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THE INFLUENCE OF $C_4A_3\bar{S}$ CONTENT AND W/S RATIO ON THE PERFORMANCE OF CALCIUM SULFOALUMINATE-BASED CEMENTS

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ABSTRACT

The effect of the variation in $C_4A_3\bar{S}$ content (expressed as $C_4A_3\bar{S}/C_5S_2\bar{S}$ weight ratio ranging from 1:5 to 3:1) on the ternary system $C_4A_3\bar{S}$-$C_5S_2\bar{S}$-$C\bar{S}$ having a constant $C\bar{S}/C_4A_3\bar{S}$ ratio of 0.5, has been studied. At the fixed w/s ratio of 0.4 the mechanical strength of the system at early ages (1–28 days) increased with higher $C_4A_3\bar{S}$ content. However, depending on the curing conditions, compositions containing more than 50% $C_4A_3\bar{S}$ showed expansion, cracking and loss of strength at later ages, due to the insufficient water used. Moreover compositions with more than 20% $C_4A_3\bar{S}$ and increasing $C_4A_3\bar{S}$ content gave progressively lower mechanical strength, when hydrated with the fixed water/reactants ($C_4A_3\bar{S}$ + $C\bar{S}$) ratio of 0.86, i.e. 10% more than the stoichiometric water requirement. Thus, both $C_4A_3\bar{S}$ content and w/s ratio must be optimized in order to achieve satisfactory performances at early and later ages. The best behaviour was obtained with cements containing 30–40% $C_4A_3\bar{S}$ hydrated with a w/s ratio ranging from about 0.35 to 0.50. *Copyright © 1996 Elsevier Science Ltd*

Introduction

The key component of calcium sulfoaluminate-based cements is the compound calcium sulfoaluminate ($C_4A_3\bar{S}$), due to its ability of generating ettringite ($C_6A\bar{S}_3H_{32}$) when combined with water, lime and/or calcium sulfate. The $C_4A_3\bar{S}$ hydration has been extensively studied in the past (1-15): depending on both the rate of formation and microstructure of ettringite, calcium sulfoaluminate-based cements can be employed as shrinkage-resistant, self-stressing and high early strength cements (16–17). While in the first two applications the well known expansive properties of ettringite are exploited, with the latter binders the process of rapid–hardening is due to the instantaneous formation of non-expansive ettringite which develops relatively large crystals able to provide high mechanical strength at early ages (18–27).

Non expansive ettringite derives from the hydration reaction of $C_4A_3\bar{S}$ and $C\bar{S}$ (1,4,5,12,13,15) according to the following equation:

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \qquad (1)$$

In these rapid-hardening cements the role played by $C_4A_3\bar{S}$ is similar to that of C_3S in ordinary portland cement (OPC). For this reason the rapid-hardening calcium sulfoaluminate-based cements are also termed non-alitic cements (27). Due to the fact that $C_4A_3\bar{S}$ requires synthesis temperatures 200–300°C lower than that required for the formation of C_3S, cements incorporating it are also called low-energy cements (21). Taking into account that for the synthesis of these cements industrial wastes and by-products can also be utilised instead of natural materials (28,29), and that the friable calcium sulfoaluminate clinker requires lower grinding energy than OPC clinker, the term 'energy saving cements' (21) is also applied to these binders.

Depending on the composition and proportioning of the raw materials used for their manufacture, calcium sulfoaluminate-based cements may also contain other compounds, e.g. C_2S, C_4AF, C_3A, and $C_5S_2\bar{S}$, whose synthesis occurs simultaneously with $C_4A_3\bar{S}$ and at about the same temperature range.

The compounds C_2S, C_4AF and C_3A behave similarly in $C_4A_3\bar{S}$-based cements as they do in OPC. C_2S generates C-S-H and therefore contributes to the strength of cement at medium and longer ages and it also contributes to the durability of the hydrated cements. Both C_4AF and C_3A generate hydration products which give little contribution to the mechanical strength and in fact interfere with ettringite by promoting its transformation to monosulfate ($C_4A\bar{S}H_{12}$) at later ages.

The compound $C_5S_2\bar{S}$ (or $2C_2S \cdot C\bar{S}$) is a double salt of C_2S and $C\bar{S}$, which forms at ~800–1200°C, and decomposes to the above two components at temperatures greater than 1280°C (28). $C_5S_2\bar{S}$ is a poorly hydraulic phase; its loss on ignition is only ~7 and 12% after 5 and 24 months of hydration, respectively (24).

The stoichiometry of reaction [1] for the full formation of ettringite requires a high w/s ratio of 0.78, which can induce excessive porosity into the hydrated cements based only on $C_4A_3\bar{S}$ and $C\bar{S}$. Cements which contain other solid phases, together with $C_4A_3\bar{S}$ and $C\bar{S}$, requiring relatively small amounts of water, have low porosity, can produce strong and dense structures and show high durability. Alternatively, a too low $C_4A_3\bar{S}$ content in calcium sulfoaluminate-based cements could reduce the concentration of ettringite in the hydration products under a critical level, and therefore markedly reduce the mechanical strength of the system.

The objective of this paper is to investigate the role of $C_4A_3\bar{S}$ content and w/s ratio in regulating the behaviour of calcium sulfoaluminate-based cements. In order to elucidate the contribution given by the $C_4A_3\bar{S}$ phase alone, cements having three components, $C_4A_3\bar{S}$, $C_5S_2\bar{S}$ and $C\bar{S}$, were studied. Neglecting the hydration of $C_5S_2\bar{S}$, only the reaction [1] was taken into consideration: the $C\bar{S}/C_4A_3\bar{S}$ weight ratio was kept constant and equal to 0.5, close to that required by stoichiometry of equation [1]; the $C_4A_3\bar{S}$ content was varied from about 15 to 55%. The above cements were investigated in two series of hydration tests, first by keeping constant the water/total solids ($C_4A_3\bar{S}$ + $C\bar{S}$ + $C_5S_2\bar{S}$) ratio and, secondly, by increasing w/s ratio, while keeping constant the water/reactants ($C_4A_3\bar{S}$+ $C\bar{S}$) ratio.

Experimental

The raw materials (viz. calcium carbonate, phosphogypsum, fly ash and bauxite) used for the experiments were the same as in previous investigations (22,24).

The compositions were calculated so as to give fired clinkers containing a wide range of $C_4A_3\bar{S}$ contents. This was achieved by varying the $C_4A_3\bar{S}/C_5S_2\bar{S}$ weight ratio from 1:5 to 3:1, while keeping the $C\bar{S}$ content constant at 0.5 (stoichiometric, 0.45), with respect to $C_4A_3\bar{S}$. The compositions investigated were identified with the sysmbols FA-0 to FA-5, and are shown in Table 1. The oxide compositions were calculated for the main clinker phases only, while the ferrous (e.g. brownmillerite) and other minor phases which may have formed were ignored.

The raw mixes were blended, fired at ~1200°C then ball-milled dry to pass a 53 μm sieve, with a residue of <5%. All the synthesized clinkers were analysed by XRD: only the three main components, $C_4A_3\bar{S}$, $C_5S_2\bar{S}$ and $C\bar{S}$, were identified.

First, specimens were cast with a fixed w/s (water/ total solids) ratio of 0.4 at about optimum consistency. The second series of investigations was performed by increasing w/s ratios, i.e. using a constant water/reactants ($C_4A_3\bar{S}$ + $C\bar{S}$) ratio of 0.86 (10% more than that required by the stoichiometry of the reaction [1]).The choice of 0.86 for this ratio was suggested for ease of handling. In spite of this, the casting of specimens FA-0 and FA-1 (w/s ratios of 0.20 and 0.29, respectively) was difficult. Therefore a commercial water-reducing admixture (1% by weight of solids) was added to both compositions. The calculated w/s ratios are presented in Table 2.

All the hydrated specimens were analysed by XRD and TGA/DTA, and their ettringite contents were calculated from the TGA/DTA traces. The other phases detected in the hydration products were aluminum hydroxide, unhydrated $C_5S_2\bar{S}$ and (for systems high in $C_4A_3\bar{S}$, hydrated with low w/s ratios) unreacted $C_4A_3\bar{S}$ and $C\bar{S}$. Compressive strength and shrinkage/expansion measurements were made according to procedures previously described (22,24).

TABLE 1

Weight Ratios, Weight and Oxide Compositions (%) of Ternary System $C_4A_3\bar{S}$-$C_5S_2\bar{S}$-$C\bar{S}$ Investigated

Composition	FA-0	FA-1	FA-2	FA-3	FA-4	FA-5
			$C_4A_3\bar{S}/C_5S_2\bar{S}/C\bar{S}$ *weight ratio*			
	1:5:0.5	1:3:0.5	1:2:0.5	1:1:0.5	2:1:1	3:1:1.5
			Weight (%)			
$C_4A_3\bar{S}$	15.4	22.2	28.6	40.0	50.0	54.5
$C_5S_2\bar{S}$	76.9	66.7	57.1	40.0	25.0	18.2
$C\bar{S}$	7.7	11.1	14.3	20.0	25.0	27.3
			Oxide composition (%)			
CaO	53.69	51.64	49.72	46.28	43.26	41.90
SiO_2	19.23	16.68	14.28	10.00	6.25	4.55
Al_2O_3	7.72	11.13	14.33	20.05	25.06	27.32
SO_3	19.36	20.55	21.67	23.67	25.43	26.23

TABLE 2
Calculated w/s Ratios Employed in the Second Series of Hydration Tests

Composition	FA-0	FA-1	FA-2	FA-3	FA-4	FA-5
$C_4A_3\bar{S}+C\bar{S}$	1.50	1.50	1.50	1.50	3.00	4.50
Water	1.29	1.29	1.29	1.29	2.58	3.87
Total solids	6.50	4.50	3.50	2.50	4.00	5.50
w/s ratio	0.20	0.29	0.37	0.52	0.65	0.70

Results and Discussion

Table 3 shows the compressive strengths of the five compositions, marked FA-1 to FA-5, hydrated with a fixed w/s ratio of 0.4. It can be seen that the compositions develop progressively higher mechanical strength at early ages and the strength is about stabilised at 28 days curing, with the exception of composition FA-5, which give somewhat lower mechanical strength than FA-4. Compositions FA-2 and FA-3 developed particularly good mechanical strength and dimensional stability (the specimens expanded slightly, up to 0.19%, to 1 year), whereas those containing the highest amounts of $C_4A_3\bar{S}$ showed strength loss accompanied by cracking and expansion after 28-56 days curing.

Fig. 1 shows the concentration of ettringite with age for compositions FA-1, FA-3 and FA-4. For the sake of clarity the data concerning compositions FA-2 and FA-5 have been omitted because they are very close to those of FA-3 and FA-4, respectively. For the same reason the points at three days are not plotted.

It is seen that ettringite forms rapidly and within 1 day it develops ~70–85% of its final values. Depending on the initial content of $C_4A_3\bar{S}$, the compositions investigated show different trends to reach steady values with curing time. With compositions FA-1, FA-2 and FA-3 the values of ettringite content after 3–7 days remained about constant (within experimental error) to the end of curing period studied. With compositions FA-4 and FA-5, a rapid

TABLE 3
Compressive Strength* (MPa, standard deviation in parentheses) of Compositions FA-1 to FA-5 Cured at 23°C, 100% RH; w/s = 0.4;
$C_4A_3\bar{S}/C_5S_2\bar{S}$ Weight Ratios are Given in the Heading in Brackets

Days curing	FA-1 [1:3]	FA-2 [1:2]	FA-3 [1:1]	FA-4 [2:1]	FA-5 [3:1]
1	22.7 (1.2)	40.1 (1.9)	53.2 (3.4)	74.8 (1.6)	63.4 (2.5)
3	25.7 (0.5)	47.3 (2.0)	65.3 (1.6)	84.5 (4.5)	71.8 (3.3)
7	27.6 (0.4)	52.4 (4.1)	71.7 (4.4)	86.4 (2.5)	72.7 (3.9)
28	33.3 (1.6)	62.5 (2.6)	79.4 (3.0)	87.6 (2.7)	74.7 (6.2)
56	32.5 (3.7)	60.3 (3.5)	74.1 (10.0)	†66.9 (16.1)	74.6 (6.8)
90	36.8 (0.9)	62.7 (2.9)	67.2 (8.5)	†47.6 (12.3)	†57.2 (20.8)
180	34.3 (4.9)	63.3 (4.7)	64.6 (9.2)	-	-
365	37.7 (2.1)	62.2 (4.7)	60.4 (5.6)	-	-
730	39.3 (5.1)	64.3 (7.3)	71.2 (11.1)	-	-

* Average of 6 specimens.

† Specimens expanded, measurements discontinued

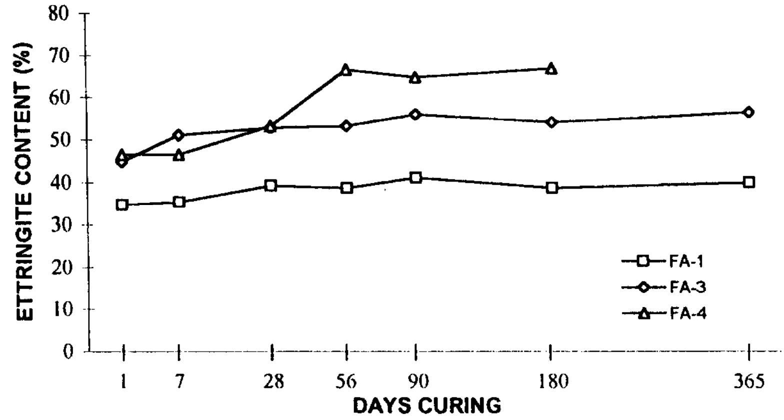

FIG. 1.

Relationship between ettringite content (%) and days curing (square root scale) for compositions FA-1 to FA-5 cured at 23°C, 100% RH; w/s 0.4.

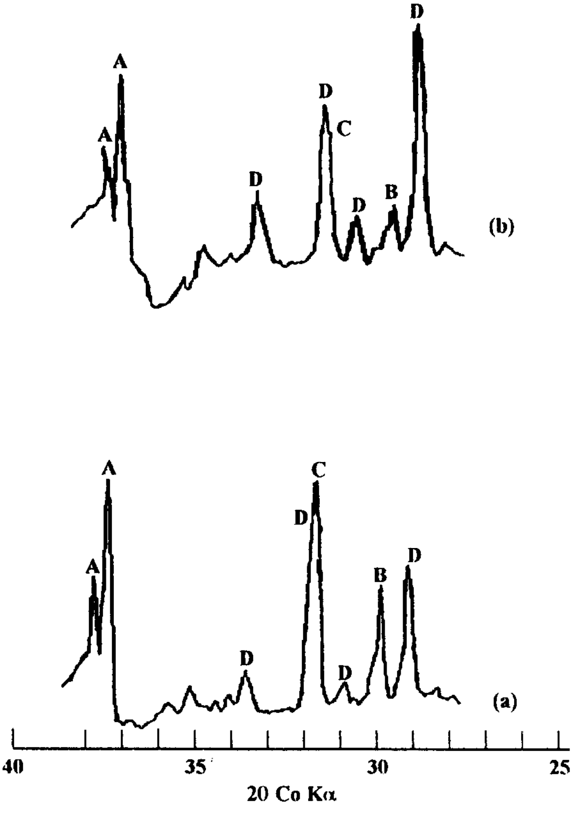

FIG. 2.

XRD diagram for composition FA-4 hydrated for (a) 28 days and (b) 56 days; A = $C_5S_2\bar{S}$; B = $C_4A_3\bar{S}$; C = $C\bar{S}$; D = $C_6A\bar{S}_3H_{32}$.

TABLE 4

Compressive Strength* (MPa, standard deviation in parentheses) of Compositions FA-0 to FA-5 Cured at 23°C, 100% RH; w/s Ratios Ranging from 0.20 to 0.70; $C_4A_3\bar{S}/C_5S_2\bar{S}$ Weight Ratios are Given in the Heading in Brackets

Days curing	FA-0 [1:5]	FA-1 [1:3]	FA-2 [1:2]	FA-3 [1:1]	FA-4 [2:1]	FA-5 [3:1]
w/s	0.20	0.29	0.37	0.52	0.65	0.70
1	35.7 (1.0)	55.4 (2.2)	36.3 (2.1)	35.8 (0.8)	27.8 (1.0)	21.8 (1.2)
3	42.3 (1.0)	72.3 (4.4)	48.7 (6.8)	49.5 (2.0)	41.0 (0.8)	34.0 (0.9)
7	45.0 (2.0)	81.0 (9.7)	59.4 (5.0)	59.7 (4.2)	46.2 (2.6)	37.7 (1.6)
28	57.9 (3.0)	79.4 (8.5)	61.8 (4.6)	70.7 (4.8)	54.6 (3.3)	39.3 (3.5)
56	61.5 (4.1)	90.0 (5.8)	66.8 (7.6)	70.5 (3.4)	57.3 (5.3)	42.3 (4.0)
90	65.6 (1.3)	79.3 (11.5)	66.2 (2.9)	70.9 (4.2)	52.0 (8.5)	44.1 (3.4)
365	79.0 (7.4)	92.7 (9.9)	80.6 (12.0)	78.0 (5.1)	53.1 (2.7)	41.6 (4.4)

* Ave of 6 determinations

increase in the content of ettringite was observed after 28–56 days, when the specimens cracked and expanded. This increase, associated with a decrease in the amount of unreacted $C_4A_3\bar{S}$ and $C\bar{S}$, was also noted by XRD (Fig. 2).

When submitted to dry conditions (21°C, 67% RH) no differences in behaviour were observed from composition to composition: all the specimens continuously shrank slightly up to 1 year (when shrinkage values ranging from 0.39 to 0.48% were obtained), after which time their shrinkage became constant.

The results of mechanical strength, ettringite content and shrinkage can be interpreted on the basis of the amount of added water. In fact, the $C_4A_3\bar{S}$-rich compositions, as shown in

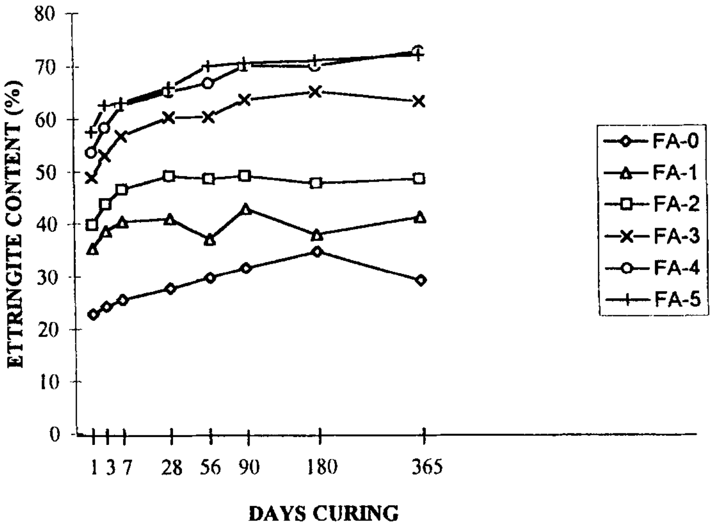

FIG. 3.

Relationship between ettringite content (%) and days curing (square root scale) for compositions FA-0 to FA-5 cured at 23°C, 100%RH; water/reactants 0.86.

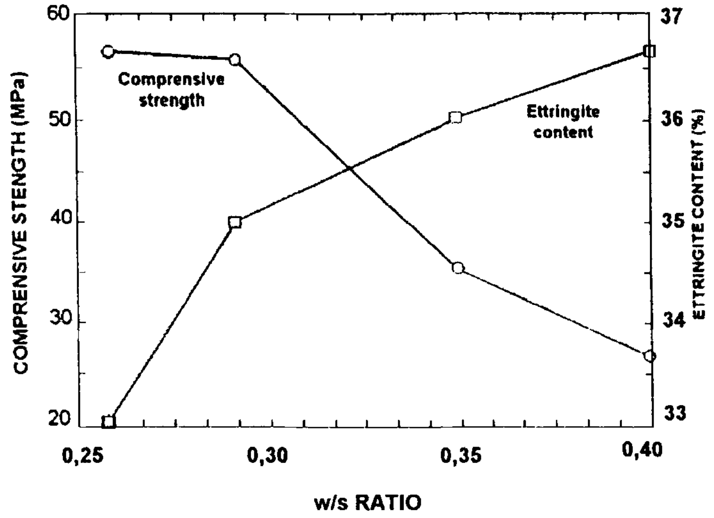

FIG. 4.

One-day compressive strength (Mpa) and ettringite content (%) of composition FA-1, cast with different w/s ratio.

Table 2, need more water for completing the hydration reaction. For systems FA-4 and FA-5 the hydration reaction was stopped for lack of water and the compositions did not reach their potentially attainable mechanical strength related to their higher $C_4A_3\bar{S}$ content. Expansion, cracking and loss of strength of wet FA-4 and FA-5 specimens observed are associated with the formation of 'secondary ettringite'. This delayed formation occurs on the surface of the specimens, due to the absorption of water from the atmosphere at 100% RH during wet curing and it is derived from the renewed hydration of $C_4A_3\bar{S}$ and $C\bar{S}$ still unreacted. This hydration is accompanied by the onset of tensions between the inner and outer parts of the cast specimens.

In dry conditions, however, hydration reaction cannot proceed, secondary ettringite formation cannot occur and the specimens remain dimensionally stable.

A confirmation of the validity of the previous hypothesis on the negative effect of insufficient water on the $C_4A_3\bar{S}$-rich compositions can be given by the analysis of the behaviour at different w/s ratios, shown by the six compositions reported in Table 1, during the second series of hydration tests. In Table 4 are listed the strength data of the above compositions cured from 1 to 365 days.

It can be seen that composition FA-1, with a low $C_4A_3\bar{S}$ content of 22.2% and w/s of 0.29, gives the highest mechanical strength. Moreover the compositions containing the highest amounts of $C_4A_3\bar{S}$ give lower mechanical strength than composition FA-0 with the lowest $C_4A_3\bar{S}$ content. Fig. 3 shows the concentration of ettringite with age for the six compositions.

Ettringite forms rapidly within 1 day and then its concentration continues to increase slightly in a regular way to the end of curing period studied. Furthermore, the ettringite content increases with increased $C_4A_3\bar{S}$ content. The data presented in Table 4 and Fig. 3 clearly show that the w/s ratio has a far greater influence on the mechanical strength of these compositions than their $C_4A_3\bar{S}$ content and their corresponding ettringite concentration. In fact, with the exception of composition FA-0, the mechanical strength increases with decreasing w/s ratio. Composition FA-0 does not show the highest mechanical strength because its content of ettringite generated is insufficient to provide a mechanical strength higher than that of composition FA-1.

The sensitivity of the above $C_4A_3\bar{S}$-containing compositions to small changes in w/s ratios, is further illustrated in Fig. 4 for composition FA-1.

Finally all the compositions investigated, including FA-4 and FA-5, were dimensionally stable under wet conditions, and no cracking and expansion has occurred. In fact, contrary to the previous case, sufficient water was available for all the compositions to allow for the full formation of ettringite.

Conclusions

In calcium sulfoaluminate cements the $C_4A_3\bar{S}$ content and w/s ratio are strictly interrelated parameters inasmuch as the stoichiometry of the $C_4A_3\bar{S}$ hydration requires a high w/s ratio for the full formation of ettringite. Both the aforementioned parameters are critical in regulating the behaviour of calcium sulfoaluminate-based cements.

The amount of $C_4A_3\bar{S}$ has to be optimised because it must generate an adequate concentration of ettringite in the hydration products without requiring excessive amount of water for the reaction. The best compromise could be achieved with $C_4A_3\bar{S}$ contents ranging from about 30 to 40%.

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