Experimental Studies of Hydration Mechanisms of Sulfoaluminate Clinker

A. Alaoui[1], V. H. Nguyen[1], L. Divet[2], A. Feraille[1], R. Le Roy[1]
[1]*ENPC LAMI, Marne la Vallée, France ;* [2]*LCPC, Paris, France*

1. Introduction

Calcium sulfoaluminate (CSA) cements are made commercially by intergrading to a fine powder together with added gypsum, a CSA clinker having yeelimite ($C_4A_3\overline{S}$), belite (C_2S) and an aluminate rich ferrite as its major minerals. The performance and use of CSA cement in civil engineering and as special cements during the last decade have been reviewed recently [[1-9]]. Sulfoaluminate clinker presents a very interesting alternative to Portland clinker regarding sustainable development. As a matter of fact, clinkering sulfoaluminate cements produces less carbon dioxide [1], [18]. CSA systems exhibit also interesting properties such as high early age and long term strengths, and low shrinkage [19].
Knowledge of the early hydration of CSA cements is important because early hydration relates not only to the behavior of fresh concrete but also to the final mechanical properties and durability of the hardened concrete. In this respect CSA cements do not differ from other cement types, for example Portland cement, although the time-scale to achieving strength is shortened owing to rapid hydration kinetics of CSA types. The key component of CSA is the compound calcium sulfoaluminate ($C_4A_3\overline{S}$), due to its ability of generating ettringite ($C_6A\overline{S}_3H_{32}$) when combined with water and calcium sulfate ($C\overline{S}$).

This study aims to a better understanding of the hydration mechanisms of the mix sulfoaluminate clinker - gypsum, versus stochiometry in order to control some durability indicators of the system.
In this paper, we first present a review on the hydration of these cements, then the used materials and the experimental program. We then present obtained results and discuss them to finally conclude.

2. Review on hydration mechanisms

The $C_4A_3\overline{S}$ hydration has been extensively studied in the past [[5, 7, 10-16]]. The hydration of $C_4A_3\overline{S}$ depends on whether calcium sulfate and calcium hydroxide are also present, and progresses at temperatures up to 75° C as follows [7, 14] :

- In pure water $C_4A_3\overline{S}$ yields monosulfate ($C_4A\overline{S}H_{12}$) and aluminum hydroxide (AH_3) as products of hydration:

$$C_4A_3\overline{S} + 18H \rightarrow C_4A\overline{S}H_{12} + 2AH_3 \quad (1)$$

- If mixed at a molar ratio of at least 1:2, mixes of $C_4A_3\overline{S}$ and gypsum ($C\overline{S}H_2$) yield ettringite alone, and a combination of ettringite and monosulfate if the amount of gypsum is reduced. In both cases, aluminum hydroxide is simultaneously formed as a reaction product:

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + 36\,H \rightarrow C_6A\overline{S}_3H_{32} + 2AH_3 \quad (2)$$

$$2C_4A_3\overline{S} + 2C\overline{S}H_2 + 52\,H \rightarrow C_6A\overline{S}_3H_{32} + C_4A\overline{S}H_{12} + 4AH_3 \quad (3)$$

- In the presence of sufficient amounts of both gypsum and calcium hydroxide, ettringite is formed as the unique reaction product:

$$C_4A_3\overline{S} + 8C\overline{S}H_2 + 6CH + 74\,H \rightarrow 3\,C_6A\overline{S}_3H_{32} \quad (4)$$

$$AH_3 + 3CH + 3C\overline{S}H_2 + 20\,H \rightarrow C_6A\overline{S}_3H_{32} \quad (5)$$

The calcium hydroxide in reactions 4 and 5 may be derived from the hydration of belite (C_2S). The C_2S hydration forms the C-S-H and the portlandite CH:

$$2C_2S + 4H \rightarrow 3C\text{-}S\text{-}H + CH \quad (6)$$

The objective of this paper is to investigate the role of $C_4A_3\overline{S}$; $C\overline{S}$ contents and water to cement ratio (W/C) in regulating the behavior of calcium sulfoaluminate-based cements. The SO_3/Al_2O_3 ($\overline{S}/A$) ratio was varied to allow to find the optimal gypsum quantities.

3. Experimental program

Different tests were performed on concrete to estimate the influences of the $\overline{S}/A$ ratio and water to cement ratio, W/C, on the chemical, physical and mechanical properties. The concrete was composed of siliceous aggregates and cement made of a mix of sulfoaluminate clinker and gypsum.

3.1 Materials and samples

a) Cement and gypsum

The cement used is a mix of sulfoaluminate clinker and gypsum. The clinker used has the chemical composition which is presented in Table 1. From the chemical analysis, we determine the SO_3/Al_2O_3 ratio ($\overline{S}/A$ ratio) of the sulfoaluminate clinker (CSA). This leads to the value of 0.56. We then add gypsum to this clinker in order to obtain desired values of $\overline{S}/A$ (i.e. 1.1, 1.64 and 2.17). These ratios are selected based on similar work on the mortar of [17]

component	PF	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	P_2O_5	SrO	SO_3	Na_2O	K_2O
% mass	0,75	7,35	31,51	1,65	1,58	0,04	41,15	0,76	0,14	0,19	13,80	0,19	0,51

Table 1 : Chemical composition of sulfoaluminate clinker

Following the mineralogical analysis, this clinker consisted of the following major hydraulic phases:

- $C_4A_3\overline{S}$ (calcium sulfoaluminate): 53 %
- Calcium silicates: (majority C_2S + trace of C_3S): 18 %
- $C\overline{S}$ (Calcium sulfate): 12 %

Other constituents are mainly calcium aluminates ferrite, titan and residual siliceous and constitute about 15%.
BLUE SULYKAL DH gypsum is used. The chemical composition is presented in Table 2

Chemical composition	P_2O_5	SO_3	CaO	K_2O	Na_2O	Fe_2O_3	Al_2O_3	SiO_2	F
% mass	0,06%	46,87%	32,25%	0,01%	0,15%	0,01%	0,02%	0,36%	0,01%

Table 2 : Chemical composition of gypsum

b) Aggregates

The siliceous aggregates Palvadeau are used to avoid undesired reactions. Three types of sand and two types of gravel are used. The compositions of the granular skeleton for the concrete formulations were determined by Beton-Lab software to achieve the best compacity. Their characteristics are given in Table 3. The final granulometry of concrete is presented on Figure1.

Aggregates	Diameter (mm)	Kg/m^3 of concrete
S1: Sand Palvadeau 0/0.315	0 - 0.315	80
S2: Sand Palvadeau 0.315/1	0.315 – 1	130
S3: Sand Palvadeau 1/4	1 – 4	330
G1: Gravel Palvadeau 4/8	4 – 8	300
G2: Gravel Palvadeau 8/12	8 – 12	805

Table 3: Characteristics of aggregates

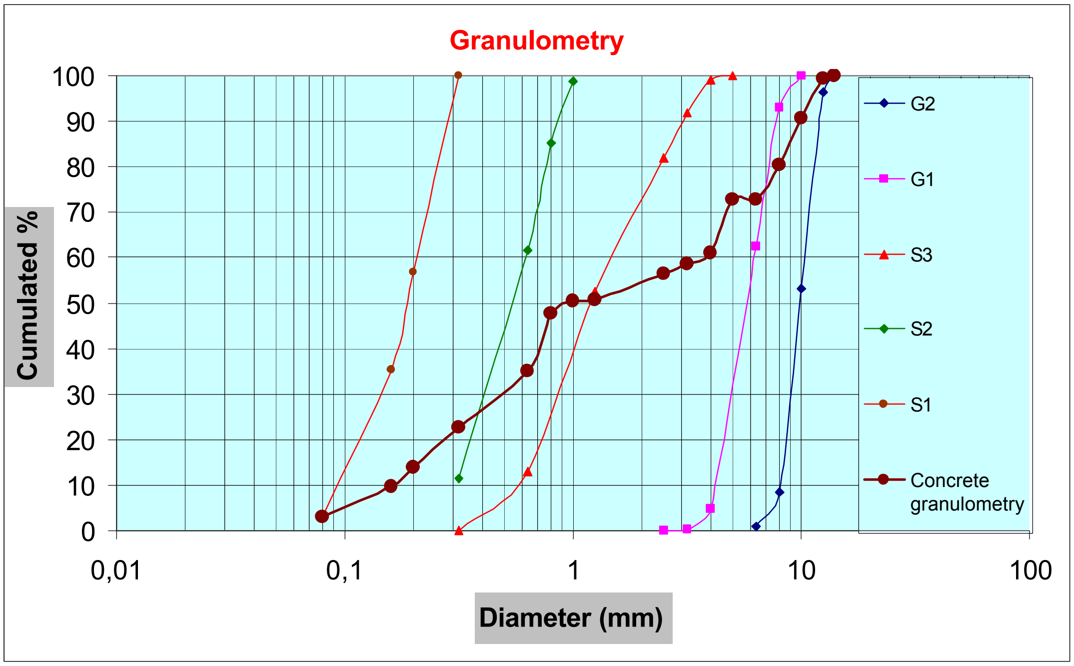

Figure 1: Granulometry of aggregates and concrete

c) Samples

In our experimental program, tests are performed on concrete cylinder specimens to evaluate the hydration temperature, expansion and compressive strength of the concrete. The standard cylindrical specimen is 11 cm in diameter by 22 cm long. The samples are then conserved in a conservation room at 20°C and more than 95 % of humidity.

3.2 Concrete composition

All concrete were made using 400 kg of cement (mix of gypsum and CSA), for $1m^3$ of concrete.
Studied formulations are presented in Table 4, where the water to cement ratio (W/C) varies from 0.6 to 0.7; and $\overline{S}/A$ ratio is respectively 0.56, 1.1, 1.64 and 2.17.

Formula	AE	BE	CE	DE	AF	BF	CF	DF
$\overline{S}/A$	0,56	1,1	1,64	2,17	0,56	1,1	1,64	2,17
W/C	0,6	0,6	0,6	0,6	0,7	0,7	0,7	0,7
CSA (kg)	400	310	254	215	400	310	254	215
Added gypsum (kg)	0	89	145	184	0,00	89	145	184
% of added gypsum	0	22	36	46	0	22	36	46
Water (kg)	246	246	246	246	286	286	286	286

Table 4 : Composition of studied formula (for a $1m^3$ of concrete)

3.3 Experiments

a) <u>Slump test</u>

The slump test is performed on newly mixed concrete. To perform the test, we use a slump cone (also known as Abrams cone). Measures are performed at the end of mixing and at ages 30 min, 1 hour, 1 hour and 30 min and when possible 2 hours.

b) <u>Expansion test</u>

This test allows measuring the expansion of the specimen put into water. The samples are conserved immersed in water. The principle of this test consists in jointing studs on three generators of the specimen placed at 120° (see Figure). On each generator, the initial distance between the two studs (l_0) is almost equal to 10 cm and is precisely measured. We then measure the evolution of this distance between the two studs (l) to determine the expansion: $e = \frac{l - l_0}{l_0}$

Figure 2: Jointing the studs on the specimen

c) <u>Exothermal test</u>

Newly mixed concrete is poured into the sample mold and placed into the calorimeter. This test setup for the hydration temperature measurements is shown in Figure 3. The temperature inside the specimen was measured by a thermocouple placed in the centre of the specimen. After the filling of the mold, the whole set is transferred to the conditioned room and the thermocouple connection is plugged in the acquisition system. The measurements were continuously controlled by the acquisition system.
These tests were performed on formula AE, BE, CE and CF.

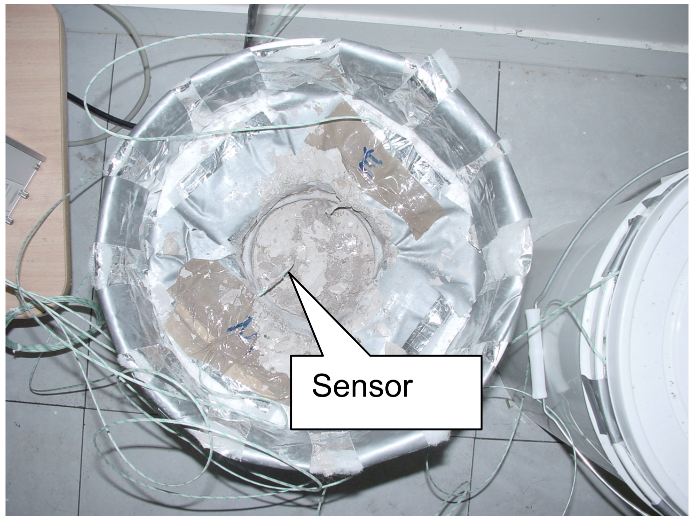

Figure 3: Calorimeter for exothermal test

d) <u>Water porosity</u>

The measurement of porosity to water is carried out on cylindrical sections of concrete cylinder specimens of age higher than 28 days. Three samples are used for each concrete formula.

After a first drying of the samples, we determine their weight. This weight is used as value of reference (initial dry weight).

The samples are then placed in vacuum cell in which we maintain a vacuum of 50 mbars during 5 hours. Then, we allow the water transfer into the cell until the sample is totally immersed. The reduced pressure is maintained for 20 hours.

After this period of time, we pressurize slowly the cell to reach the ambient pressure. A second weighing is then conducted with the sample totally immersed in water. We determine the apparent weight in water (water weight). Next step consists in a light drying using a wet sponge, and a rapid new weighing. This third weighing permits us to determine the wet weight of the sample in the air (air weight).

The last stage consists in drying the sample until the complete stabilization of its weight. We thus determine the final dry weight.

With these weight values, we can calculate the volume of the sample, the porosity f of the material and its apparent density r.

4. Results and discussion

4.1 Slump

Slump measured values of different formulations are given in Table 5.

Concrete formula	W/C	$\overline{S}/A$	0'	30 min	1 h	1h 30 min	**2 h**
AE	0.6	0.56	18	6,5	-	-	**-**
BE	0.6	1.1	20,5	13,5	4,5	3	**-**
CE	0.6	1.64	19,5	17	9	6	**3,5**
DE	0.6	2.17	18	9,5	-	-	**-**
AF	0.7	0.56	21	-	-	-	**-**
BF	0.7	1.1	23	18	-	-	**-**
CF	0.7	1.64	22,5	19	4	-	**-**
DF	**0.7**	**2.17**	**24**	**19,5**	**16**	**-**	**-**

Table 5: Slump values (in cm) for concrete formula

As we can notice, at the fixed value of W/C = 0.6, when the $\overline{S}/A$ ratio increases, the workability is improved and the setting time is also increased until the value $\overline{S}/A$ = 1.64.
At the fixed value of W/C = 0.7, both the workability and the setting time are improved when increasing the $\overline{S}/A$ ratio.
But for a fixed value of $\overline{S}/A$ ratio, increasing the water content leads to a shorter setting time, except for $\overline{S}/A$ = 2.17, which is very unusual for concrete!
We can also notice that for $\overline{S}/A$ = 0.56 (no added gypsum to the CSA) the setting time is extremely short (less than 30 min with W/C = 0.7!).

4.2 Expansion test

The measures were conducted for more than five months and are still continued. For each concrete formula, three samples are equipped and we present results on figures 4 and 5. The mean value corresponds to nine measures (three samples with three pairs of studs). The error bar represents twice the standard deviation of the measures.
As we see on the figures, for both values of W/C, concrete formula with $\overline{S}/A$ = 0.56 are instable and lead to an expansive concrete. We can thus think that part of the ettringite formed during the hydration is a secondary ettringite, known to be expansive.

For other values of $\overline{S}/A$, the strain is quite moderate, mainly expansive except a slight shrinkage for formula DE.
But the great surprise came from the "explosion" of all samples of formula CF after immersion into water, as shown on the image! This is the reason why no expansion

result is available for this formula. We try to explain this observation in the next section.

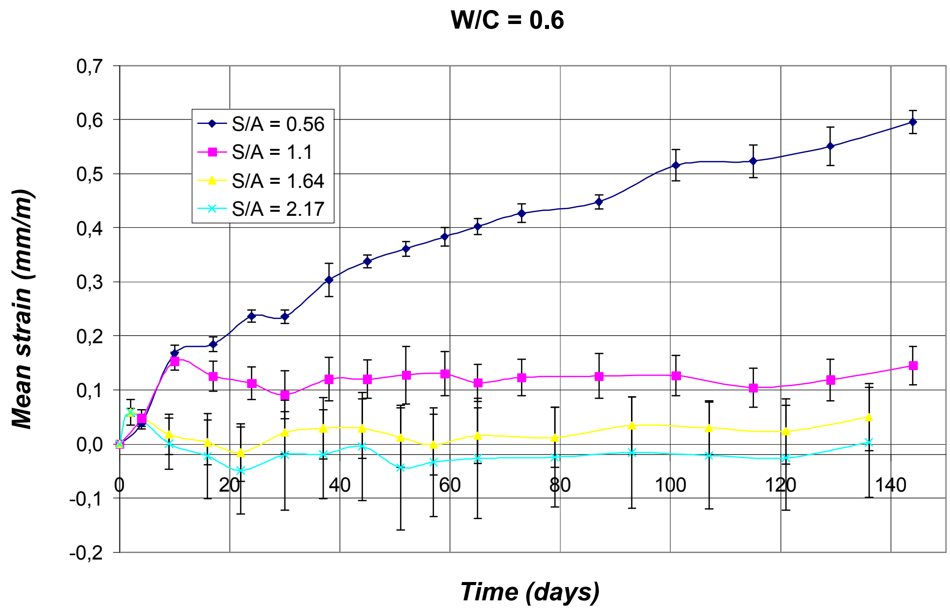

Figure 4: Expansion evolution for concrete formula at W/C = 0.6

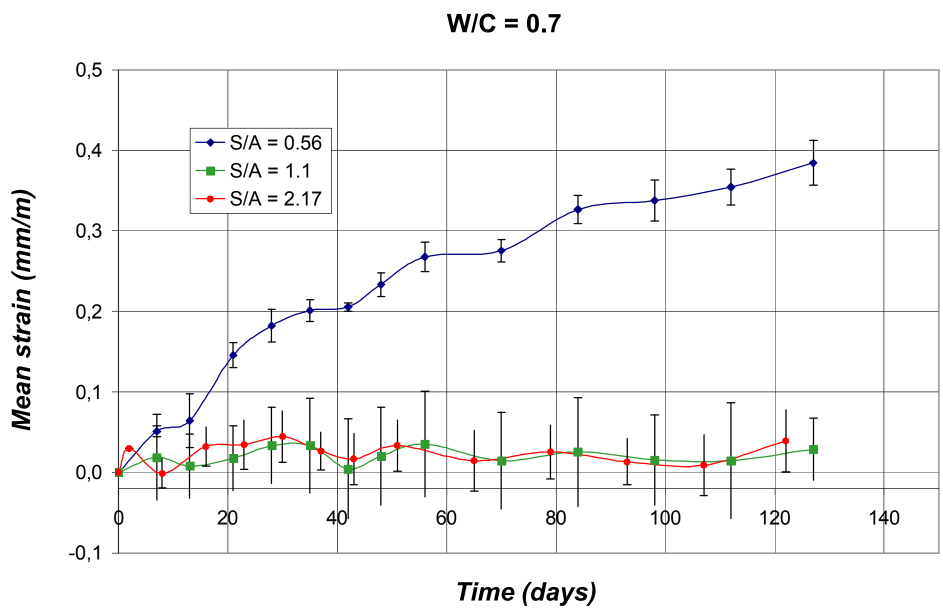

Figure 5: Expansion evolution for concrete formula at W/C = 0.7

4.3 Exothermal test

The evolution of temperature inside the sample was measured by a thermocouple placed in the centre of the specimen. The measured curves, for formula AE, BE, CE and CF are presented on figure 6. Formula AE, BE, CE were chosen due to the longer setting time observed from slump tests and to evaluate the effect of $\overline{S}/A$ ratio, and formula CF is chosen to try to explain the instability that occurred with the expansion test.

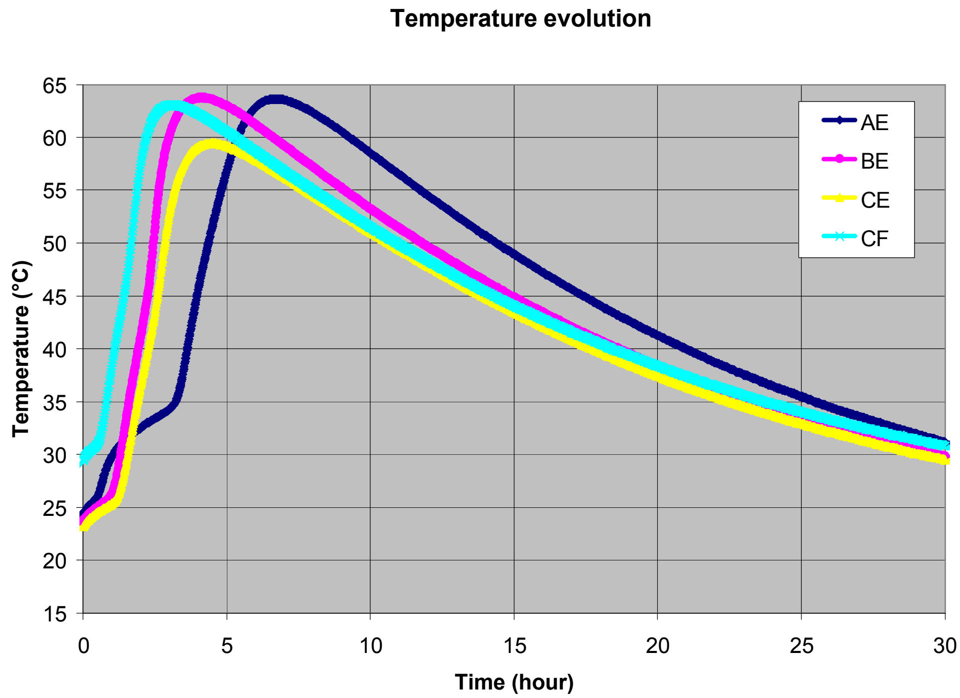

Figure 6: Temperature evolution during the hardening of concrete.

As we can notice, the peak temperature is nearly constant around 63 °C, except for formula CE for which the peak temperature is around 60°C. But the hydration kinetic varies a lot:

- Indeed, for formula AE (with no added gypsum), the hydration takes place in three phases and the total time to achieve the hydration is quite long (about 6 hours and 30min). We also notice that there exist a specific phase that may correspond to the production of monosulfate (equation (1))
- For both BE and CE formula, we can observe two phases in the hydration kinetic corresponding to phase 1 et 3 of the hydration of AE. As phase 2 has disappeared, the hydration time is shortened and is around 4 hours and a half. Adding more gypsum (formula CE) leads to a slight decrease in peak temperature and a slight increase in hydration time (duration up to peak temperature), but the total hydration energy is almost constant.
- Finally for formula CF, the first phase is very rapid and leads to a very short hydration time of about 3 hours. This can explain the rapid loss of workability for this concrete formula between 30 min and 1 hour as we measured a slump fall from 19 cm to 4 cm.

The whole observations are summarized in table 6, where we can compare peak temperature during hydration, hydration time and what we called “Energy up to Peak temperature" corresponding to the integral of temperature with respect to time.

Formula	Peak temperature	Hydration time (hours)	"Energy up to Peak temperature"
AE	63,60	6,50	1126581,0
BE	63,80	4,23	812096,4
CE	59,50	4,50	802668,6
CF	63,00	2,97	655987,2

Table 6: Summary of important hydration factors

We can conclude that the hydration time is the most critical parameter with respect to hydrates stability in the material. However, energy plays also an important role compared to expansion stability, as formula AE developed 32,8% more energy during the hydration phase.

4.4 Water porosity

Results are presented in table 7. The mean value of porosity is high in regard with general values for similar concretes based on Portland cements (almost twice the value).

Concrete formula	W/C	$\overline{S}/A$	f (%)	r (***10^{-3} kg/m^3***)
AE	0.6	0.56	12.52	**2.2**
BE	0.6	1.1	19.42	**2.16**
CE	0.6	1.64	21.92	**2.11**
DE	0.6	2.17	23.40	**2.06**
AF	0.7	0.56	18.15	**2.16**
BF	0.7	1.1	22.94	**2.07**
CF	0.7	1.64	19.46	**2.16**
DF	**0.7**	**2.17**	**22.0**	**2.1**

Table 7: Water porosity values and apparent density of concrete formula

As we can notice, at the fixed value of W/C = 0.6, when the $\overline{S}/A$ ratio increases, porosity also increases and the apparent density decreases.
But at value W/C = 0.7, there is no clear tendency even if for the instable formula CF, the porosity value is lowered.

5. Conclusion

This experimental study enabled us to highlight important parameters controlling the hydration and the behavior of sulfoaluminate cements. We confirmed the importance of both water to cement ration and $\overline{S}/A$ ratio on rheological and physical behavior of these cements, due to their interaction during the hydration phase. However, an increase in the water to cement ratio can lead to a reduction in workability, which is against the intuition and deserves a more thorough exploration.

One very important result is that instability related to ettringite formation during the concrete hardening is either due to a very rapid hardening (case CF where the hydration time is less to 3 hours) or to very exothermic hydration (case AE, where we noticed non stabilized expansion of samples).

We have also been able to find optimal values of water to cement ration and $\overline{S}/A$ ratio with respect to the stability of concrete, and it corresponds to formula BE (W/C= 0.6 and $\overline{S}/A$ =1.1).

Of course, these results must be validated by chemical and physical analyses on cement pastes during hydrati on, which is programmed for next year.

6. Reference

[1] Ambroise, J. and J. Pera, *Développement de matériaux de construction à partir de phosphogypse*. 2003, U.R.G.C Matériaux INSA de Lyon.

[2] Beretka, J., et al., *Energy-saving cements obtained from chemical gypsum and other industrial wastes.* Waste Management, 1996. **16**(1-3): p. 231-235.

[3] Beretka, J., et al., *Hydraulic behaviour of calcium sulfoaluminate-based cements derived from industrial process wastes.* Cement and Concrete Research, 1993. **23**(5): p. 1205-1214.

[4] Beretka, J., et al., *Utilization of industrial wastes and by-products for the synthesis of special cements.* Resources, Conservation and Recycling, 1993. **9**(3): p. 179-190.

[5] Beretka, J., et al., *Influence of calcium sulfoaluminate over-bar content and W/S ratio on the performance of calcium sulfoaluminate-based cements.* Cement and Concrete Research, 1996. **26**(11): p. 1673-1681.

[6].Brown, A.D.R. *Application of calcium sulfoaluminate cements in the 21st century*. 1993. Dundee, UK: Publ by E. & F.N. Spon, London, Engl.

[7] Odler, I., *Special inogranic cement*. Mordern concrete technology, ed. A. Bentur. Vol. 8. 2000, New York: E & FN SPON.

[8] Pera, J. and J. Ambroise, *New applications of calcium sulfoaluminate cement.* Cement and Concrete Research, 2004. **34**(4): p. 671-676.

[9] Singh, M., S.N. Upadhayay, and P.M. Prasad, *Preparation of special cements from red mud.* Waste Management, 1996. **16**(8): p. 665-670.

[10] Kasselouri, V., et al., *Study on the hydration products of a non-expansive sulfoaluminate cement.* Cement and Concrete Research, 1995. **25**(8): p. 1726-1736.

[11] Mehta, P.K., *Mechanism of expansion associated with ettringite formation.* 1973. **3**(1): p. 1-6.
[12] Zhang, L. and F.P. Glasser, *Hydration of calcium sulfoaluminate cement at less than 24 h.* Advances in Cement Research, 2002. **14**(4): p. 141-155.
[13] Janotka, I., et al., *The hydration phase and pore structure formation in the blends of sulfoaluminate-belite cement with Portland cement.* Cement and Concrete Research, 2003. **33**(4): p. 489-497.
[14] Hanic, F., I. Kapralik, and A. Gabrisova, *Mechanism of hydration reactions in the system C_4A_3S-CS-CaO-H_2O referred to hydration of sulphoaluminate cements.* Cement and Concrete Research, 1989. **19**(5): p. 671-682.
[15] Barnier, *Synthèse et étude de l'hydratation de ciments a base de silicate dicalcique sulfate*. 1986, Ecole des Mines de Paris.
[16] Cottin, B., *Hydratation et expansion des ciments.* Ann. Chim. Fr, 1979. **4**: p. 139.
[17] Sudoh, G., T. Ohta, and H. Harada. *High strength cement in the CaO-Al_2O_3-SiO_2-SO_3 system and its applications*. in *7è congrès de la chimie des ciments* 1980. Paris.
[18] Feraille F. et al. *New cements for sustainable development* , ICCC'2007, Montréal, Canada.
[19] Alaoui A. et al. *Experimental study of sulfoaluminate concrete based materials*, CONSEC'07, Tours, France