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Investigation into relations among technological properties, hydration kinetics and early age hydration of self-leveling underlayments

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ABSTRACT

Technological properties such as flow value, setting times, compressive strength and early age dimensional stability as linear shrinkage and expansion have been studied for two types of self-leveling underlayments (SLU) in which the kind of calcium sulfates was varied. The influence on hydration kinetics has been measured by isothermal heat flow calorimetry. The results obtained for the technological properties change significantly when different kinds of calcium sulfates are used. The basic trend for the results changes when the composition changes from a calcium aluminate cement system to a Portland cement system. Additionally, there was an interesting relationship to final dimensional stability and shape of heat evolution curve. Moreover the time to reach plateau of dimensional stability was related to the development of compressive strength. In the meanwhile, using hemihydrate in Portland cement systems caused low compressive strength and significant expansion. On the other hand, in the results of XRD measurements, the first genesis of Ettringite corresponded to the first shrinkage of SLU. Interesting results related with technological properties and hydration kinetics or the results of XRD other than these above results were obtained.

1. Introduction

In recent years, self-leveling underlayments (SLU) with high flow ability and self-smoothing properties are often used on a concrete floor in various fields, such as new-building construction and repair work. As for the place where it is used, office buildings, apartments, stores, schools, hospitals, factories, parking lots, vessels, etc. are greatly varied. Moreover, the customer's performance demand is increasing. Advance of performances, such as workability, rapid drying, rapid hardening, shrinkage compensation, smooth nature, etc. is desired. Thus, for SLU becoming diversified and high performance materials, there is a serious need for understanding fundamental mechanisms.

Meanwhile, calcium aluminate cement (CAC) is known as a highly efficient material, and is an indispensable material in the construction field. In the dry mix mortar industry (tile cements, self-leveling screeds…), CAC is the essential part of the hydraulic binder and is used as a formulation constituent, i.e. as a chemical reactant. This is why this industry is also called “Building Chemistry Industry”. SLUs of a CAC system usually consist of three binders (CAC, Portland cement (OPC) and calcium sulfates (C$)) which react with water, and exhibit together improved hardening characteristics, faster drying and better dimensional stability as compared to SLUs with only OPC as binder [1]. There are three types of C$ – anhydrite, dihydrate and two modifications as alpha-hemihydrate and beta-hemihydrate – which were used with the mixed binders for different SLU compositions. Upon water contact, anhydrite and dihydrate harden very slowly. But, if alpha-hemihydrate and beta-hemihydrate are mixed with water, they react more quickly and harden. Furthermore, the rate of dissolution and hydration speed of beta-hemihydrate is quicker than alpha-hemihydrate [2]. Thus, when different C$ are used for SLUs, although sometimes against common formulation understanding, natural performances of SLUs themselves differ largely. In order to grasp the fundamental features of SLU, it is very interesting to evaluate the influence of different types of C$ indispensable to SLU combination.

The purpose of this study out of commercial formulations is to grasp what kind of correlation is among technological properties, hydration kinetics and the results of XRD in SLUs. In this study, the influence of C$ on properties such as workability, setting time, strengths, dimensional stabilities, hydration kinetics, and XRD in SLUs based on two binders has been investigated.

2. Literature

In these latter days, there has been some theoretical interest in characteristic features of SLUs. Kighelman et al. have reported for the relation between heat of hydration and generation of Ettringite [3]. In addition, Zurbriggen et al. have demonstrated about “hydration balls” which are typical damages of SLU in storage [4]. Moreover Kighelman

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et al. have analyzed porosities and abrasions from the point of view of SLU's layers [5].

The cause of shrinkage or expansion in mortars is chemical reactions, surface tension of gap water being displaced in a cementitious matrix (drying shrinkage) and plastic shrinkage in the not yet solid material. Bier et al. investigated shrinkage and shrinkage compensation at early ages in binders containing OPC, CAC and C$ [6]. They demonstrated that shrinkage curves could be divided into three phases with a significant shrinkage compensation only being achieved with compositions rich in CAC and sulfate and fast setting mortar systems showing rather high shrinkage as compared to plain OPC or CAC mortars.

Taylor has reported about the general heat evolution of Portland cement paste [7]. According to him, the process may be divided into five stages for the initial reaction, the induction period, the acceleratory period, the deceleratory period and the final period of slow reaction. Furthermore, he has demonstrated the nature of hydration reactions at various peaks in the heat evolution curve.

However, heat evolution curves for binders composed of several active materials show several distinct peaks [1,8,9]. Evju and Hansen [8] for example demonstrated those peaks in the heat evolution curves for materials consisting of CAC, OPC and beta-hemihydrate. They are caused by the formation of Ettringite, the replacement of gypsum, and the formation of C_2AH_8.

3. Experimental

3.1. Formulations of SLU

Formulations of SLUs used in this study are based on two typical combinations which are shown in Table 1. For each formulation the used C$ are shown in Table 2.

The denomination of Ettringite system and CAH–CSH system is used as reported in the past [10,11]. Ettringite system contains mainly CAC with an addition of C$. The properties of this binder mix are dominated by a controlled quick and massive precipitation of Ettringite, which transforms a high amount of mixing water into crystalline bonded water. CAH–CSH system mainly consists of OPC, accelerated by CAC. The aluminium ions are incorporated into the hydrates C_4AH_{13} and Ettringite.

Formulations A to D belong to the region of Ettringite system and formulations E to H belong to the region of CAH–CSH system. In order to grasp the influence of C$ in both systems, the mineral composition and the amount of admixtures for each system were perfectly kept constant. Major modifications in properties were achieved by modifying only the $CaSO_4$ type according to Table 2. Plasticizer, accelerator, retarder and stabilizer were used as admixtures. Water powder ratio was 0.24. The compositions correspond to those reported by Emoto and Bier [1].

The combinations of raw materials for SLUs were dry mixed before the corresponding experiments.

Table 1
Formulations of SLU.

Materials (%)	Ettringite system	CAH–CSH system
Ciment Fondu Lafarge	20	12
Cement CEM I 42.5 R	4	19
Calcium sulfate	7	7
Quartz sand (0.2–0.5 mm)	38	41
Fine grained limestone	28	20
Redispersible powder	2	2
Admixture	0.5	0.5

Table 2
Each of formulations and used calcium sulfates.

Ettringite system formulation	CAH–CSH system formulation	Used calcium sulfate
A	E	Alpha-hemihydrate
B	F	Beta-hemihydrate
C	G	Anhydrite
D	H	Dihydrate

3.2. Methods

Measurements of workability, setting time, compressive strength, dimensional stability, hydration kinetics through calorimetry and X-Ray diffraction were performed for each formulation.

3.2.1. Workability and setting time

Workability was measured using a mini-slump cone. This test as an index of fluidity was measured based on EN 12706 and the mini-slump cone specified by JIS R 5201. The measurements were started immediately after mixing. The spread width in two perpendicular directions on a glass plate was measured without drops after the spread of SLU stopped. The acquired value was recorded as a flow value.

Setting time was measured based on EN 196-3.

3.2.2. Compressive strength

In the experiments compressive strength was measured according to DIN EN 196 standards. Compressive strengths were tested at 6, 12 and 24 h, and 7 days.

3.2.3. Dimensional stability

In this study, the "Schwindrinne" was used for measuring the shrinkage or expansion of SLUs. The used mould is 25 cm in length and a rectangular cross section of 38 mm by 60 mm. The shrinkage or expansion was monitored from immediately after a mixing up to 24 h.

3.2.4. Hydration kinetics

Calorimetric tests as an index of hydration kinetics were measured by using the conduction calorimeter of a triple type. The evolution of heat of hydration was monitored for one day. Characteristic events in heat evolution curves such as inflection point and upward peak are schematically shown in Fig. 1.

3.2.5. X-ray diffraction

For some formulations X-ray diffraction patterns were measured with an X'PERT Pro MPD PW 3040/60 diffractometer from Panalytical with a fast detector in order to check the hydrate formation continuously from mixing.

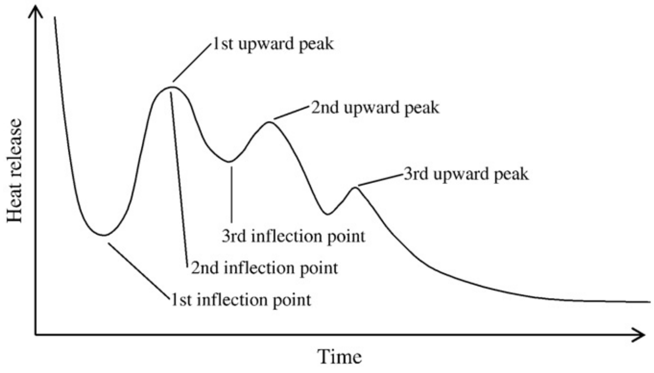

Fig. 1. Defined inflection point and upward peak for heat evolution curves in this study.

4. Results

4.1. Workability and setting time

The flow values and setting times for each formulation are shown in Table 3.

4.1.1. Ettringite system

Formulation B with beta-hemihydrate as $CaSO_4$ material shows the lowest flow ability as compared to the formulations with alpha-hemihydrate, anhydrite or dihydrate, respectively. Flow values are around 30 cm except for B, which shows with a 5 cm lower value a quite significant difference. Generally, flow values are lower than those for the CAH–CSH system.

About setting time, initial set of all formulations is around 50 min and final set around 60 min. The values for the difference between final and initial set (Δ set) are around 15 min. Only formulation B shows slightly lower values for initial, final and Δ set. Additionally, setting time of Ettringite system is much shorter than that of CAH–CSH system except for G.

4.1.2. CAH–CSH system

Comparable to the Ettringite system flow ability exhibited by formulation F with beta-hemihydrate as $CaSO_4$ material shows the lowest values. And the tendency for the different flow values caused by different $CaSO_4$ modifications is also the same as in the Ettringite system. Flow values are around 34 cm except F. The absolute difference between the flow value of F and other formulations is smaller than for the Ettringite system.

In the result of setting time, CAH–CSH system completely differs from Ettringite system. Initial set for all formulations except G range from around 1.5 h to 2 h. Contrary to that the initial set for G is around 30 min. Similarly, final set for all formulations except G range from around 2 h to 3 h, while final set for G is around 1 h. The values for the difference between final and initial set (Δ set) are around 55 min except G, whereas that of G is around 30 min. Setting time of Ettringite system is much shorter than that of CAH–CSH system except G, although the setting time of G is very different from the other formulations in CAH–CSH system.

4.2. Compressive strength

The compressive strength development up to 24 h which was obtained for the Ettringite and CAH–CSH system is shown in Fig. 2.

In Ettringite system, the compressive strength of all formulations shows a sharp rise at 6 h, followed by a slow down thereafter. For all formulations, no cracks were detected up to seven days of age. On the other hand, in the CAH–CSH system, the strength development is different as compared to the Ettringite system. The compressive strength of G with anhydrite as C\$ material is the highest value amongst the other formulations, which is completely contrary to the results of the Ettringite system. The compressive strength of G shows a sharp rise at 6 h followed by a slower increase afterwards. The compressive strength of H with dihydrate shows its sharp rise at 12 h, and follows then G. Formulations E with alpha-hemihydrate and F with beta-hemihydrate did not show any significant increase in strength over 24 h and stay at around 3 to 4 N/mm^2. In addition, the hardened SLU of E and F shows pronounced cracks for both sets of specimens from compressive strength and dimensional stability tests, respectively.

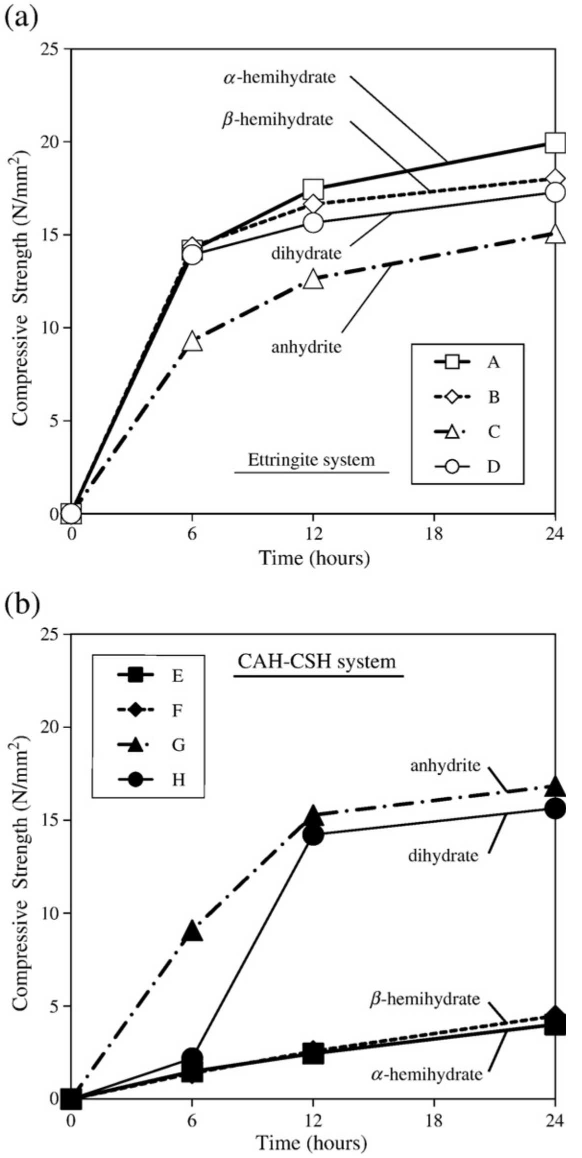

Fig. 2. Compressive strength development; sulfate source indicated in the diagram: (a) Ettringite system, (b) CAH–CSH system.

Table 3
The flow value and setting time.

Formulation		Flow value (cm)	Setting time (hh:mm)		
			Initial	Final	⊿ Final − initial
Ettringite system	A	30.6	0:50	1:05	0:15
	B	25.3	0:46	0:58	0:12
	C	30.3	0:52	1:07	0:15
	D	30.7	0:51	1:05	0:14
CAH–CSH system	E	34.5	1:59	2:52	0:53
	F	32.6	1:26	2:15	0:49
	G	34.0	0:34	1:01	0:27
	H	34.7	1:50	2:48	0:58

4.3. Dimensional stability

The dimensional stability up to 24 h obtained for Ettringite system and CAH–CSH system is shown in Fig. 3.

In the Ettringite system, all formulations except C with anhydrite as C\$ material exhibit expansion, with the expansion of B with beta-hemihydrate being the largest. The dimensional stability curves for all formulations reach a stable plateau within the first 6 h.

In the CAH–CSH system and corresponding to the Ettringite system, all formulations except G with anhydrite as C\$ material show

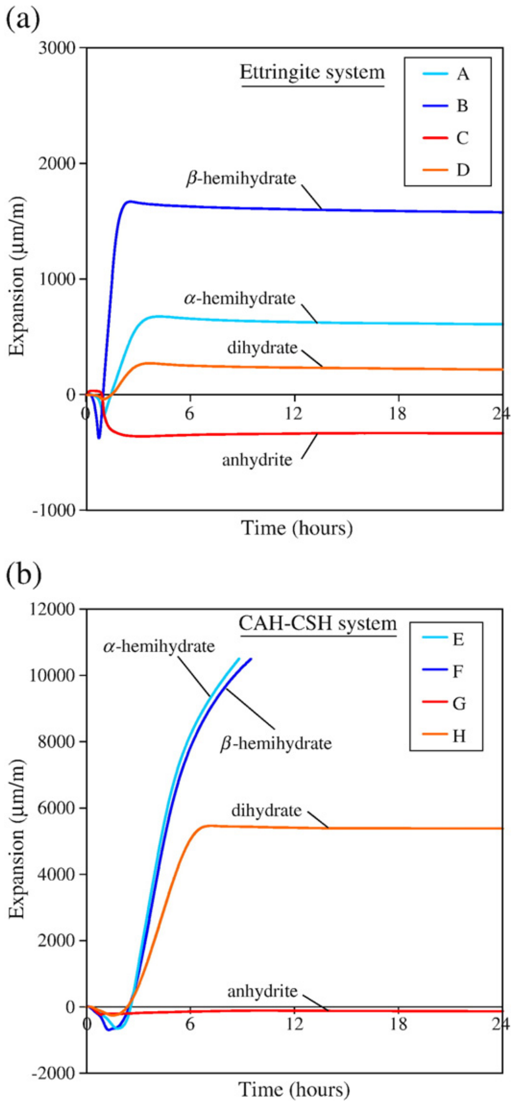

Fig. 3. Dimensional stability; sulfate source indicated in the diagram: (a) Ettringite system, (b) CAH–CSH system.

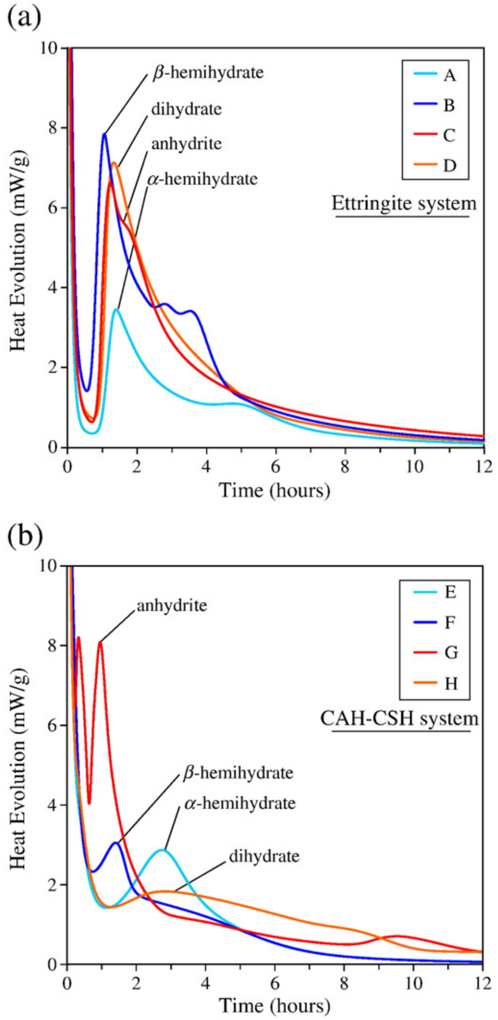

Fig. 4. Rate of heat evolution curves; sulfate source indicated in the diagram: (a) Ettringite system, (b) CAH–CSH system.

expansion. The expansion trend is especially pronounced for E with alpha-hemihydrate and F with beta-hemihydrate with almost the same curves up to 10,500 μm/m expansion. As a result cracks are observed and the measurement could only be conducted beyond 8 h. Formulation H showing a plateau in expansion reached well after 6 h. The maximum expansion, however, is larger than the one for formulation D. The delay to reach maximum expansion for H as compared to D seems to be related to the difference observed in 6- and 12-h compressive strength development. Formulation G behaves with no expansion similar to formulation C of the Ettringite systems.

4.4. Hydration kinetics

The rate of heat evolution as a function of time for the Ettringite system and the CAH–CSH system are plotted in Fig. 4.

For the formulations A, B and C, two or more exothermic upward peaks are observed after the first inflection point. Formulation C has a second exothermic upward peak as a shoulder immediately after the first upward peak. The interval between these peaks in the formulation C is about 30 min. However, in formulations A and B, the first and second upward peaks are clearly separated with the second peak appearing at about 2 h to about 3.5 h after the first one. On the other hand, formulation D only shows one clear exothermic upward peak.

Meanwhile, in the CAH–CSH system, the heat evolution curves are clearly different from those of the Ettringite system. Two exothermic upward peaks in the heat evolution curves are observed only for formulation G. Formulation H shows only a broadly distributed, weak heat flow after the first inflection point with two very small upward peaks at about 3 and 8 h. Moreover, formulations E and F have only one clear exothermic upward peak.

For formulations E and F, generation of heat is hardly seen after about 8 h. In addition total generation of heat in formulations E and F , are smaller than other formulations.

5. Discussion

5.1. Flow and setting time

For the Ettringite system and the CAH–CSH system, the maximum of heat evolution and 1/flow value are plotted in Fig. 5. In addition, max of heat evolution appeared within 5 min after mixing.

In both Ettringite system and CAH–CSH system, max of heat evolution are related very much to 1/flow value. Flow value increases

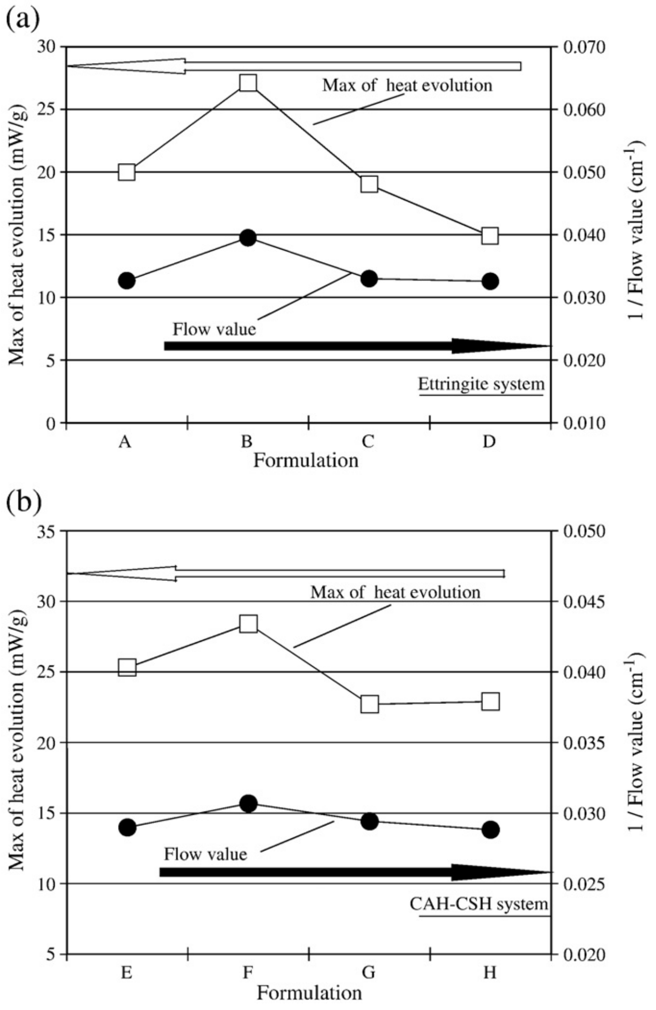

Fig. 5. Maximum of the heat evolution and 1/flow value: (a) Ettringite system, (b) CAH–CSH system.

with a decrease in max of heat evolution, conversely flow value decreases with an increase in max of heat evolution. From this result, it is concluded that heat release value correlates well with flow value. The tendency for the different flow values caused by different C$ modifications is also the same in both systems.

Additionally, in both systems, formulations B and F, containing beta-hemihydrate exhibit low flow values. In general, beta-hemihydrate is considered to be a more porous surface as compared to other C$ materials [12]. Therefore, one of the consequences seems to be the fact that beta-hemihydrate has a higher water demand. As a result, it is thought that the formulations containing beta-hemihydrate show the lower flow values for the same amount of mixing water as the other formulations.

Setting time of Ettringite system is shorter than that of CAH–CSH system except G, although the setting time of G is very different from the other formulations in CAH–CSH system. It seems that this is due to the influence of the different ternary systems and admixtures. Especially for admixtures, in order to grasp the influence of C$ and both systems, the amount of admixture for each system were perfectly kept constant. It is thought that these things influenced the result of setting time. However, for the formulation with anhydrite in the Ettringite system the set is the slowest. In the CAH–CSH system this trend is inversed. This effect is unknown and should be resolved by additional experiments.

5.2. Compressive strength, dimensional stability and hydration kinetics

What the relation between 24 h compressive strength and heat evolution curve is concerned, it turns out that low compressive strengths are found for formulations E and F. Compressive strengths at 24 h in the other formulations exceed 15 N/mm^2. Compared to heat evolution curves, the formulations that have higher compressive strength at 24 h can be seen two or more exothermic upward peaks, or their total heat generation is larger than that of formulations E and F. This fact indicates that 24 h compressive strength is low when heat release is not active.

The relation between 6 h compressive strength and dimensional stability expressed as the time to reach a plateau of dimensional stability is shown in Fig. 6. The 6 h compressive strength increases to more than 9 N/mm^2 when a plateau is reached within 6 h. However, when the dimensional stability curve increases without reaching a plateau or the rate of dimensional change slows down within 6 h, compressive strength values stay very low with is less than 3 N/mm^2. This seems due to the fact that a plateau in dimensional stability curves indicates that the hydration reactions slow down and the hardening body reaches a stable structure.

On the other hand, attention is also paid to the relation between final dimensional stability and heat evolution curve. For the different SLU formulations investigated only formulations C in the Ettringite system and G in the CAH–CSH system show two exothermic upward peaks clearly and closely. These are the compositions using anhydrite as a sulfate source and their dimensional stability curves show shrinkage finally. According to XRD results, it seems that the second exothermic upward peak for those formulations shows the formation of monosulfate. It is thought that the generation of monosulfate or its timing influence expansion and shrinkage of dimensional stability. On the other hand, all other formulations, where a second exothermic upward peak doesn't appear or the time between the two upward peaks becomes long (h), the dimensional stability curves show pronounced expansion finally.

5.3. Early hydrate formation, dimensional stability and hydration kinetics

Early hydrate formation from X-ray diffraction has been measured for formulations with anhydrite and beta-hemihydrate and is compared to the heat evolution curves in Fig. 7. For formulations C and G, containing anhydrite and exhibiting shrinkage, monosulfate is detected besides Ettringite at early times of around 1 h. For formulation G monosulfate appears with the second peak in the heat flow curve. On the other hand, for formulations B and F, containing beta-hemihydrate and showing finally expansion no monosulfate, but rather Ettringite is observed. The lime rich formulation F also shows the precipitation of gypsum.

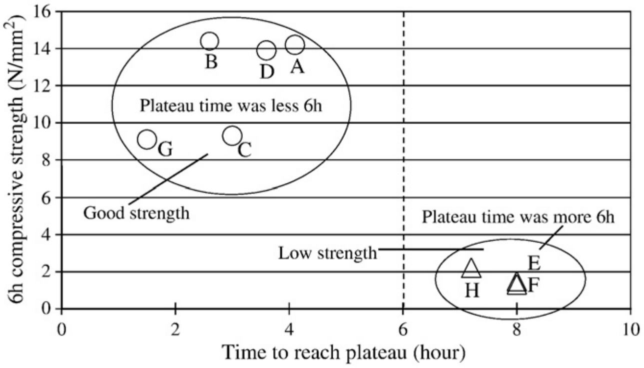

Fig. 6. 6 h compressive strength and time to reach plateau of dimensional stability.

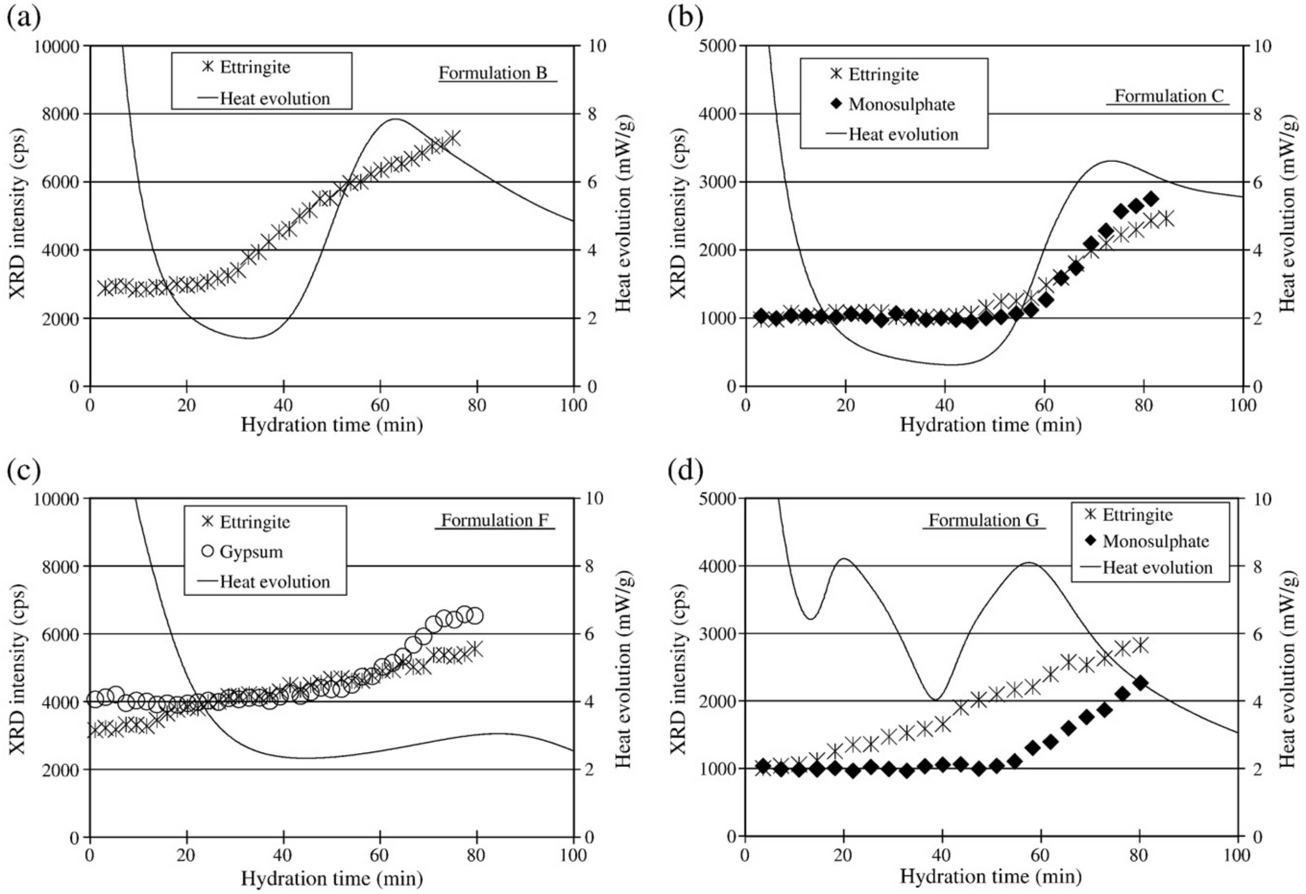

Fig. 7. Generation for some kind of hydrate and heat evolution curve in the early hydrate: (a) Formulation B, (b) Formulation C, (c) Formulation F, and (d) Formulation G.

Moreover, it seems that the second exothermic upward peak in the formulations with anhydrite is due to monosulfate formation. Therefore, although other formulations have to be checked, there is a possibility that the generation of Monosulfate and/or the timing of that event are related to shrinkage. Incidentally, generally it is said that the specific gravity of monosulfate is larger than that of Ettringite (monosulfate is 1.80 g/cm^3, Ettringite is 1.73 g/cm^3) [13].

Except formulation F the beginning peak in heat flow and the increase in Ettringite or monosulfate are generally in agreement. In formulation F, a weak peak in heat flow curve is seen at the time of gypsum formation. In general the beginning of peak in heat flow is in agreement with the time of beginning hydrate formation. In addition, gypsum is observed in formulation F, where at early times many cracks were observed. This result reaffirms that using beta-hemihydrate in SLU is difficult depending on conditions.

The correlation between generation of Ettringite and dimensional stability is shown in Fig. 8. In all formulations, the beginning Ettringite formation corresponds to the time when the dimensional stability curves change to shrinkage during the plastic phase. Initial and final sets occur always after or at the drop on shrinkage curves. Shrinkage changes to expansion only after the initial set when the specimen starts to form a firm matrix. But it seems that Ettringite formation first leads to shrinkage due to water consumption by the hydrates. After a firm matrix starts forming expansion can take place in the absence of monosulfate formation (samples B and F).

In addition, it is thought that changes in dimensional behavior indicate the formation of major hydrates leading to the transition from the plastic to the elastic state. Thus, from the point of view of matrix formation the very interesting relations reported in Ref. [14] are confirmed. Further studies will concentrate on the chemical and physical mechanisms during the stiffening and hardening period.

6. Conclusion

This study investigated the influence of $CaSO_4$ materials on properties such as workability, setting time, compressive strength, dimensional stability, hydration kinetics and generation of early hydrate in SLU based on CAC–OPC–C$. The obtained conclusions are shown below.

1. In both Ettringite system and CAH–CSH system, the maximum of heat evolution is related to flow value. Different C$ modifications show the same influence on flow in both systems.
2. Compressive strength starts to increase significantly once a plateau is reached in the dimensional stability curve.
3. Dimensional stability of the anhydrite formulations showed shrinkage in both Ettringite system and CAH–CSH system.
4. In CAH–CSH system, the hemihydrate formulations showed strong expansion and the hardened mortar for those formulations showed pronounced cracking. In addition, gypsum in formulation F is seen at by X-ray diffraction.
5. For the presented results the increase in heat flow curves at the first maximum corresponds to the time of the first major hydrate formation.
6. When two upward exothermic peaks in heat evolution curves are clear and close, the dimensional stability curves showed finally shrinkage. Also, monosulfate could be detected for the second peak of heat flow in formulations C and G.
7. X-ray diffraction results show for all formulations investigated that the time when Ettringite is first generated, corresponds to the time when dimensional stability curves drop to shrinkage. For those formulations where no monosulfate was observed, initial shrinkage finally turned into expansion.

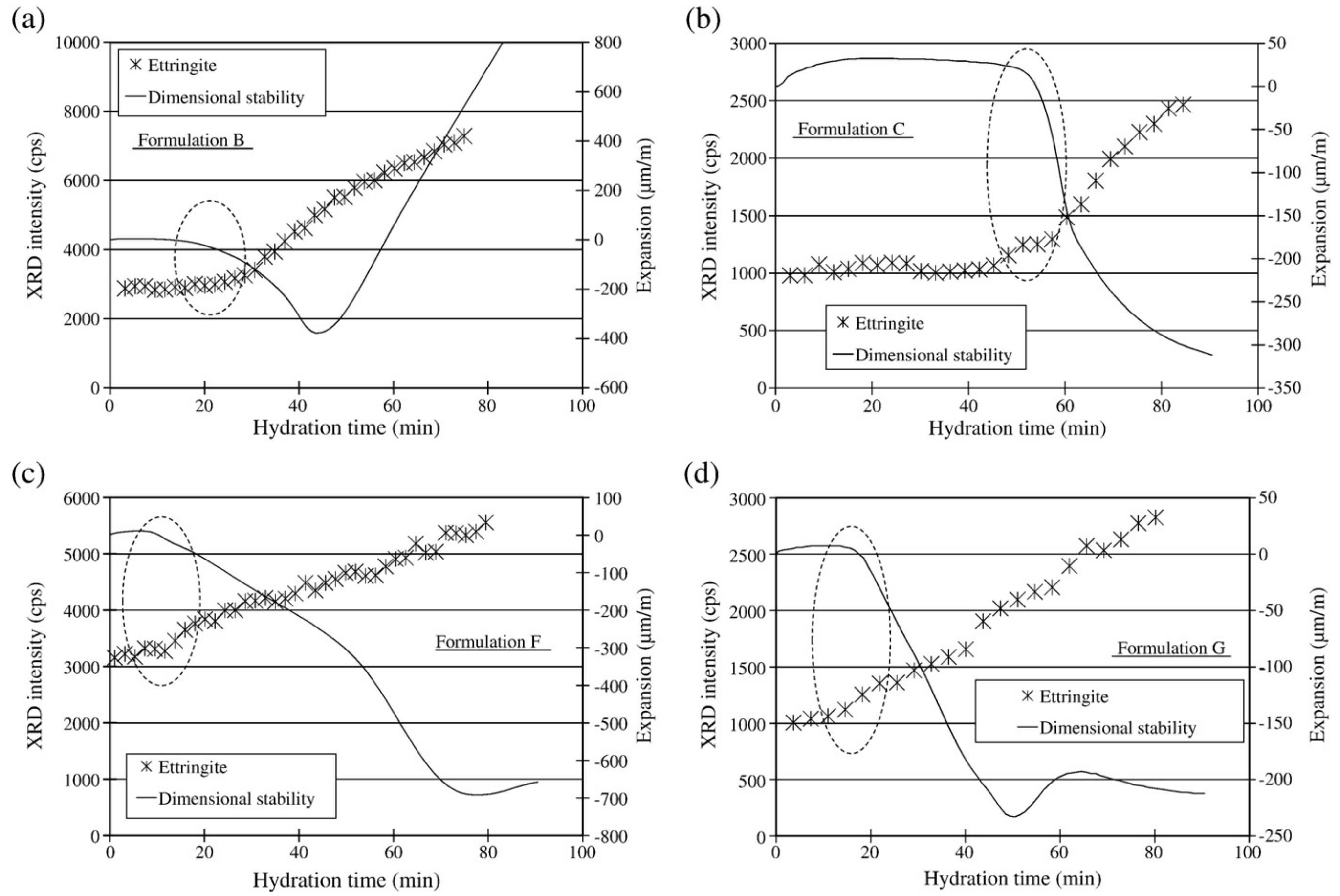

Fig. 8. Generation of Ettringite and dimensional stability in the early hydrate: (a) Formulation B, (b) Formulation C, (c) Formulation F, and (d) Formulation G.

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