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LONG-TERM BEHAVIOUR OF HYDRAULIC BINDERS BASED ON CALCIUM SULFOALUMINATE AND CALCIUM SULFOSILICATE*

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ABSTRACT

Hydration, physico-mechanical and carbonation studies have been carried out on the ternary system of calcium sulfoaluminate ($C_4A_3\bar{S}$), calcium sulfosilicate ($C_5S_2\bar{S}$) and anhydrite ($C\bar{S}$), synthesised by single firing at 1200°C. The raw materials used were natural materials, viz. limestone, bauxite and clay, and also industrial process wastes and by-products, viz. phosphogypsum, fly ash and blast furnace slag.

These clinkers containing calcium sulfoaluminate and calcium sulfosilicate can be produced at about 1200°C, i.e. at temperatures 200–250°C lower than OPC clinker. The fired clinker is relatively soft and friable, it is easy to grind, and consequently the whole process results in considerable saving of energy. The ground clinker hydrates rapidly and has good cementitious properties. Good early (1 day) paste strengths of 35–50 MPa, and 28-day strengths of 58–76 MPa were obtained, when the materials were tested in a wet state. Dry testing gave 50–80 MPa strengths after 1-day curing, and up to 103 MPa after 28 days curing for the composition containing fly ash. All the compositions had very good dimensional stabilities, similar to OPC pastes. The dried pastes had good resistance to atmospheric carbonation to 1 year, although the ettringite component of the specimens tended to carbonate. However, even after extensive accelerated carbonation, about 67% of the original mechanical strength of the specimens was still retained.

Apart from energy saving, the use of industrial process wastes assists in the reduction of the cost of the raw materials, the clinkering process, and the cement produced. Large-scale utilisation of industrial process wastes and by-products also contributes to the reduced exploitation of natural resources. The decreased generation of CO_2 during firing can contribute to the reduction of the greenhouse effect.

* In this paper the terminology adopted in cement chemistry, viz. C = CaO, S = SiO_2, A = Al_2O_3, $\bar{S}$ = SO_3, H = H_2O etc., has been used.

Introduction

The hydration of calcium sulfoaluminate ($C_4A_3\bar{S}$) to form ettringite ($C_6A\bar{S}_3H_{32}$), is well documented. Ettringite is one of the main components of expansive, shrinkage-resistant, rapid hardening, high early strength and low energy cements (1–3). Very little is known, however, about the hydraulic and physico-mechanical properties of calcium sulfosilicate ($C_5S_2\bar{S}$). Its existence has been observed by several researchers (4,5,6–11), but mainly as a minor phase in portland cement clinkers in the presence of gypsum impurities or mineralisers and more abundantly in sulfoaluminous cement clinkers.

$C_5S_2\bar{S}$ has been identified by many investigators as an inert or very slowly hydrating phase, which most probably contributes neither to strength nor to the durability of cementitious systems.

It has been reported, however, that $C_5S_2\bar{S}$ present in significant quantities contributes to some undesirable setting and hardening characteristics of expansive cements (6,8). Furthermore, it has also been noted that $C_5S_2\bar{S}$ cannot contribute to the initial expansive properties of expansive cement, and even reduces their expansive potential (8).

Previous investigations (12–14) on systems containing reactive $CaSO_4$, CaO, Al_2O_3 and SiO_2 revealed that in some cases, at about 1200°C, $C_5S_2\bar{S}$ formed as a second major phase instead of β-C_2S and $C\bar{S}$, in addition to $C_4A_3\bar{S}$. Upon hydration, this cement produced very high mechanical strength at early and later ages. The dimensional stability of the system was also good and, depending on the composition, the ΔL of the dry specimens was 0.17–0.30% after 1 year. Therefore, it was decided to investigate the long-term physico-mechanical behaviour of the $C_4A_3\bar{S}$-$C_5S_2\bar{S}$-$C\bar{S}$ system obtained by firing mixes containing commercial materials and industrial process wastes such as phosphogypsum, fly ash and blast furnace slag. Particular attention has been paid to the hydration of $C_5S_2\bar{S}$, and the hydration of the entire system.

It is known that ettringite has relatively low resistance to CO_2 attack (15–24), but there is a lack of data about the durability of the ettringite-containing cements. Accordingly, it was decided to examine the long-term carbonation of the above $C_4A_3\bar{S}$-$C_5S_2\bar{S}$-$C\bar{S}$ system under normal atmospheric conditions at room temperature, and under accelerated conditions in a carbonation chamber.

Experimental

Raw materials

The principal chemical compositions of the raw materials used for the experiments are shown in Table 1. The pure analytical reagent materials used for some of the experiments were not analysed.

Table 1. Major chemical components (%) of raw materials used

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	P_2O_5	H_2O
$CaCO_3$, AR	55.70	n.a.	n.a.	0.02	0.25	n.a.	43.80*
Phosphogypsum	32.60	0.06	0.13	0.01	45.40	0.63	19.95
Fly ash	4.80	56.80	25.50	4.20	0.40	n.a.	0.40
Bauxite	n.a.	5.00	54.50	11.90	n.a.	n.a.	n.a.
Blast furnace slag	41.13	33.17	14.15	1.57	2.58	n.a.	0.15
Burdwood clay	1.08	46.80	34.50	1.33	0.10	n.a.	14.69

* CO_2

Composition of mixes

The compositions of the various mixes containing fly ash, blast furnace slag and clay, identified with the symbols FA, BS and CL, respectively, are listed in Table 2. The compositions were calculated so as to produce clinkers containing $C_4A_3\bar{S}$, $C_5S_2\bar{S}$ and $C\bar{S}$, in the weight ratio of 1:1:0.5, after firing.

Table 2. Composition of mixes FA, BS and CL (wt%)

Material	FA	BS	CL
$CaCO_3$	34.72	25.23	35.40
Phosphogypsum	33.54	34.23	33.62
Fly ash	9.60	—	—
Bauxite	22.14	23.30	18.97
Blast furnace slag	—	17.24	—
Clay	—	—	12.01
Total	100.00	100.00	100.00

Synthesis and procedures

The raw materials for compositions FA, BS and CL were sieved to pass a 150 μm sieve and blended. They were then placed in fire-clay crucibles and fired in an electric kiln for 4–8 h (depending on the amount processed) at about 1200°C with pauses of 1 h at 850°C and 1 h at 1000°C, to allow for the escape of CO_2 from the carbonate, and H_2O from the hydrated alumina in bauxite. After firing, the slightly sintered and friable products were crushed, ball milled dry for about 16 hours, then sieved to pass a 53 μm sieve, with residue of <5% on the sieve.

The $C_5S_2\bar{S}$ for hydration studies was synthesised from previously prepared β-C_2S and $C\bar{S}$ by firing at 1200°C for 2 h, followed by milling the product to pass a 53 μm sieve. For the synthesis of β-C_2S and $C\bar{S}$, pure AR chemicals were used.

All the sintered materials were analysed by XRD.

Physico-mechanical properties

For compressive strength and density measurements, 25 mm cube specimens with a w/s ratio of 0.4 were cast. For shrinkage/expansion measurements, 100 × 12.5 × 12.5 mm bars with a w/s ratio of 0.4 were cast. The specimens were demoulded after 4 hours, cured at 23°C and 100% RH from 1 day to 1 year. The specimens were removed at various time intervals and tested immediately for compressive strength (WET). The specimens were also tested (DRY) after drying for 21 days in a room set at 21°C, 67% RH (constant temperature room—CTR) to constant weight. The specimens were analysed by XRD and TGA/DTA. The densities of the WET and DRY specimens were calculated by conventional methods.

One set of expansion bars was cured for 24 hours at 23°C, 100% RH, then allowed to age in a CTR for 1 year. Their dimensional changes were measured (DRY) at various time intervals. A second set of specimens was kept at 23°C, 100% RH for 1 year, and their dimensional changes were measured (WET) as before. It is worth noting that in the industry, shrinkage/expansion measurements are carried out only when the specimens are drying out, i.e. DRY.

Carbonation experiments

For the determination of *atmospheric carbonation*, three sets of 25 mm cube specimens were cast as described before, using w/s = 0.5 for composition FA, and w/s = 0.4 for compositions BS and CL. The specimens were cured for 28 days at 23°C, 100% RH. One set was tested WET for compressive strength and density; the second and third sets were placed in a CTR at 21°C, 67% RH and one was tested after 21 days (DRY); and the other set was allowed to carbonate in the CTR for 1 year and tested after 6 months and 1 year.

For the measurement of *accelerated carbonation*, composition FA only was used, with w/s = 0.4. Three sets of cubes were cast and cured for 28 days. One set was tested WET; another two sets were dried for 21 days as before, and one was tested DRY; and the other set was placed in a carbonation chamber (4% CO_2) for 1, 2, 7 and 28 days, and tested for compressive strength and density.

After carbonation all the specimens were analysed for changes in their mineralogical composition and ettringite content using XRD and TGA/DTA techniques.

Results and Discussion

XRD analysis confirmed that in the fired compositions FA, BS and CL, the main mineralogical phases were $C_4A_3\bar{S}$, $C_5S_2\bar{S}$ and $C\bar{S}$. Very small quantities of tricalcium aluminate (C_3A) were also present, but no β-C_2S or any reactants were identified in the clinkers. The iron oxide component of the raw materials, particularly the bauxite, was converted to traces of brownmillerite (C_4AF).

XRD analysis revealed that the calcium sulfosilicate synthesised for the hydraulic studies was virtually pure $C_5S_2\bar{S}$.

Physico-mechanical properties of cast specimens

The compressive strength of the specimens containing fly ash (FA), blast furnace slag (BS) and clay (CL), respectively, are shown in Figs 1–3. It can be seen that all the compositions, particularly FA and CL, developed very good early (1 day) strength after testing WET. Their strengths gradually increased up to about 90 days (FA being higher than CL). After this time the strengths became about constant to 1 year, with the exception of FA whose strength slightly decreased after 90 days curing. The strength of sample BS did not reach the maximum value at 90 days, but increased further to 1 year.

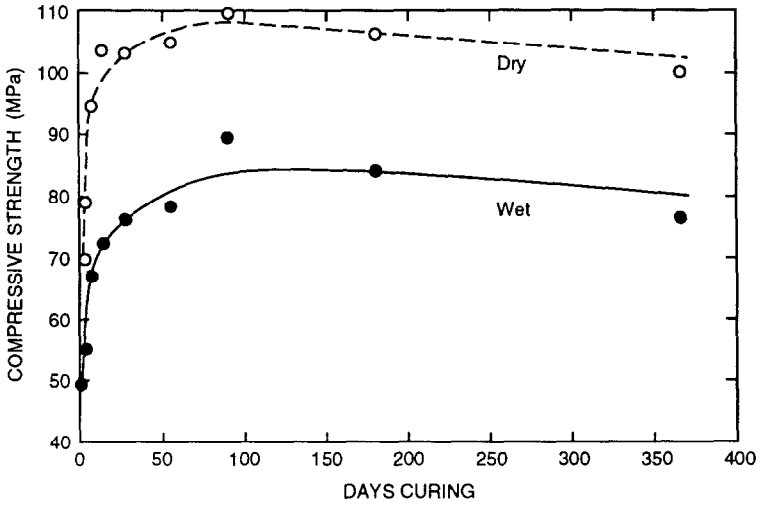

FIG. 1
Relationship between compressive strength and days curing for composition FA, tested WET and DRY: W/S = 0.4; average of 6 specimens.

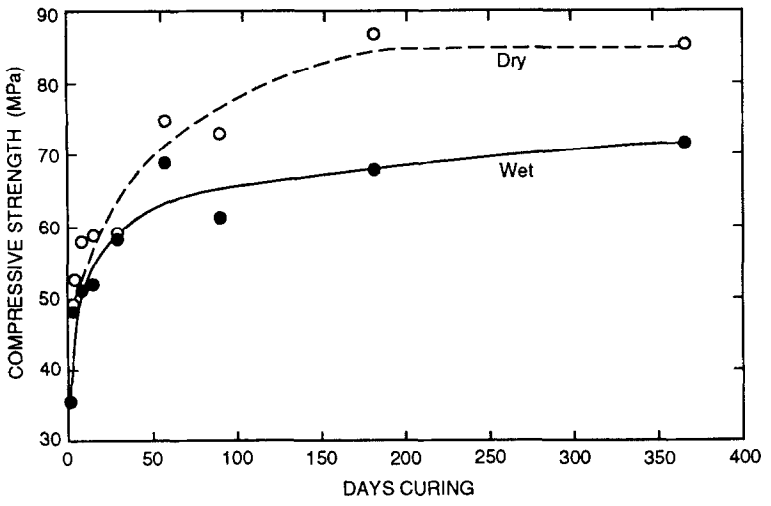

FIG. 2
Relationship between compressive strength and days curing for composition BS, tested WET and DRY: w/s = 0.4; average of 6 specimens.

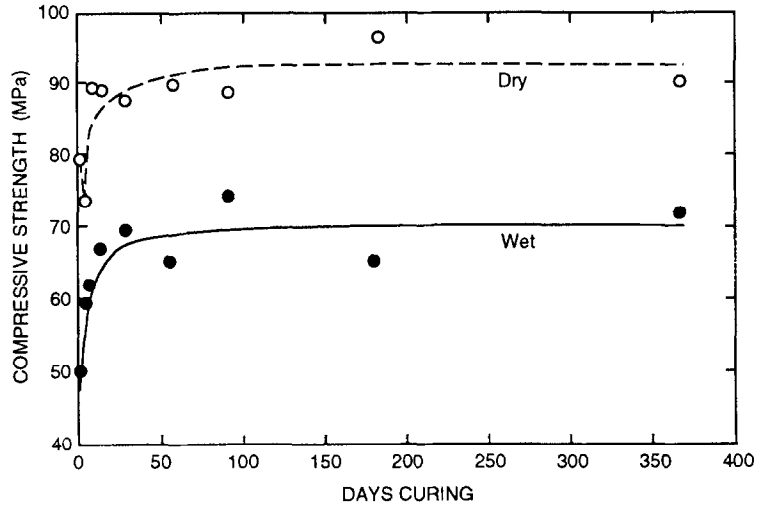

FIG. 3
Relationship between compressive strength and days curing for composition CL, tested WET and DRY: w/s = 0.4; average of 6 specimens.

All the specimens had much higher mechanical strength after drying (tested DRY) than after wet testingas expected. However, the mechanical strengths of the dried specimens of FA tended to decrease slightly after reaching a maximum value at 90–180 days curing.

The mineralogical compositions of FA, BS and CL, cured for up to 1 year, were determined by XRD after each curing period. Due to the similarity of the XRD traces for all three compositions, only those for composition FA, cured for 1 and 28 days, respectively are shown in Fig. 4. The results indicate that all three compositions hydrated rapidly, and the main hydration product

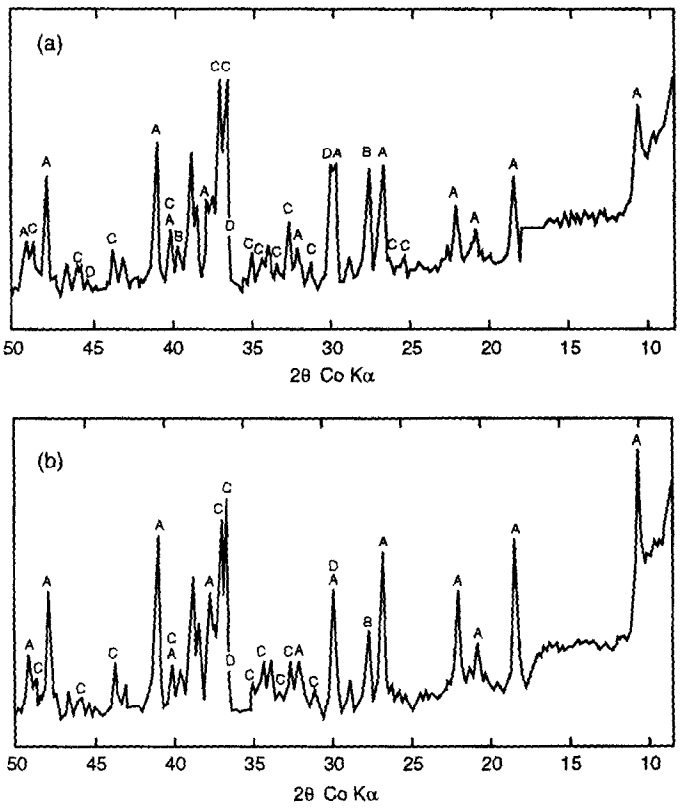

FIG. 4

XRD diagrams for composition FA hydrated for (a) 1 days, and (b) 28 days, showing the presence of major mineralogical phases: A = $C_6A\bar{S}_3H_{32}$; B = $C_4A_3\bar{S}$; C = $C_5S_2\bar{S}$; D = $C\bar{S}$.

(ettringite) formed within 1 day. Furthermore, all three compositions contained about the same amounts of $C_5S_2\bar{S}$, unreacted $C_4A_3\bar{S}$ and $C\bar{S}$, as well as small quantities of C_3A.

After 28 days hydration, the reflections for the main hydration product (ettringite) become stronger for all three compositions investigated. However, the intensities for $C_5S_2\bar{S}$ were about the same as after 1 day curing, indicating that $C_5S_2\bar{S}$ did not undergo extensive hydration. In all three systems investigated, small quantities of unreacted $C_4A_3\bar{S}$, $C\bar{S}$, and C_3A, were still present, and the reactants were not fully consumed at 1 year.

The hydrated specimens were also analysed by thermal analysis (TGA/DTA) at the various stages of hydration. Again, due to the similarity of the TGA/DTA traces for all three compositions, only those for composition FA hydrated for 28 days are shown in Fig. 5. It can be seen, that the characteristic endotherm due to the partial dehydration of ettringite is predominant in the temperature range of 50–180°C, with a maximum at about 120°C. The second endothermic peak in the range of 190–340°C, with a maximum at about 260°C, is due to the dehydration of alumina gel formed in the system during the reaction between $C_4A_3\bar{S}$ and $C\bar{S}$, i.e. ettringite formation.

The ettringite content of the specimens hydrated from 1 day to 1 year has been calculated from the characteristic endothermic peak, and the results are presented in Table 3. The results indicate that 80-85% of the main hydration product (ettringite) forms in 1 day in all three compositions

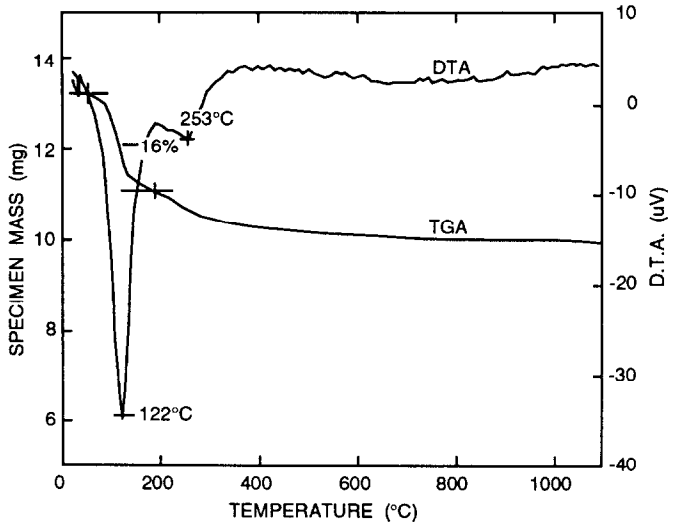

FIG. 5
Thermal analysis (TGA/DTA) diagram for composition FA hydrated for 28 days showing the presence of the major mineralogical phase (ettringite).

Table 3. Ettringite content (%) of hydrated compositions FA, BS and CL cured for various times; w/s = 0.4; measured on WET and DRY specimens

Days curing	FA		BS		CL	
	WET	DRY	WET	DRY	WET	DRY
1	44.3	42.1	40.6	37.6	45.5	50.9
3	46.7	43.9	41.8	39.4	50.6*	44.6*
7	42.1	46.7	43.3	42.7	51.2	50.6
14	49.4	47.6	47.3	43.3	53.9	47.3
28	48.5	47.6	46.7	47.9	49.4	48.2
56	42.7	47.6	48.8	47.6	49.4	48.2
90	48.5	47.0	49.7	48.2	48.5	46.7
180	49.7	46.7	50.6	50.3	53.9	49.1
365	54.3	50.9	52.4	51.8	52.1	50.0

* 4 days

examined. Further curing slightly enhanced the formation of ettringite to the end of the curing period studied, i.e. 1 year. Variations in the values of ettringite content measured are most probably due to experimental error. It appears that ettringite formation was a little faster in the systems containing fly ash (FA) and clay (CL) than in the system containing blast furnace slag (BS).

The quantities of ettringite determined in the WET specimens were a little higher than in the DRY specimens. This is probably due to the higher stability of ettringite in wet rather than dry conditions (25,26), and also to the ongoing formation of ettringite in the wet state.

The dimensional changes of the specimens containing fly ash, blast furnace slag and clay are shown in Figs 6–8, respectively. It can be seen that all the specimens shrank relatively little during drying (DRY), and the shrinkage tended to increase only a little with curing time to 1 year. Sample BS appears to be the most dimensionally stable composition. The percentage of shrinkage was about the same order of magnitude as for OPC pastes (about 0.3% at later ages) cured under similar conditions.

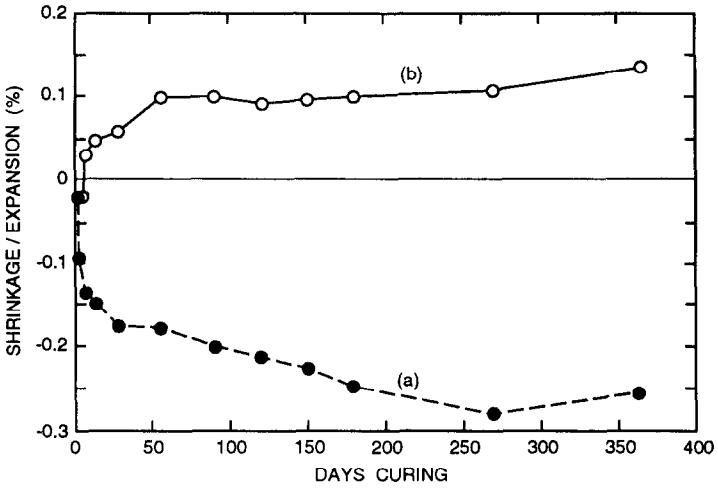

FIG. 6
Relationship between shrinkage/expansion and days curing for composition FA, cured for (a) 24 hours at 23°C, 100% RH, followed by drying at RT (DRY); and (b) cured continuously at 23°C, 100% RH (WET): w/s = 0.4; average of 6 specimens.

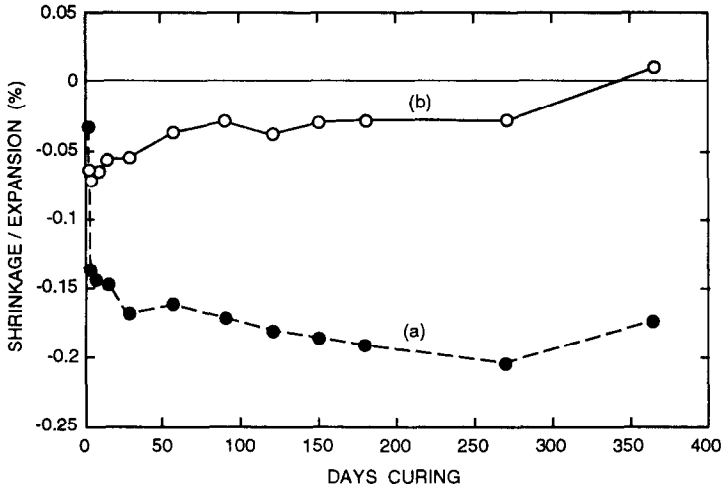

FIG. 7
Relationship between shrinkage/expansion and days curing for composition BS, cured for (a) 24 hours at 23°C, 100% RH, follower by drying at RT (DRY); and (b) cured continuously at 23°C, 100% RH (WET): w/s = 0.4; average of 6 specimens.

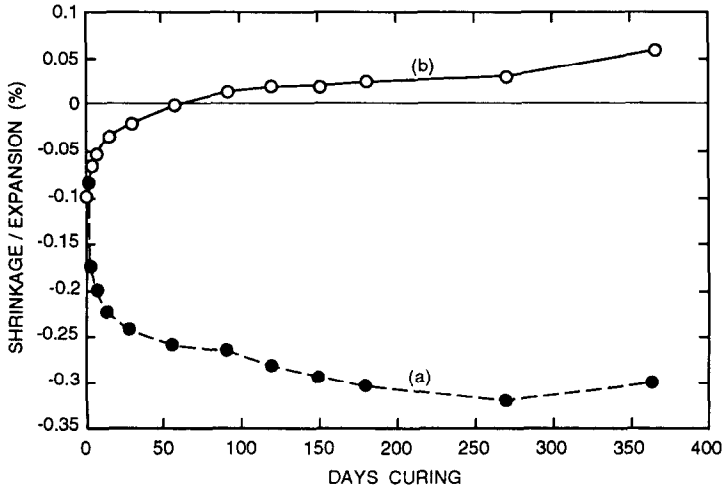

FIG. 8
Relationship between shrinkage/expansion and days curing for composition CL, cured for (a) 24 hours at 23°C, 100% RH, followed by drying at RT (DRY); and (b) cured continuously at 23°C, 100% RH (WET): w/s = 0.4; average of 6 specimens.

When the specimens were kept at 23°C, 100% RH and tested WET, the samples containing fly ash (FA) tended to expand slightly after 7 days, and those containing clay (CL) only after 56 days. The specimens containing blast furnace slag (BS) did not show any expansion up to 1 year.

Carbonation studies

Atmospheric carbonation—The results presented in Table 4 show that the strengths of the specimens increased to 180 days curing, after which time it slightly decreased to 365 days. However, all the compositions retained their mechanical strength at 1 year (60.8, 71.8 and 76.6 MPa, for compositions FA, BS and CL, respectively). These strength results, for BS and CL, were even higher than for the uncarbonated specimens. The observed decrease in strength 180 and 365 days can be attributed to the partial carbonation of ettringite by CO_2 attack. The carbonation of the above specimens was verified by XRD, indicating that after 1 year at RT the specimens carbonated only slightly, and some small quantities of carbonation products, namely calcite, vaterite (μ-$CaCO_3$) and traces of hemihydrate were present in the specimens as shown in Figs 9(a) and 9(b).

Accelerated carbonation—The results of accelerated carbonation of specimen FA in a carbonation chamber (4% CO_2) are shown in Table 5. It can be seen that the specimens carbonate with time and their strength is gradually reduced. XRD examination of the carbonated specimens after 28 days exposure to CO_2 (Fig. 9(c)) indicated that most of the ettringite in the specimens carbonated to calcite and vaterite, gypsum and hemihydrate. Alumina gel was also present as indicated by DTA/TGA. Although only ~18.5% ettringite (from the original 47.9%) was still present in the carbonated specimens at the end of exposure to CO_2, the percentage of strength retained was still relatively high (about 67%).

Table 4. Compressive strength (MPa) for compositions FA, BS and CL cured at (a) 23°C, 100% RH for 28 days, tested WET and DRY; then (b) after 180 and 365 days atmospheric carbonation: w/s ratio for FA, 0.5; for the others, 0.4. Standard deviation in parentheses

Days curing	FA		BS		CL	
	WET	DRY	WET	DRY	WET	DRY
28 (fog)	50.4 (3.7)	66.3 (2.2)	55.4 (4.2)	64.3 (4.9)	62.0 (0.7)	72.2 (4.4)
180 (CTR)	—	73.1 (3.7)	—	75.8 (1.8)	—	86.0 (7.4)
365 (CTR)	—	60.8 (4.1)	—	71.8 (4.7)	—	76.6 (2.9)

Table 5. Compressive strength and density for composition FA cured for 28 days at 23°C, 100% RH, tested WET and DRY; followed by accelerated carbonation in a CO_2 chamber containing 4% CO_2. Ettringite content is also shown before and after 28 days carbonation: w/s = 0.4; standard deviation in parentheses

	Compr. strength (MPa)		Ettringite content (%)	Strength retained (%)	Density (kg/m^3)	
	WET	DRY			WET	DRY
Before carbonation						
	75.3 (2.9)	102.0 (9.3)	47.9	100.0*	1929	1850
Days in carbonation chamber						
1	—	102.6 (6.8)		100.6	—	1827
2	—	89.6 (4.1)		87.8	—	1820
7	—	80.0 (4.3)		78.4	—	1828
28	—	67.8 (3.8)	~18.5	66.5	—	n.d.

* Dry strength, 100%, nominal

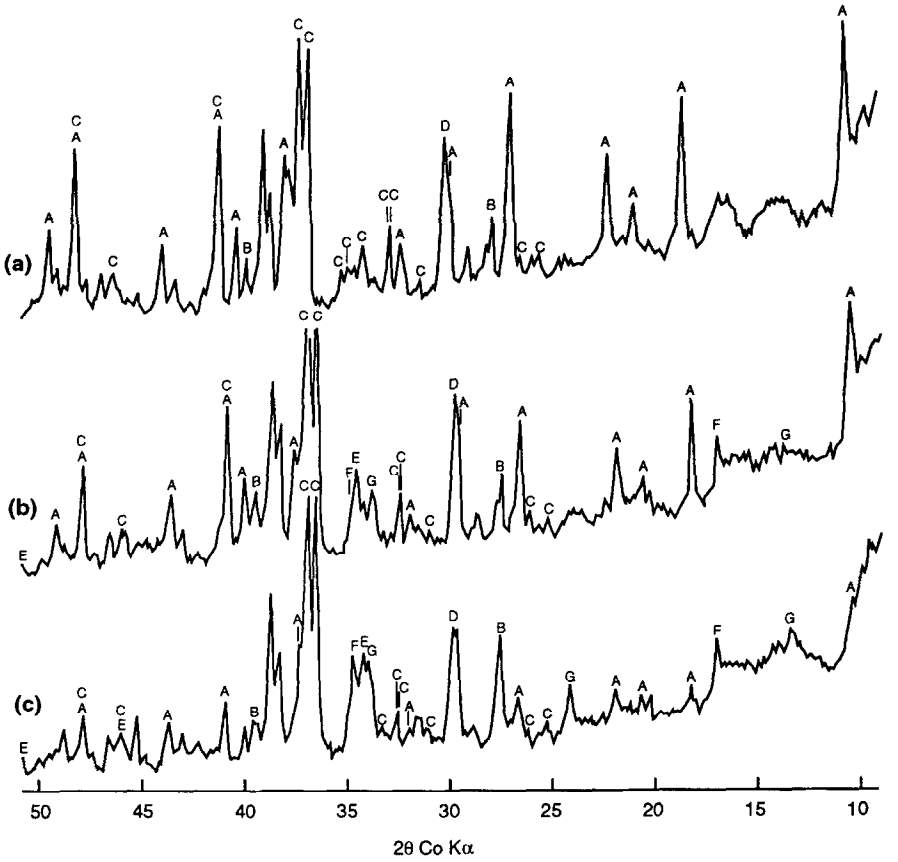

FIG. 9
X-ray diffraction diagrams of specimen FA: (a) uncarbonated; (b) carbonated for 1 year in CTR; and (c) 28 days exposure to 4% CO_2 in a carbonation chamber:
A = $C_6A\bar{S}_3H_{32}$; B = $C_4A_3\bar{S}$; C = $C_5S_2\bar{S}$; D = $C\bar{S}$; E = $C\bar{C}$; F = $C\bar{S}H0.5$; G = $C\bar{S}H_2$.

The retention of mechanical strength of these specimens can be attributed to the presence of $C_5S_2\bar{S}$. Its small prismatic crystals form strong interlocking with other cementitious phases, i.e. with ettringite and gel phases, and provide a monolithic structure to the whole system. Due to this monolithic structure, a great portion of the mechanical strength of the system is retained, in spite of the partial conversion of ettringite due to carbonation.

The densities of the specimens did not seem to have changed during carbonation.

Hydraulic properties of $C_5S_2\bar{S}$

In the literature, $C_5S_2\bar{S}$ is recognised by some authors either as a non-hydraulic or as a very poorly hydrating compound (4,5,8,27,28). Other authors (29), studying the hydration of $C_5S_2\bar{S}$ in suspensions and in pastes, have found that the hydration process commences by the partial dissolution of $C_5S_2\bar{S}$ from the surface of the grains, and is completed by the formation of $C_2S.nH_2O$, gypsum and hydro-sulfosilicate ($2(C_2S).mCaSO_4.nH_2O$, where m <1). It has also been reported (26,29,30) that $C_5S_2\bar{S}$ has better hydraulic properties and durability than β-C_2S, and after autoclaving it transforms to a rapidly hardening and high strength compound.

In order to get a better understanding of the hydraulic properties of $C_5S_2\bar{S}$, small (2 g) quantities were mixed with water (w/s, 1:1), then placed in plastic envelops and cured at 55°C and 100% RH for up to 2 years, then examined by XRD and TGA/DTA.

XRD examination of the unhydrated material and the material in contact with water and hydrated for up to 2 years (not shown) provided no clear evidence that hydration of the sample had taken place. However, TGA/DTA examination of the same specimens after 7 days, 150 days and 2 years hydration (Figs 10(a)–10(c)) indicated that some changes had occurred in the material during these periods. In particular, after 7 days hydration (Fig. 10(b)) a small endothermic peak became evident in the temperature range 50–100°C. This endothermic peak gradually increased in intensity as a result of hydration to 2 years (Fig. 10(d)). The loss of weight calculated from this peak was small, and increased only to about 2.0% in 2 years. At 150 days hydration (Fig. 10(c)), three very small endothermic peaks appeared with minima at about 500, 680 and 950°C, respectively. The peaks at 500 and 680°C, due to the formation of other hydrated phases, have also increased in intensity with curing time. The peak at 500°C has gradually shifted to about 450°C; while the

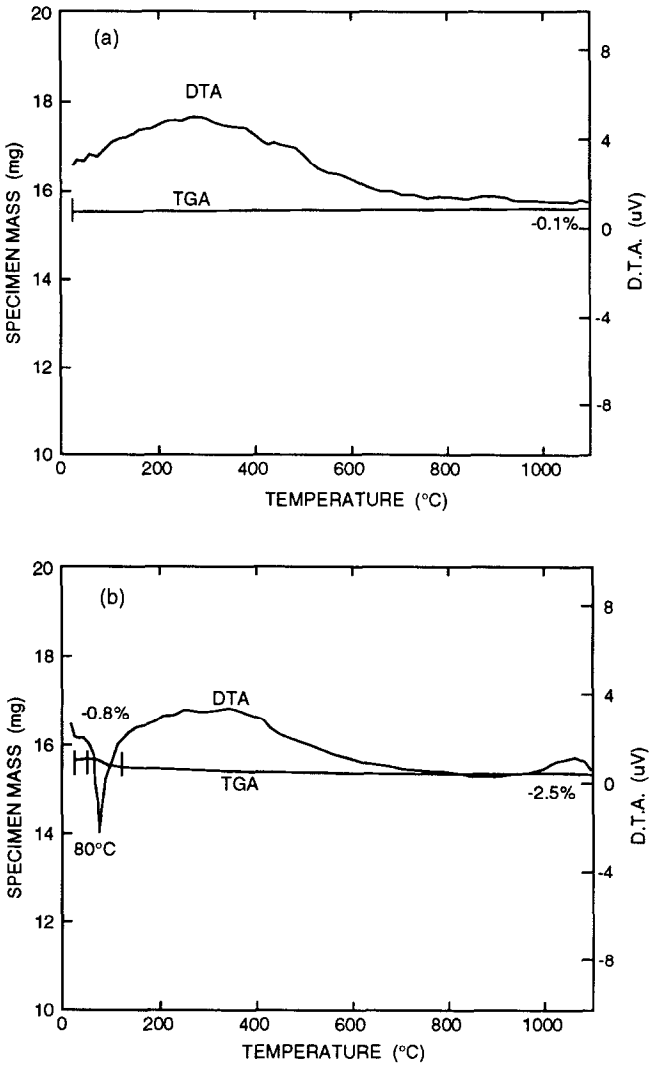

FIG. 10
Thermal analysis (TGA/DTA) diagrams for $C_5S_2\bar{S}$: (a) unhydrated; (b) hydrated for 7 days; (c) hydrated for 150 days; and (d) hydrated for 2 years at 55°C, 100% RH.

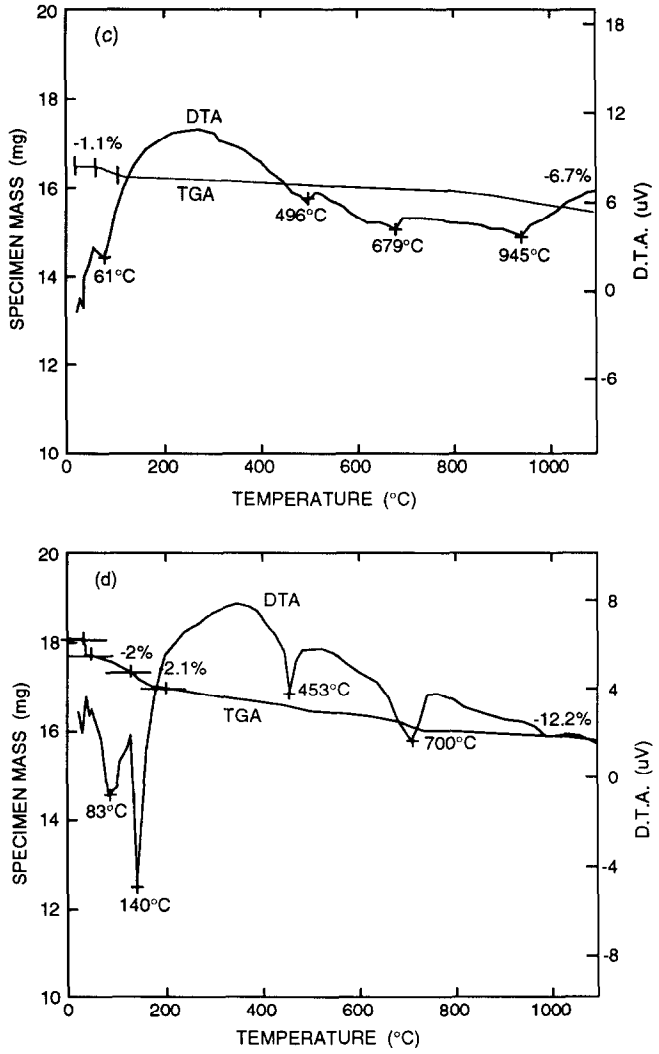

FIG. 10
continued

peak at 680°C has shifted to 700°C and become broader at the end of the curing period of 2 years (Fig. 10(d)). These two peaks could probably be due to calcium hydroxide and calcium carbonate, respectively. The peak at 950°C disappeared after 150 days curing.

Furthermore, the peak at 140°C, which appeared between 150 and 270 days, is probably due to the newly formed gypsum or hemihydrate. This peak increased in intensity to 2 years, and the weight loss amounted to 2.1%.

The total loss of weight from the sample gradually increased with curing time. In particular, up to 1100°C, the sample hydrated for 7 days lost 2.5%; and in 2 years, 12.2%. These weight losses, and the appearance of new peaks which increased in intensity during curing, indicated that hydration of $C_5S_2\overline{S}$ took place, and this hydration, although slow, was more extensive with longer curing times.

Further evidence of the hydration of $C_5S_2\overline{S}$ was obtained by measuring the total of free and bound water in the specimens hydrated as before. This was carried out by heating the specimens at

1000°C for 8 hours. The corresponding weight losses were as follows: 7 days, 3.1%; and 2 years, 12.1%. These weight loss results are in good agreement with those obtained by TGA/DTA.

The above findings confirm that $C_5S_2\bar{S}$ can hydrate, but at a very slow rate. Consequently, $C_5S_2\bar{S}$ is expected to contribute to the strength of cementitious systems particularly at later ages.

Conclusions

Cements comprising $C_4A_3\bar{S}$, $C_5S_2\bar{S}$ and $C\bar{S}$, in the weight ratio of 1:1:0.5, can be synthesised from commercial materials and industrial process wastes, viz. phosphogypsum, fly ash and blast furnace slag, in a single firing, at a temperature of about 1200°C, which is about 250–300°C lower than that used for clinkering portland cement. The resulting clinkers are soft and friable and can be ground by using little energy.

The cements are reactive, hydraulic and rapid-hardening, and provide high mechanical strengths at early ages (35–50 MPa in 1 day, tested WET) and also at later ages (57–76 MPa at 28 days, tested WET). The cements have good dimensional stabilities, similar to OPC pastes. The dimensional stability of the system is most probably due to the presence of $C_5S_2\bar{S}$. The strength of these cements at early ages is due to the formation of ettringite ($C_6A\bar{S}_3H_{32}$), and the ultimate strength is due to the presence of ettringite as well as the formation of cementitious phases from the hydration of $C_5S_2\bar{S}$.

The dried pastes aged for 1 year have moderately good resistance to carbonation to 1 year at ordinary atmosphere and room temperature, but they partially carbonated under severe exposure conditions in a carbonation chamber. Although the ettringite is partially converted by carbonation, the mechanical strength of the systems are still retained to about 67%.

By altering the ratio of $C_4A_3\bar{S}$-$C_5S_2\bar{S}$-$C\bar{S}$ in the raw mixes, cements with different physico-mechanical properties can be designed, and are being investigated.

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