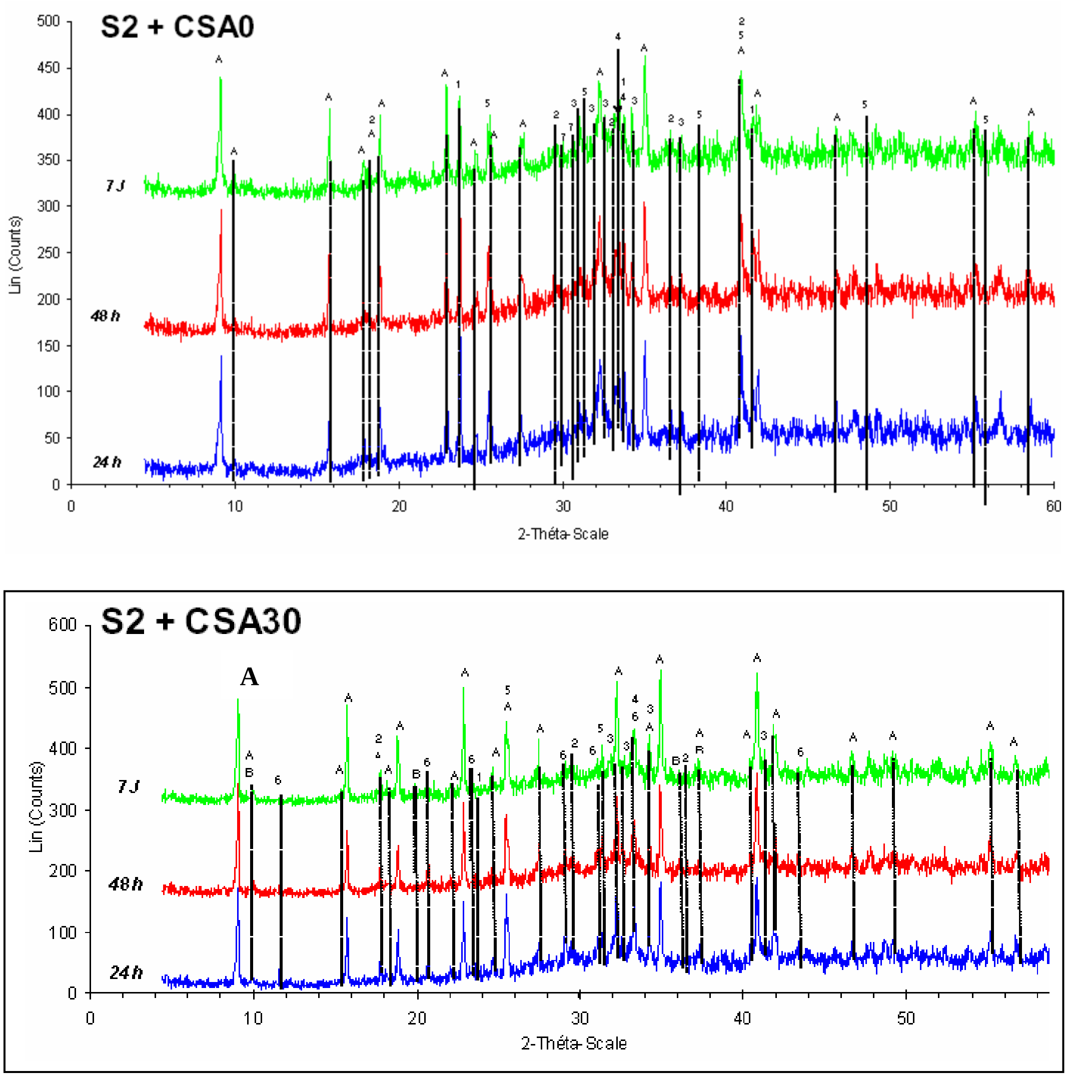


Figure 6 — Evolution of compressive strength versus time.

In order to understand the appearance of cracks, the microstructure was investigated by X-ray diffraction. The results are presented in Fig. 7.



1 -	Yeelimite
2 -	Mayenite
3 -	C_2S
4 -	Merwinite
5 -	Anhydrite
6 -	Gypse
7 -	Calcite

A -	Ettringite
B -	Afm
C -	Gibbsite
D -	Calcium carbo-aluminate

Figure 7 — Microstructure of cements.

As shown in Fig.7, all gypsum is consumed at 24 hours in the sample containing S2 + CSA0, and the production of ettringite is very regular versus time. The sample does not crack. Residual gypsum is still found in the sample S2 + CSA30, at 24 and 48 hours. After 7 days, it disappears and leads to the formation of delayed ettringite which precipitates in an established matrix, leading to cracking. When ettringite precipitates very early, as in (S2 + CSA0), it is not swelling, and no crack appears.

5. Preparation of colored concrete blocks.

Until now, the manufacturer prepared his blocks with a mixture of white portland cement (CEM II-A) and metakaolin. Metakaolin is introduced in the binder to prevent efflorescence. The composition of one tonne of concrete for blocks is given in Table 5.

Table 5 — Composition of one tonne of concrete for blocks.

Compound	Content (Kg)
Sand 0/5 mm	430
Sand 0/2 mm	140
Coarse aggregate 4/8 mm	300
CEM II-A	80
Metakaolin	50
Magnesium stearate	0.8
Chemical admixture	0.2
Water content	5.7%

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Instead of using (CEM II-A + metakaolin), a new binder was introduced in the recipe, consisting in:

- either 60% S2 + 40% CSA15,
- or 50% S2 + 50% CSA.

This second binder was chosen to see if an increase in the CSA content had a significant influence on the performances of the blocks. In any case, the mixture (60% S2 + 40% CSA15) was cheaper.

The content of other compounds was maintained. Blocks were cast and their compressive strength was measured at 24 hours and 7 days of age. The results obtained are shown in Table 6. This Table points out the accelerating effect of CSA15. At 7 days, all blocks presented similar performances.

Table 6 — Compressive strength of concrete blocks.

Binder	Compressive strength (MPa)	
	1-d	7-d
CEM II-A : 80 Kg Metakaolin: 50 Kg	5.2	8.9
S2: 78 Kg CSA15: 52 Kg	6.2	8.7
S2: 65 Kg CSA15: 65 Kg	7.5	9.0

6. Conclusions

Based on the above results, the following conclusions can be made:

1. Calcium sulfoaluminate cement is a strong accelerator of slag cement, especially at 24 hours.
2. The mechanism of acceleration depends upon the composition of slag cement.
3. For each type of slag cement, it is necessary to adjust the proportions between calcium sulfoaluminate clinker and gypsum.
4. The introduction of calcium sulfoaluminate cement in the recipe of concrete blocks increases the compressive strength at one day of age and does not modify the performance at seven days.

7. References

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