

Formation and Hydration of Low-CO₂ Cements Based on Belite, Calcium Sulfoaluminate and Calcium Aluminoferrite

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Abstract

Clinkers based principally on belite, calcium sulfoaluminate and calcium aluminoferrite were made at 1300°C from a raw mix based on limestone, kaolinite, gypsum and haematite. The inclusion of dopants stabilized belite in the α -form, which led to a greater hydraulic reactivity. Cements made from such clinkers with 8-12% gypsum were more easily grindable than OPC and offered potential CO₂ emissions reductions of 20-30% in manufacturing, while giving performance not far from that of OPC. It is shown that these “BCSAF” cements initially set due to ettringite formation but that later hardening is mainly due to belite hydration.

1 Introduction

The manufacture of Portland cement produces large amounts of CO₂ due to the high CaCO₃ content of the raw mix required by the high lime contents of modern alite-rich OPC clinkers. Decarbonation of CaCO₃ typically produces about 0.53 tons of CO₂ per ton of OPC clinker and also accounts for most of the energy requirement of clinker formation in an efficient modern dry-process kiln system [1]. Current societal concerns about industrial greenhouse gas emissions have led the European cement industry to commit to significant specific CO₂ emissions reductions, but the only currently proven approaches to this end consist of increased use of cementitious materials, replacement of “conventional” fuels and raw materials with renewable or recycled fuels or raw materials, and maximizing kiln thermal efficiency. All three of these approaches are likely to reach their practical limits during the coming decade, so additional approaches are certain to be needed for the longer term.

Clinkers rich in belite and calcium sulfoaluminate (C₄A₃S or “ye’elinite”) can be produced from kiln feeds with significantly lower CaCO₃ contents than OPC, resulting in proportionately lower total CO₂ emissions. Such clinkers can be made from a wide variety of reasonably abundant raw materials provided that significant levels of iron oxide and other minor components are included, leading to the presence of additional phases, principally a calcium aluminoferrite solid solution [2]. Cements made from such clinkers generally give high strengths at early ages due to the reactivity of the sulfoaluminate phase, but later strength development is

often slow. We have recently shown that certain minor components can help solve this problem, in part by stabilizing the belite in the α' form.[3]

Although hydration mechanisms for belite-sulfoaluminate cements have been proposed in literature [4,5], very little work has been carried out on the effect of the proportion of belite and its reactivity on the hydration of such cements. However, the work of Palou and Majling [6,7] shows a large influence of particle size on the hydration kinetics. It might be expected that, in belite-sulfoaluminate-ferrite (BC \hat{S} AF) clinkers containing an intimate mixture of the three main anhydrous phases (C₂S-C₄A₃ \hat{S} -ferrite) of different intrinsic reactivities, there would perhaps be a “synergistic effect”, i.e. the minerals may well complement and accelerate each other in hydration. This paper presents work aimed at better understanding the hydration of such cements.

2 Experimental procedure

2.1 Raw materials

The basic raw materials used to make the clinkers were a very pure limestone, a kaolinite clay, a natural gypsum and reagent grade Fe₂O₃. The chemical compositions of the first three are given in Table 1. Additional minor ingredients were used to modify the clinker reactivity [3].

Table 1: Chemical compositions of the principal raw materials

%	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	TiO ₂	K ₂ O	Na ₂ O	LOI
Limestone	55.7	0.01	0.08	0.03	0.05	0.19	0.01	0.01	0.01	43.7
Clay	0.14	41.9	40.3	0.66	0.34	0.08	0.87	0.16	0.12	16.0
Gypsum	32.7	1.05	0.15	0.08	44.6	0.11	0.02	0.02	0.02	21.4

2.2 Chemical and mineralogical composition of clinker

The chemical composition of the target “pure” BC \hat{S} AF clinker is indicated in Table 2. The corresponding raw mix contained 60.01% limestone, 28.34% clay, 6.58% gypsum and 5.07% Fe₂O₃. The phase composition of the resulting clinker was estimated using a calculation procedure based on the solid solutions determined by Touzo and Glasser [8].

Table 2: Chemical and phase composition of the target clinker (mass %)

Chemical composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	TiO ₂	K ₂ O	Na ₂ O
	52.48	17.60	16.90	7.79	4.51	0.21	0.37	0.08	0.06

Estimated phase composition	belite	ye'elite	ferrite	others
	51	29	19	<1

2.3 Clinker Formation

All raw materials (except gypsum) were dried in an oven at 100°C for 4 hours and then ground to pass 80µm before being batched. After being weighed and combined, the mixture was thoroughly homogenized by a successive dilution method using a blender. The feed was then made into 5-10 mm nodules with 8% water in a rotating granulator. The nodules were dried at 100°C overnight. Nodulised feed was clinkered in 250g batches in platinum crucibles, heating to 975°C at 15°C/min and then holding for 30 minutes, then heating at 5°C/min to 1300°C and again holding for 30 minutes, followed by air quenching. This protocol was found to give a free lime content of < 0.2% and good clinker phase formation.

The main difference between the doped and undoped clinkers was the stabilization of most of the belite in the α form by the dopant. This can be clearly seen by comparing the X-ray diffractograms of the two clinkers:

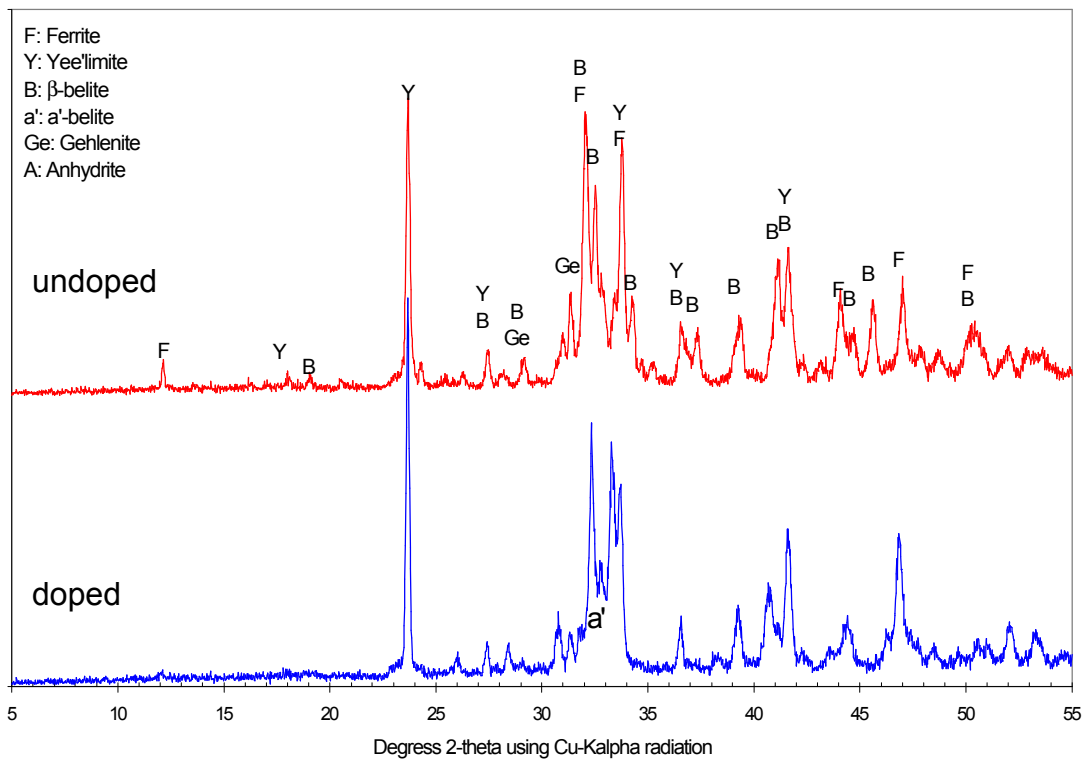


Fig. 1: Diffractograms for doped and undoped BC&SAF clinkers

2.4 Cement preparation

Clinker was ground with 8% added gypsum in a laboratory ball mill of 1 kg capacity. The grindability was evaluated by the number of revolutions required to reach the target Blaine specific surface (BSS) of 380m²/kg.

The BC \hat{S} AF cements ground more easily than a typical OPC. The grinding time to obtain a BSS of 380m²/kg for undoped BC \hat{S} AF was about 40% of that needed for a typical OPC. For the doped clinker it increased to about 65%, probably because of increased clinker liquid phase formation.

2.5 Mechanical and rheological performance

Cement performance was evaluated using “micromortars” composed of 500g cement, 500g Palvadeau 0~0.315mm quartz sand and 250g water. They were mixed in a Kenwood mixer for 1 min at low speed, then 1 min at high speed. The consistencies of the fresh mortars were evaluated by a flow test. Their setting times were compared by the Vicat method. The strengths were determined on 2x2x10cm prisms demoulded at 6 hours and cured in water to the corresponding testing time. Dimensional changes in water were also monitored. All tests were made at 20°C. A CEM I – 52.5 OPC was also tested similarly for comparison purposes.

Fresh mortar results, (Table 3), show that the undoped BC \hat{S} AF cement micromortar was less workable than the OPC control, and set very much more quickly, whereas the doped BC \hat{S} AF micromortar was initially more workable but still set slightly more quickly than the OPC control.

Table 3: Consistency and setting time

Cement	Initial Consistency	Setting time (h)
OPC (CEM I –52.5R)	workable	~ 5.0
Undoped BC \hat{S} AF	stiff	~ 1.0
Doped BC \hat{S} AF	fluid	~ 4.0

BC \hat{S} AF micromortar compressive strengths (Fig. 2) were higher than the OPC at 6 hours, the undoped BC \hat{S} AF giving very high values compared to the doped clinker; but by 1 day the OPC had caught up. At 7 days, both BC \hat{S} AF cements were about 40% weaker than the OPC, but the doped BC \hat{S} AF cement then accelerated and by 28 days was within about 15% of the control, whereas the undoped BC \hat{S} AF hardly gained any strength after 7 days. It is to be pointed out that an interground gypsum content of 8% used in both BC \hat{S} AF cements in these tests is not necessarily the optimum calcium sulfate content.

Linear expansion in water was monitored on 2x2x16cm micromortar bars. None of them expanded by more than 200 μ m/m over two years.

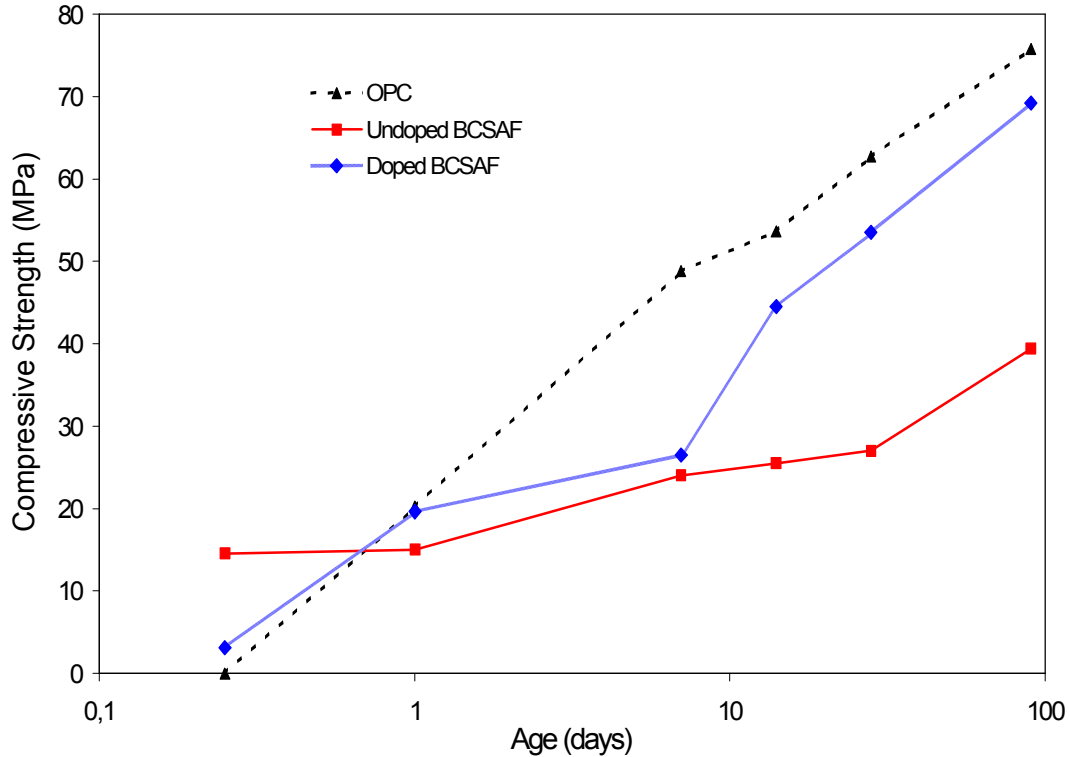


Fig. 2: Strength development of BCŞAF micromortars, vs. OPC

3 Hydration mechanism studies

3.1 Methods

The cements used in the hydration mechanism studies were similar to those described above, except that they were ground with 12% gypsum. The BSS was 380 ± 8 m²/kg except where noted otherwise.

3.1.1 Calorimetry

A pure paste was prepared from 3g cement and 1.5g water (W/B=0.5) and stirred manually for 30s. Then 2g was put in the calorimeter (at 20°C).

3.1.2 Conductivity and aqueous phase composition

Electrical conductivities were measured at 20°C on cement suspensions with water/binder ratio of 20. At selected times (based on the conductivity measurements), the aqueous phase was extracted by filtering. The elemental composition of the liquid phase was determined by ICP.

3.1.3 Hydration followed by semi-quantitative XRD

Pastes were made with pure calcium fluoride as an internal standard, added at a 1:6 mass ratio to cement. Pastes made at $w/c=0.50$ were “stopped” using acetone-ether procedure before XRD analysis. Well-separated XRD peaks were used and compared to the main fluorite peaks, allowing the relative changes to be monitored. The peaks for the anhydrous clinker phases were calibrated against the estimated phase composition of the initial cement. When necessary for increased sensitivity, selective dissolution methods were applied; salicylic acid in methanol was used to dissolve calcium silicates; and hot KOH/sugar solution was used to dissolve aluminates and aluminoferrite phases.

3.2 Calorimetry Results

Results for both undoped and doped BC \hat{S} AF at $380\text{m}^2/\text{kg}$ BSS plus doped BC \hat{S} AF at $550\text{m}^2/\text{kg}$ BSS are shown in Fig. 3. The main observations are:

1. An initial strong exotherm (“peak 1”) attributable to rapid initial hydration. This peak could not be evaluated quantitatively due to the use of an external mixing procedure and the time required for the calorimeter to reach thermal equilibrium.
2. An “induction period” characterized by low heat generation. Clinker doping lengthened this period by about 3 hours. An increase in doped cement BSS from 380 to $550\text{ m}^2/\text{kg}$ shortened it by about 2 hours.
3. The first acceleration period, giving rise to peak 2.
4. A second acceleration, giving rise to peak 3, which is higher than peak 2 in the undoped case, but lower with the doped clinker.
5. The shape of the curves is very different in comparing undoped and doped cements at the same BSS, whereas increasing the BSS for the doped cements did not change the overall shape of the curve.

3.3 Liquid phase evolution

Conductivity curves for the undoped and doped BC \hat{S} AF suspensions at $w/c = 20$ are shown in Fig. 4. In general, these seem to parallel the calorimetry curves, although the time scale is different, presumably due to the higher dilution. The sharp conductivity minimum observed at about 3 hours with the undoped BC \hat{S} AF and 8 hours with the doped BC \hat{S} AF appears to be related to the second heat peak, and the sharp conductivity maximum observed at about 4 hours with the undoped BC \hat{S} AF and 11 hours with the doped BC \hat{S} AF appears to be related to the third heat peak. To understand the conductivity curves better, a full solution analysis was conducted for the doped BC \hat{S} AF case, as shown in Fig. 5.

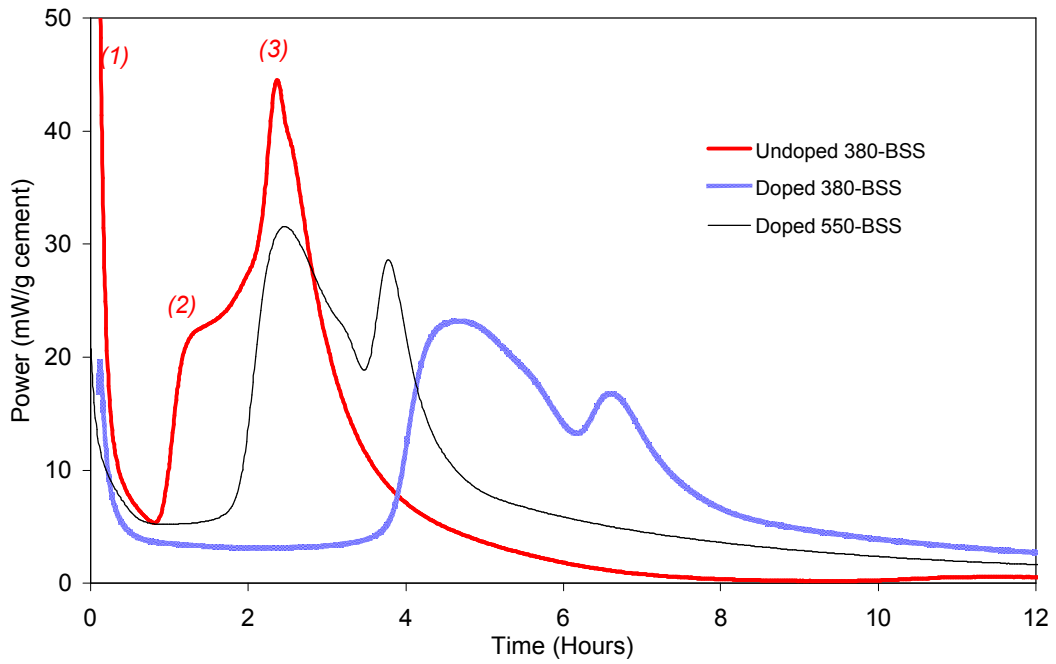


Fig.3: Calorimetry on BC⁺SAF cements pastes at w/c = 0.5

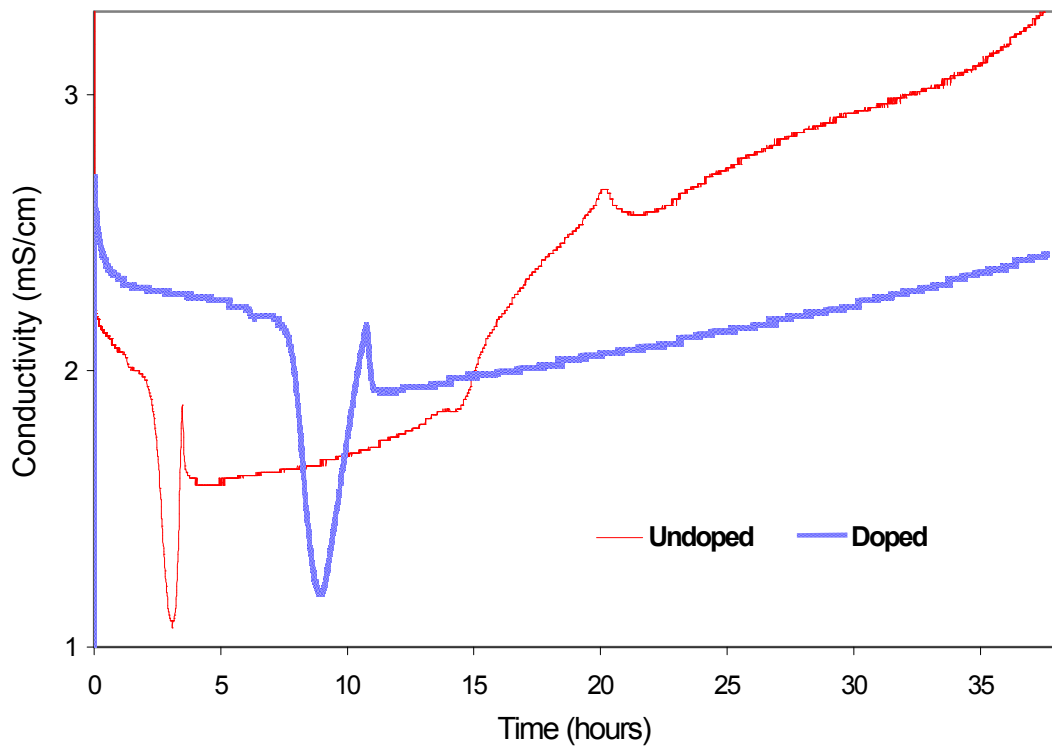


Fig. 4: Conductivity of BC⁺SAF cement slurries at w/c=20

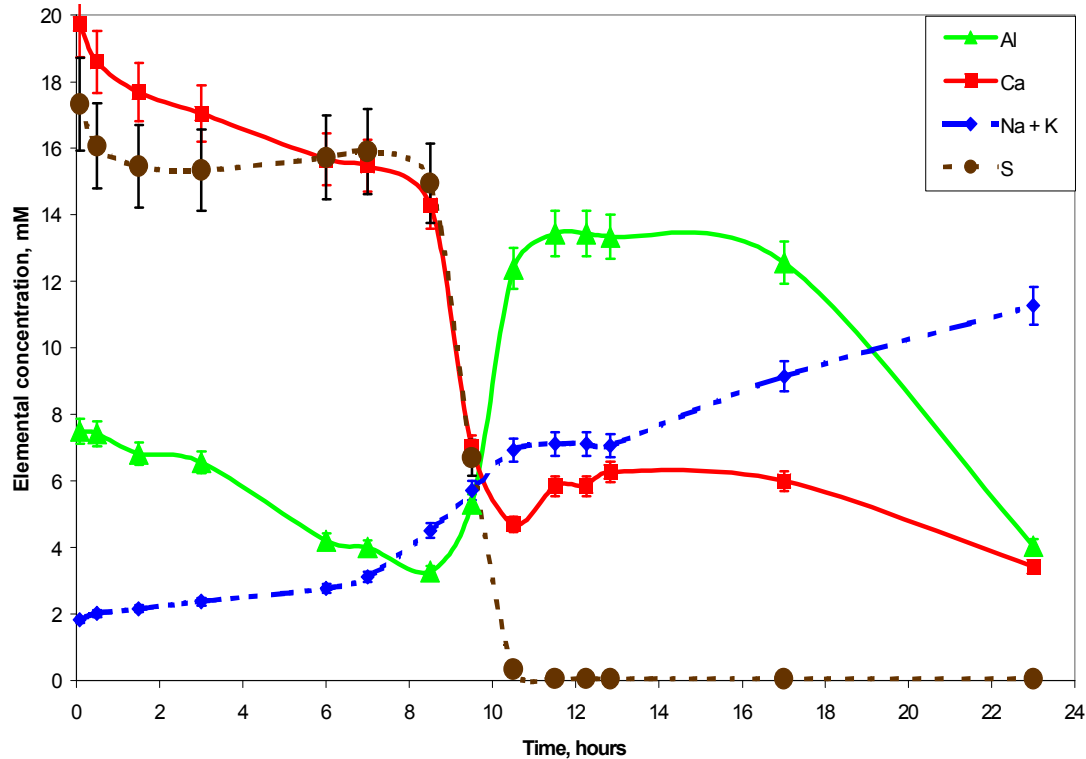


Fig. 5 : Liquid phase composition of doped BC&AF cement slurry (w/c=20)

The liquid phase appears to be saturated with respect to gypsum from the very beginning; there may even be a slight supersaturation in the first hours. The excess of calcium plus alkali cations over sulfate anions can be accounted for by the presence of aluminium, presumably as $\text{Al}(\text{OH})_4^-$. Note that the presence of significant levels of alkali ions is related to the dopant used to stabilize α -belite; thus, the slow release of alkalis probably indicates slow belite hydration, although the early-age alkali release may be related to traces of alkali sulfate and/or alkali in the aluminates phases. Note also that silica concentrations were only about $5\text{-}8\mu\text{M}$ initially, increasing to about $22\mu\text{M}$ by 23 hours, whereas sulfate (assumed equal to total sulfur concentration) fell to a steady value of about $60\mu\text{M}$ after 11 hours. Iron concentrations were always below the limit of detection.

The sharp conductivity drop at about 8 hours appears to correspond to the disappearance of sulfate from the solution, coupled with a strong diminution in the calcium concentration. This is consistent with the exhaustion of the supply of gypsum. At the same time, the aluminate concentration increases sharply, which would be consistent with the change from an ettringite-gypsum pseudo-equilibrium towards one between ettringite and another phase, such as monosulfoaluminate. The apparently low concentrations of hydroxide and silicate ions suggests that aluminium hydroxide should also be present amongst the solid phases.

The sharp but small conductivity peak occurring at about 11 hours seems to correspond to as sudden but small increase in dissolved calcium, which might be due to renewed hydration of the ferrite phase after gypsum exhaustion. After that, there is a slow increase in alkali concentration, probably indicative of slow belite hydration. And after 17 hours, aluminium concentrations begin to fall far more rapidly than calcium concentrations, suggesting that the ye'elimite phase may be almost exhausted by then.

3.4 Solid phase evolution

The results of the XRD analyses are summarized in Fig. 6:

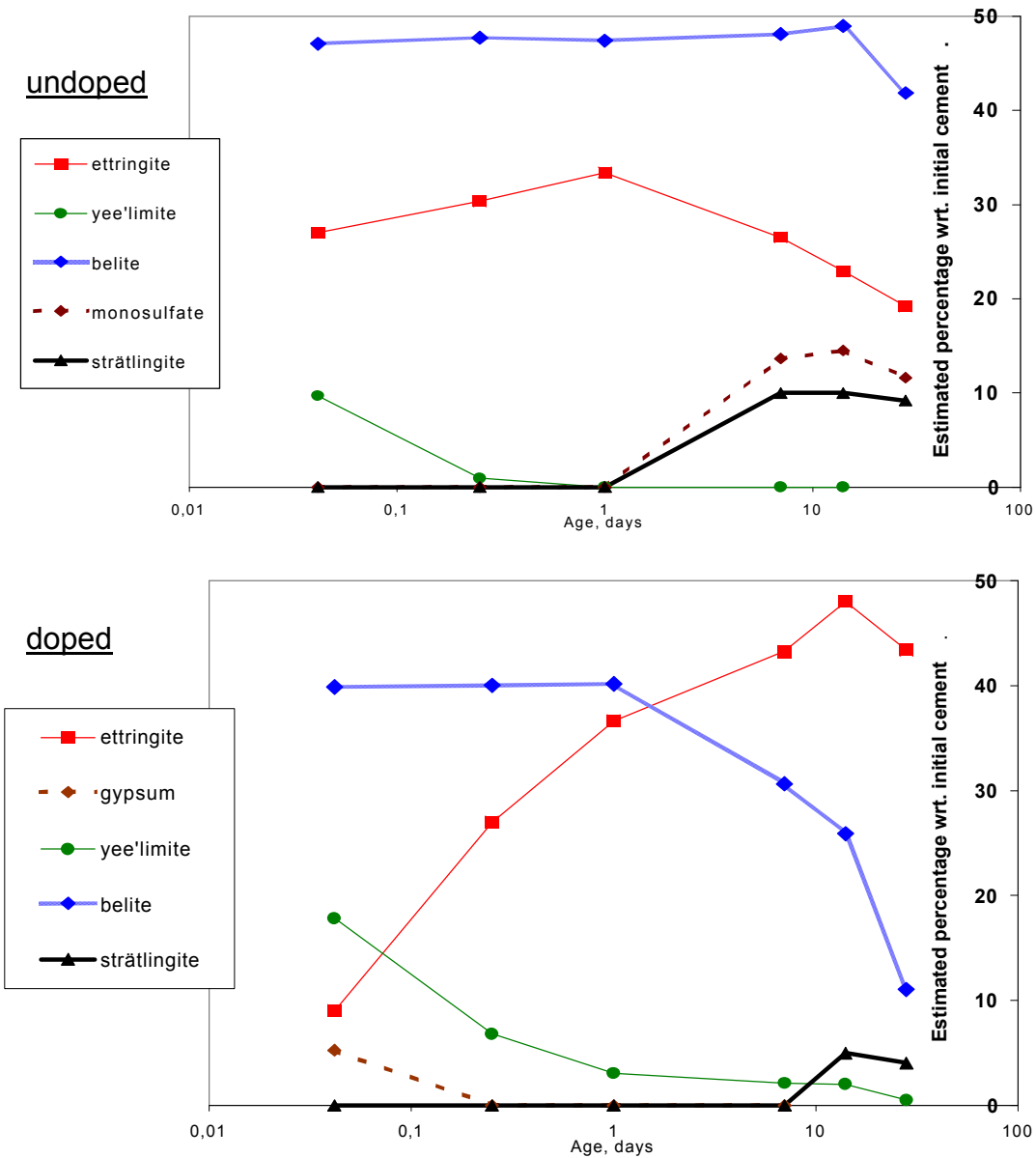
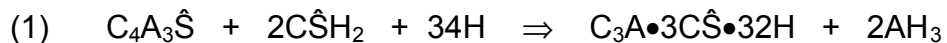


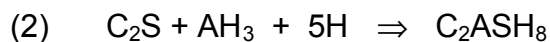
Fig. 6. Semiquantitative XRD analyses of hydrating BC&AF pastes

The phase compositions are estimated very roughly as mass percentages relative to the initial cement, (unhydrated initial values not shown in the graphs). It can be seen that the initial rate of ettringite formation is much greater in the undoped case, and no gypsum is detectable by the time of the first measurement (1 hour). Ye'elimite also disappears rapidly and is almost gone by 6 hours. By comparison, the doped cement still contains a lot of gypsum at 1 hour, and even at six hours it still has about one quarter of its original ye'elimite content. These observations suggest that the reaction between ye'elimite and gypsum to form ettringite (Eq. 1) is somehow retarded by the clinker dopant, (which may not be directly related to its role in the stabilization of α -belite; this remains to be studied).

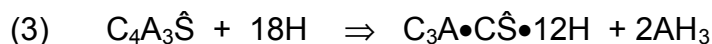


Note that we assume that this reaction must give rise to aluminium hydroxide, although this has not been directly confirmed. It is also not yet clear how much the ferrite phase participates in the formation of ettringite; the ferrite phase was not accurately measurable in our XRD experiments.

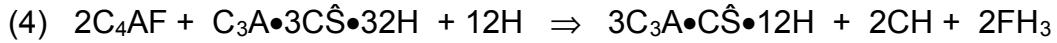
The XRD data also clearly confirm that the α -belite in the doped clinker hydrates faster than the β -belite in the undoped clinker. About 70% of the belite in the doped clinker has reacted by 28 days, while only about 15% of the belite in the undoped control has reacted by that time. This increased belite reactivity can explain the good strength development of the doped cement after the first few days. Moreover, it seems that the amount of ettringite obtained with the doped cement is higher and it persists for much longer. This is hard to explain on the assumption that the maximum amount of ettringite that can form should depend on the amount of sulfate in the cement, which is not significantly changed by doping; so it may be due to the limitations of the analytical method. We therefore do not attempt to explain the apparent quantitative differences; but the fact that the ettringite forms more slowly and persists longer is also consistent with the apparent absence of "monosulfate"-AFm-phase formation in the doped cement. The formation of strätlingite in both cases might be assumed to be due to a reaction such as Eq. 2, but this cannot explain why there appears to be less of it formed in the doped cement:



Formation of monosulfoaluminate after the exhaustion of the gypsum supply might be due either to reaction of residual ye'elimite, as in Eq.3:



Or else to reaction of ferrite phase with ettringite:



In this latter case the excess solid volume created per mass of cement reacted is very small, and this, coupled with slow belite hydration, could explain why the strength of the undoped cement does not increase very much during the period when AFm phases are forming.

4 Discussion

The disappearance of anhydrous phases and appearance of hydrates as observed by XRD make qualitative sense but the quantitative values are probably not sufficiently precise to be useful. However, the observations that the doped clinker has a less reactive ye'elite phase and a more reactive belite phase than the undoped clinker are totally consistent with the rheological and mechanical performance of the cements. It is somewhat more difficult to reconcile them with the calorimetric curves and aqueous phase data. It seems likely that peak 2 in the calorimeter curves corresponds to the exhaustion of gypsum; but, if this is so, it is hard to understand why ettringite appears to continue forming for quite a long time after that peak. Moreover, the existence of the third heat peak is not easily explained. It seems unlikely to be due to belite hydration, which leaves us with the alternative that it might be related to hydration of the ferrite phase.

Regarding the reduction of CO₂ inherent in the manufacture of BC[^]SAF cements, the clinker (Table 1) contains only 52.5% CaO, compared to a typical modern OPC clinker at about 66%. Moreover, about 3% of this CaO is supplied as calcium sulfate rather than limestone. Thus, one would expect the overall CO₂ emissions per unit clinker to be reduced by about 25%, based on the amount of limestone that must be decarbonated in the kiln. Regarding fuel-derived CO₂ emissions, it is difficult to estimate them accurately until the manufacturing process has been demonstrated on an industrial scale. But, if we assume that these clinkers could be made in a modern preheater kiln, the clinkering energy should be reduced roughly in proportion to the diminution in feed limestone content (since endothermic limestone decarbonation is the major energy sink in clinkering). Given that the optimal gypsum addition levels for BC[^]SAF cements currently appear to be in the range 8-12%, as compared to OPC at 4-6%, one can expect to obtain a further CO₂ emissions savings of around 5% in the cement.

5 Conclusions

It is demonstrated that "BC[^]SAF" clinkers based principally on belite, calcium sulfoaluminate and calcium aluminoferrite can be made at temperatures of about 1300°C from common raw materials, and, when certain dopants are included, can be used to make cements that perform somewhat like ordinary portland cements in mortar tests. The reduction in

total CO₂ emissions for the manufacture of such cements is expected to be about 20-30% compared to pure OPCs of similar performance, assuming that modern energy-efficient cement kilns can be used.

Unlike OPC, BC^oSAF cements initially set due to ettringite formation. Clinker dopants are required, both to retard early ettringite formation so as to obtain reasonable workability times, and also to activate the belite phase so that steady strength development will continue after set.

It is clear that a great deal further careful study will be required to fully understand the hydration of these interesting and novel cements, and thus to be able to better optimise their compositions and thereby further decrease manufacturing CO₂ emissions for equal concrete performance.

6 Acknowledgements

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7 References

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