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High-performance cement matrices based on calcium sulfoaluminate–belite compositions

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Abstract

Cement clinkers with a mineralogy based on $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, Ca_2SiO_4 (belite) and $C_2(A,F)$ (ferrite) are made in China: annual production is $>10^6$ tons/year. This cement is interground with 16–25% gypsum. The product has very rapid strength gain and examples removed from service in seawater are found to give remarkable protection to embedded steel after 14 years service in the intertidal zone. The chemistry and physics of sulfoaluminate cement hydration are described. Self-desiccation is more readily achieved in ettringite-rich cements than in traditional OPC formulations. It is concluded that the self-desiccated state, once achieved, is very difficult to resaturate and that the dry internal environment is partly responsible for the virtual absence of corrosion of embedded steel, even in chloride-rich environments.

Keywords: Calcium sulfoaluminate; Ettringite; High performance; Steel corrosion; Durability

1. Introduction

Interest in non-Portland, high-performance cements continues to be high. Portland cement concretes are a satisfactory product with which to engineer composites, but cement production generates much CO_2 and has high-energy requirements. Moreover, the matrix is relatively inflexible with respect to its chemical, microstructural and rheological properties. On the other hand, Portland cements are cheap; economic and technical constraints make it difficult to challenge their dominance. Among possible rivals, sulfoaluminate–belite cements are relatively cheap and have low energy requirements.

However, these compositions are relatively unfamiliar to engineers. Their main constituent, calcium sulfoaluminate, or $C_4A_3\bar{S}$, has been known as a cementing phase for many decades, but its potential in nonexpansive cement formulations has only recently been achieved. As a result of research at the China Building Materials Academy, an optimised formulation based on a clinker containing $C_4A_3\bar{S}$, belite (C_2S), ferrite and anhydrite ($CaSO_4$) was developed in the 1970s. Production has now expanded to $>10^6$ tons/year and several variants of this basic clinker are being manufactured, including normal, high early strength and high iron oxide types. In this paper, we describe some of the properties of the normal type of sulfoaluminate–belite clinkers.

2. Manufacture

Calcium sulfoaluminate cements, shorthand $C\bar{S}AC$, are made in rotary kilns. In China, small capacity kilns, once used for Portland cement production, tend to be diverted to $C\bar{S}AC$ production. Raw materials include limestone, bauxite or aluminous clay and gypsum: coal is normally used as fuel. However, other alumina sources have been used, for example, “red mud,” a largely unwanted by-product of the Bayer process for alumina purification. Table 1 (Column 1) gives a chemical analysis of a representative clinker.

Calcining temperatures attain 1300–1350 °C in the hot zone. This estimate has been made from microstructural examination of clinker and comparison of the mineralogical state or condition of clinker with relevant phase diagrams [1] and was subsequently confirmed to the writers as correct on a visit to a $C\bar{S}AC$ plant in China.

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Table 1
Analyses of commercial calcium sulfoaluminate cement

Oxide, wt.%	Clinker	Clinker blend
SiO_2	9.25	8.08
Al_2O_3	29.36	24.56
Fe_2O_3	4.29	3.62
CaO	42.91	41.10
MgO	2.78	2.86
SO_3	9.45	14.50
TiO_2	1.21	1.50
LOI	0.51	3.51
Sum	99.75	99.37

The resulting clinker is porous and friable relative to OPC clinker and, on that account, it is readily ground. Whereas OPC is normally interground with a few weight percent of $CaSO_4$ (including gypsum, hemihydrate or anhydrite or mixtures), $C\bar{S}AC$ is typically interground with 16–25% $CaSO_4$: Column 2, Table 1 shows an analysis of the finished product. As expected, calcium remains approximately constant, sulfate increases, while other major oxides of the clinker are generally diluted by the large calcium sulfate addition. The slight increases in MgO and TiO_2, which appear contrary to the general trend, reflect day-to-day variability of clinker and gypsum compositions.

The mineralogy of the $C\bar{S}AC$ clinker before gypsum addition is compared with OPC in Table 2. Some phases are present in both cement types, e.g., belite and ferrite. However, C_3S and C_3A, characteristic of Portland cement, are absent in $C\bar{S}AC$, whereas $C_4A_3\bar{S}$ is characteristic of $C\bar{S}AC$. The $C\bar{S}AC$ clinker may additionally contain anhydrite, $CaSO_4$, as well as minor amounts ($<5\%$) of gehlenite, $C_{12}A_7$ and periclase; the latter is usually kept low, $<1-2\%$, by careful selection of raw materials. The ferrite phase of $C\bar{S}AC$ is quite rich in Al: its mean Al/Fe ratio is usually close to 2. The ferrite phase of $C\bar{S}AC$ also includes much of the total TiO_2, although acid dissolution residues also disclose the presence of some perovskite $Ca(Ti,Al,Fe)O_3$, indicating that not all Ti is accommodated in ferrite.

The energy balances and CO_2 emissions depend on the efficiency of the kiln and fuel. An indication of these balances is shown in Table 3, giving ΔH values required per kilogram of phase. On account of the low Ca content, relative to OPC, CO_2 emissions are markedly reduced in $C\bar{S}AC$ clinkers. Further economy in specific fuel consumption and CO_2 release results from the high level of gypsum addition, 15–25%, typically made to the clinker, as well as the low energy requirements for grinding the composite.

Table 2
Comparison of clinker mineralogies

Phase/cement	OPC	$C\bar{S}A$[a]
C_2S	Yes	Yes
$C_2(A,F)$	Yes	Yes
$CaSO_4$[b]	Yes	Yes
C_3S	Yes	No
C_3A	Yes	Trace
C_4A_3S	No	Yes

[a] Shorthand for calcium sulfoaluminate.

[b] Including gypsum and hemihydrate. Much or all the calcium sulfate is added in the course of grinding clinker.

Table 3
Energy and CO_2 production

Compound	ΔH formation (kJ/kg)	CO_2 release[a]
C_3S	1848	0.58
CA	1030	0.28
βC_2S	1030	0.51
$C_4A_3\bar{S}$	800	0.22

[a] kg/mol of product.

3. Hydration

The as-received $C\bar{S}AC$ clinker, containing an estimated 18% gypsum added as a blending agent, had a specific surface area of 3840 cm^2/g. When mixed to a w/c ratio 0.43 at 20 °C, initial Vicat set occurred in 45 min and final set at 60 min. A 1:2.5 cement:sand mortar cube, cured at 20 °C at >98% r.h. had 1- and 3-day cube compressive strengths of 44.2 and 53.9 MPa, respectively: flexural strengths were essentially constant, 7.6 and 7.5 MPa at 1 and 3 days, respectively. The rapid strength gain, accompanied by rapid heat evolution, is characteristic of $C\bar{S}A$ cements. X-ray powder diffraction discloses that ettringite begins to form within 15–20 min of mixing and by 24 h is responsible for much of the strength development. At longer ages, strength continues to rise as other phases, especially belite, slowly hydrate. Gypsum is consumed rapidly and despite large additions, 18% in this instance, it is no longer detected by XRD after ~ 48 h of hydration. In a well-made paste, formulated to low w/s ratio, the ettringite matrix is virtually featureless in backscattered electron images. The rod or needle-like morphology of ettringite, so characteristic of its appearance in the pores within OPC, is not visible in $C\bar{S}AC$ pastes owing to dense packing of separate crystals. The matrix undoubtedly contains C–S–H and, in later stages of hydration, AFm although morphologies typical of these phases are not prominent in the microstructure. The most conspicuous coarser feature of the microstructure is the presence of unhydrated clinker; at high magnification, unhydrated ferrite solid solution can also be observed persisting even in pastes which have been moist cured for ~ 10 years.

A sensitivity study discloses the importance of the amount of gypsum added to the clinker. Zhang [2] calculated mineralogical balances for complete hydration of the clinker composition shown in Table 1, treating the amount of gypsum added as an independent variable.

Fig. 1 shows how the mineralogy is affected by the content of added $CaSO_4$. Note that some phases, e.g., C–S–H, are simply diluted by sulfate calcium additions

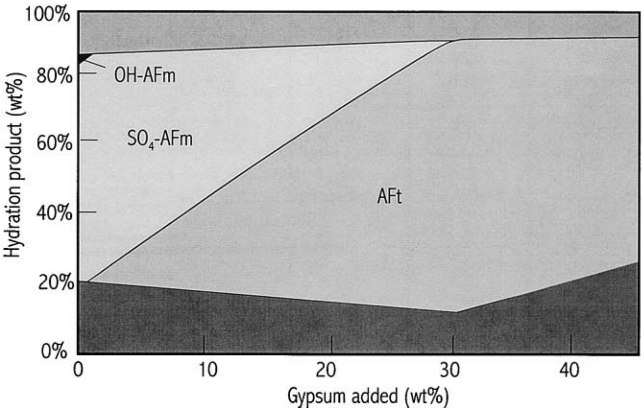

Fig. 1. Calculation of the hydrate phase composition (ferrite excluded) of a commercial calcium sulfoaluminate cement blended with varying amounts of gypsum. The commercial cement used in this study contained an estimated 18% gypsum. See Table 1 for the clinker chemistry.

whereas the content of ettringite, the main matrix former, is very sensitive to the amount of added sulfate. The manufacturer's empirical optimisation of this clinker, at 18% $CaSO_4$, ensures that ettringite is the dominant matrix former. From experience, this cement shrinks very slightly during its set, albeit rather less than an OPC. If, however, this $CaSO_4$ content of the $C\bar{S}AC$ composite is increased to 22–24%, the dimensional change is close to zero while, at or above a 24–25%, it becomes expansive. The expansive potential is usually realised within ~24 h. Thus, total $CaSO_4$, both present in clinker and also added during grinding, tends to be kept slightly below the theoretical requirement to maximise ettringite content in order to produce a cement, which, when formulated into mortar or concrete, is dimensionally neutral. Thus, formulations, developed in the first instance on an empirical basis, can be rationalised by calculation.

Set times of $C\bar{S}AC$ are typically quite short and it may be necessary in some applications to use a retarding plasticiser. Plasticisers have a dual function: to extend the workability of fresh mixes and also to reduce water contents and thereby improve ultimate strength. In general, plasticisers suitable for calcium aluminate cements tend to work well with $C\bar{S}AC$.

The chemical water demand (CWD) for complete hydration of clinker is characteristically higher for $C\bar{S}AC$ than for OPC. Zhang [2] calculated CWD for complete hydration of the cement shown in Table 1, Column 2. Since microscopy disclosed that the ferrite was essentially inert, calculation of the CWD was based on hydration of $C_4A_3\bar{S}$ and belite alone: Fig. 2 shows the results. The calculation discloses that CWD is closely related to the amount of interground gypsum and increases up to a maximum at ~30% gypsum. Since ettringite is very water-rich, and the amount of ettringite increases up to ~30% added gypsum, the rising trend of CWD is explained and the maximum CWD coincides with the maximum potential for ettringite formation. Using lightly plasticised mixes, the example cement has a rheology very similar to that of an OPC; w/c ratios in the range 0.3–0.35 give workable mortars and w/c ratios 0.35–0.45 give workable concretes. However, the CWD of $C\bar{S}AC$ mixes are substantially greater than for equivalent OPC mixes and, on that account, $C\bar{S}AC$ mixes, especially high-performance mixes made to low w/c ratios, are likely to retain much unhydrated clinker.

As a consequence of their high CWD, $C\bar{S}AC$ mixes readily undergo self-desiccation. We first envisaged that in a water-deficient environment, i.e., in the regime developed in formulations having less than the calculated CWD, AFm might simply form at the expense of the more water-rich AFt phase. But, experimentally, enhanced AFm formation is not observed in a variety of exposures, including both laboratory specimens and commercial concretes exposed to weathering for 10–15 years. Sufficient ettringite forms to consume all free water and thereafter ettringite continues to coexist with unhydrated clinker. Moisture regimes have been followed in the laboratory by casting hollow cylinders, ca. 60 mm diameter, of $C\bar{S}AC$ mortars: the cement used is shown in Table 1, Column 2. After final set, but within ~3 h of casting, a hygrometer probe was inserted into the hollow cavity and changes in internal relative humidity at the sealed probe were followed for 1.5 years. Fig. 3 shows the data. At an initial mix ratio w/c = 0.44, hydration virtually ceases after ~30 days and the internal 20°C relative humidity stabilised at ~90%. However, at w/c = 0.30, the relative humidity declined to less than 60% within 90–120 days and thereafter continued to decrease, albeit slowly, over the duration of the experiment, 575 days.

Microstructural studies disclose that some unhydrated clinker persisted at w/c = 0.44 but much more clinker, estimated to be 25% by semiquantitative image analyses

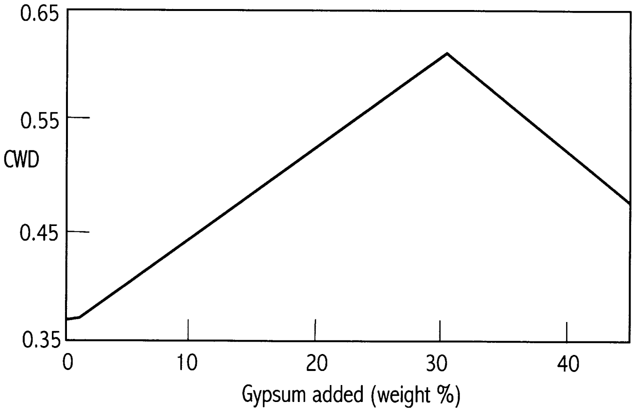

Fig. 2. Calculated chemical water (CWD) for full hydration of the clinker shown in Table 1, to which varying amounts of gypsum were added prior to grinding. The commercial cement used in this study had an added gypsum content of 18%, giving an indicated CWD ~ 0.52. The data are taken from Ref. [3].

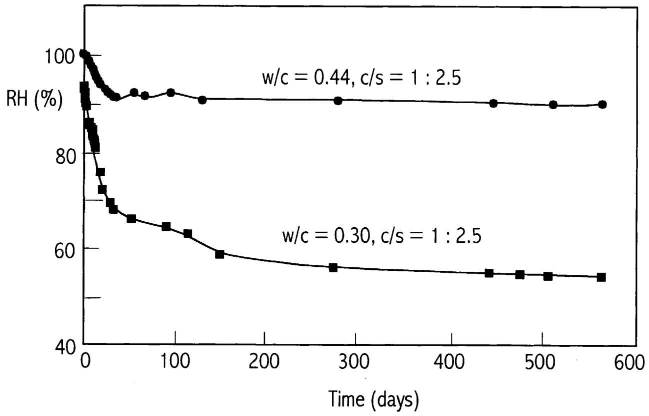

Fig. 3. Observed relative humidity achieved during hydration of the mortars made with the cement is shown in Table 1, with 18% added gypsum. Data are for cement: sand mortars, weight ratio 1:2.5, made to two w/c ratios. Note the severe self-desiccation achieved at w/c = 0.30.

and X-ray diffraction, persisted after 575 days in the mix with initial w/c = 0.3: this estimate of the amount of clinker agrees with calculations made by Zhang [2,3].

Although hydration virtually ceases at w/c = 0.44 after ~30 days, the process of pore refinement still continues. Fig. 4 shows mercury intrusion porosimetry data on a C$\bar{S}$A cement paste initially with w/c = 0.30. In the interval between 180 and 360 days, total accessible porosity diminishes and the pore size distribution shifts to smaller pore sizes.

4. In-service performance

Not surprisingly, the ultimate test of a new cement type is a documented record of in-service performance. A number of samples removed from service conditions after 10–15 years have been examined. Unfortunately, as is often the case with field concretes, not much is known about the actual concrete formulation and the quality of supervision and workmanship. However, none of the structures examined had failed, or proved inadequate for purpose, needed repair or otherwise showed signs of distress. Measured depths of carbonation were broadly similar to expectations of an OPC concrete with equivalent properties. It must also be noted that many of the structures examined were not exposed to demanding service conditions, e.g., prefabricated concrete stairs in interior service. We therefore concentrate on the performance of C$\bar{S}$AC concrete in the most demanding application available to us, in seawater.

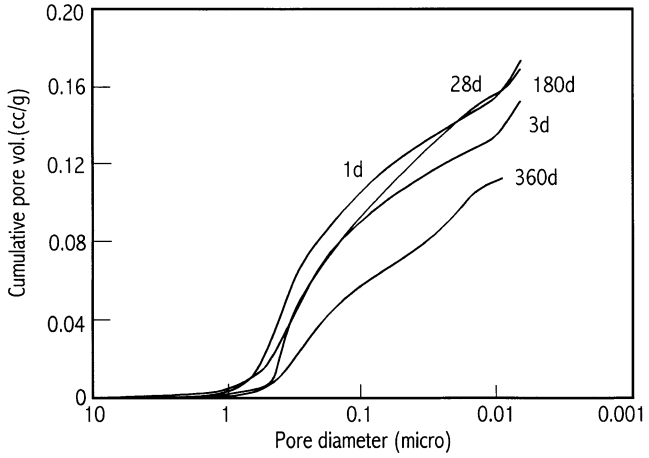

Fig. 4. Mercury intrusion porosimeter scans of the commercial cement shown in Table 1 (18% gypsum added) after hydration for various periods at self-generated humidity and 20 °C. The w/c ratio was 0.44. Note that, although no detectable hydration was observed between 180 and 360 days, the scan discloses that considerable pore refinement occurs.

A fine aggregate concrete pipe was made by centrifugal casting about 1978. Because of the centrifugation, the distribution of aggregate sizes is graded circumferentially. The exact w/s ratio is not known, but from experience of similar product, it was reduced to ~0.25 by centrifugation. In service, the pipe was used to convey gas and,

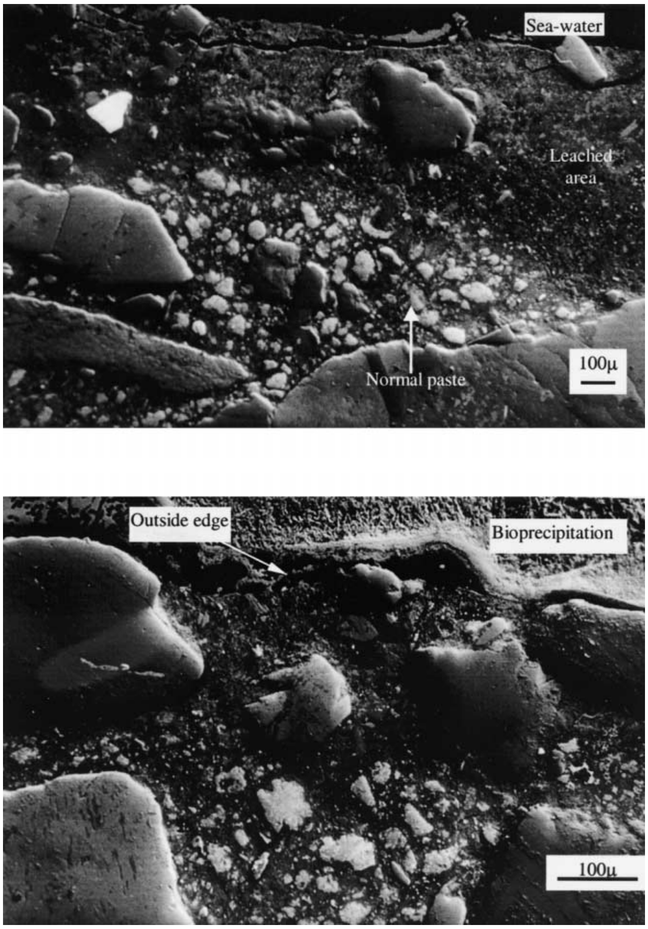

Fig. 5. Two representative cross-sections of the near surface altered zone of C$\bar{S}$AC concrete pipe after 14 years service in the intertidal zone. The coarse particles are quartz aggregate. See text for explanation of the zoning.

subsequently, process water for ~ 14 years. Physically, the pipe was located in the intertidal marine zone where it was subject to twice daily immersion. A section of pipe close to low tide was removed for physical examination. When broken, the mild steel mesh reinforcement was found to be uncorroded even though its concrete cover was as little as 7–8 mm. Fig. 5 shows a backscattered electron image of a cross-section of pipe close to the exterior surface, in alternating contact with seawater and air, and extending ~ 1 mm into the pipe. Three zones can be distinguished in the micrograph. An inner layer consists of unaltered but chloride-impregnated concrete. This comprises the whole of the matrix at depths greater than 500–1000 μm, and is characterised by the presence of abundant unhydrated cement clinker. Above this lies an altered zone, the composition of which is gradational. Supplementary microprobe analyses disclose that at or near the base of the altered zone, its chemistry is essentially identical to that of the original bulk composition. However, the nearer the surface exposed to sea water, the greater the extent of calcium depletion. All clinker in the altered zone has hydrated except towards its base, near its contact with unaltered cement.

In the outermost part of the altered layer, extending to 5–20 μm depth, extensive replacement of Ca by Mg occurs. Finally, the surface is coated by a discontinuous but strongly adherent layer of bioprecipitated $CaCO_3$.

The microprobe results also disclose that chloride has penetrated through the bulk of the paste, both altered and unaltered zones having a similar chloride content of ~ 0.1 wt.% chloride: unhydrated clinker, aggregate and $CaCO_3$ remain chloride free, so the actual chloride content of the hydrated but microscopically unaltered paste is probably on the order of ~ 0.2–0.4 wt.%.

5. Discussion

$C\bar{S}AC$ can lay claim to being a "high-performance" cement for three reasons:

- the low energy and low CO_2 emission associated with its production;
- its ability to form cements, mortars and concretes with high early and final strengths;
- its excellent durability, especially in saline marine environments, and the protection it affords to embedded mild steel.

Each aspect will be discussed in turn.

The low energy and low specific emissions of CO_2 are undoubted advantages of $C\bar{S}A$ products. The extent of benefit will, of course, depend on the thermal efficiency of the kiln but the saving in electricity requirements for grinding is a further advantage, as is the considerable dilution of clinker by calcium sulfate during finish grinding. The process is also capable of being operated with suitable by-product calcium sulfate, e.g., calcium sulfate arising from flue gas desulfurisation, which can partially or wholly replace gypsum in the kiln feed.

The high early strengths of $C\bar{S}A$ mortars and concretes do not appear to degrade with time in normal service. The principle matrix phase, ettringite, is stable relative to AFm in the thermodynamic sense. Thus, conversion reactions, as occur in high alumina cement when metastable hydroxy AFm converts to hydrogarnet, C_3AH_6, do not occur in $C\bar{S}AC$ because sufficient sulfate is added to avoid forming much AFm phase. The presence of ettringite has aroused concern because of its propensity to carbonate and, at elevated temperatures, to degrade. In practice, as judged from depth of carbonation in field exposures, carbonation does not appear to be a serious problem. Both laboratory experiments and field measurements disclose that carbonation rates in $C\bar{S}AC$ are similar than to those in OPC-based materials of comparable quality. With regard to thermal limits of ettringite stability, guidance has been given recently [4]: both temperature and relative humidity of the service environment require to be known in order to recommend conservative limits for ettringite-based cements. These limits are unlikely to be achieved under conditions of normal service.

Concern has also been expressed about the presence of unreacted clinker in hardened $C\bar{S}AC$: will it resume hydration in the future, and if so, will renewed hydration result in physical expansion? This question is of course quite general: most high-performance cements made to low w/s ratios, including OPC-based compositions, contain substantial amounts of unhydrated clinker. In fact, this clinker serves a valuable purpose. By lowering the internal relative humidity, and thereby achieving internal self-desiccation, it becomes difficult to initiate secondary hydration if and when concrete is wetted. Penetration and continued ingress of water, possibly by compression of air trapped in the pore network, is effectively halted. Fig. 5 demonstrates clearly how hydration can only proceed if accompanied by leaching: despite the concrete experiencing wet–dry cycling twice daily with corresponding suction, unhydrated clinker persists at relatively shallow depths, > 0.6–1.0 mm after 14 years exposure. Thus, rehydration, even upon cyclic immersion in sulfate-containing seawater, is not observed.

Ion penetration certainly occurs, as evidenced by homogeneous permeation of chloride through the entire thickness of the paste. Chloride is believed to diffuse by ion exchange, between OH and Cl^-, within the matrix minerals of the paste, principally AFm, but possibly also C–S–H and ettringite. However, while permeating "water" can similarly exchange with the constitutional H_2O and OH^- of paste, the cement paste cannot increase its total water content by this mechanism because pores, once emptied of water, are difficult to resaturate. This accounts for the apparent paradox that chloride, and presumably hydroxide, migrate through the paste, but that unhydrated clinker also persists. The suggested mechanisms of environmental interaction allow ion exchange to occur but not significant gain of molecular water unless other mechanisms of deterioration, such as leaching, are also operative.

Steel remains passivated within the matrix. The original state of the reinforcement at the time of placement, nearly 20 years ago, is unknown: it may already have been lightly oxidised. However, after 14 years of service, embedded steel is still fresh and the cover concrete is intact. These observations contrast with recent laboratory data of Kalogridis et al. [5]. They made a C$\bar{S}$A clinker in the laboratory, similar to the commercial clinker we used, except that sulfate was apparently all incorporated at the clinkering stage. Half-cell potentials of steel embedded in this cement were measured in tap water and in 3.5% NaCl solution. They conclude that "the low pH values... of the pore solution and the higher, compared to OPC, average pore diameters... of sulfoaluminate cement mortars of this study exposed the reinforcing steel to a high corrosion risk, as revealed by the half cell potential measurements. However, other factors, like the concentration of free chlorides in the pore solution, the oxygen access to the steel surface and the total porosity also contributed to the observed averaged corrosion rate."

We do not dispute their results, which usefully highlight regimes in which corrosion may be a hazard. However, in the case of pipe intermittently immersed in seawater for 14 years, corrosion has not occurred. We suggest that (i) the effective permeability for oxygen is in part controlled by the internal self-desiccation, which was spontaneously achieved in the Chinese samples on account of the added calcium sulfate, which, during reaction, increased chemical water demand; (ii) the pore size distribution of hydrated paste in the Chinese material is much more favourable than that of the mix used by Kalogridis et al. [5]; and (iii) it is better to incorporate reactive calcium sulfate in the mix rather than add it all to the raw meal with the resulting risk of generating unreactive deadburning anhydrite.

Existing theories of passivation of steel in concrete, including the role of chloride ions and internal oxygen activity, have yet to be applied to C$\bar{S}$AC matrices. But it is apparent that existing theory relates to corrosion in a water-saturated environment, whereas it is probable that self-desiccation in the C$\bar{S}$AC example maintains a water activity much below saturation in the vicinity of the embedded steel. This observation might be equally applicable to self-desiccating OPC-based high-performance cements.

6. Summary

C$\bar{S}$AC materials are seen as a potentially very attractive high-performance material. Rapid strength gain and durability in a range of aggressive environments make it applicable to civil engineering needs. It is chemically compatible with and adheres strongly to OPC, including carbonated OPC. It achieves self-desiccation more readily than OPC compositions and this self-desiccation affords protection against corrosion to embedded steel, even in cyclic exposure to chloride-containing seawater. Its high sulfate content makes it virtually immune to seawater sulfate attack, because its constituent phases are fully sulfated.

The content of unhydrated clinker remaining in matrices formulated to low w/c ratios is not seen as a disadvantage and, indeed, has many potential advantages with respect to chemically toughening near-surface layers undergoing leaching.

Corrosion of embedded steel remains an area which requires further research. Although practical examples demonstrate that the C$\bar{S}$A matrix can afford excellent protection, regimes of corrosion and of protection still need to be quantified and related to engineering practice.

Acknowledgments

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References

[1] O. Andac, F.P. Glasser, Microstructure and microchemistry of calcium sulfoaluminate cement, vol. 370, in: S. Diamond, S. Mindess, F.P. Glasser, L.W. Roberts, J.P. Skalny, L.D. Wakeley (Eds.), Materials Res. Soc. Proceedings, Materials Research Society, Pittsburgh, PA, 1995, pp. 135–142.

[2] L. Zhang, PhD Thesis, University of Aberdeen (2001).

[3] L. Zhang, F.P. Glasser, New concretes based on calcium sulfoaluminate cement, in: R.K. Dhir, D. Dyer (Eds.), Modern Concrete Materials: Binders, Additions and Admixtures, Thomas Telford, London, 1999, pp. 261–274.

[4] Q. Zhou, F.P. Glasser, Thermal stability and decomposition mechanisms of ettringite at < 120 °C, Cem. Concr. Res. (in press).

[5] D. Kalogridis, G.Ch. Kostrogloudis, Ch. Ftikos, Ch. Malami, A quantitative study of the influence of non-expansive sulfoaluminate cement on the corrosion of steel reinforcements, Cem. Concr. Res. 30 (2000) 1704–1731.