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A new methodology for the specification of calcium sulfoaluminate cement in concrete

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ABSTRACT

In recent years, calcium sulfoaluminate (CSA) cement has generated interest as a low-CO2 alternative to Portland cement (PC). The successful implementation of PC-type kilns for the production of CSA cement has given cement manufacturers the incentive to develop their own CSA cement products, some of which are being sold commercially through national or European technical approvals. On this basis, the European cement industry is currently considering the development of a harmonised product standard for CSA cement. For CSA cements, however, the process will likely be more challenging than it was for PC (CEM I) with so many variations of CSA cement clinker now being produced. These are usually either ye'elimite-rich or belite-rich depending on the proportions of raw materials going into the kiln. In addition, limits on the levels of additional calcium sulfate (required for full hydration of the ye'elimite phase) may need to be determined along with an appropriate methodology for the specification of these materials in concrete. This paper seeks to contribute to the development of a harmonised product standard for CSA cement by proposing a new methodology for specification in concrete applications. In this new approach, the level of calcium sulfate addition is specified as a function of the ye'elimite content of the CSA cement and the 'target' water:binder ratio for the concrete. Early mechanical and durability testing of cement pastes revealed that the new methodology led to improved CSA cement properties compared with control specimens that were formulated using a conventional approach.

1. INTRODUCTION

To meet sustainability targets, the cement industry is currently investigating novel cements that depend less on the calcination of limestone [1]. In recent years, cement producers have been developing calcium sulfoaluminate (CSA) cements as low-carbon alternatives to Portland cement (PC) CEM I for various applications. CSA cement is typically produced by burning raw materials such as limestone, clay, bauxite and gypsum at temperatures approximately 200°C lower than those required for PC. Limestone generally forms the bulk of the kiln feed however the quantity is less with sulfur and aluminium bearing minerals partially taking its place. The corresponding reduction of the limestone content in the raw meal is the main contributor to reduced CO_2 emissions in CSA cements.

One of the main barriers to the widespread uptake of CSA cement in Europe is lack of standardisation. While some manufacturers have obtained European Technical Approvals (to facilitate CE marking) it is still considered necessary to pursue a harmonised product standard to obtain widespread acceptance in construction applications. As CSA cement is a clinker-based cement, it is likely that an initial version of the product standard will draw on a template similar to the PC standard (i.e. EN 197-1). However, one of the key challenges likely to be faced during the drafting of such a standard will be in devising the main cement 'types'. For example, belite-rich CSA cement clinker results from higher proportions of silica bearing minerals in the raw feed; whereas ye'elimite-rich clinker results from lower proportions of raw silica.

Unlike CEM I, CSA cements usually require varying quantities of additional calcium sulfate to achieve dimensionally stable cement pastes with good strength development. Therefore, it is important to investigate a robust methodology for specifying CSA cement in concrete and to examine whether a prescriptive or performance based approach is a practical solution for a harmonised product standard.

In this paper, a new methodology has been proposed whereby the quantity of calcium sulfate is calculated taking account of the 'target' (or desired) water:binder (w/b) ratio to be specified for the final concrete mix. This is considered to be an improvement over the common methodology that assumes full hydration of the ye'elimite and calcium sulfate phases. It is anticipated that the outcome of this research could influence the development of a new harmonised standard for CSA cement.

2. DESCRIPTION OF THE NEW METHODOLOGY

In the literature [2], the optimum quantity of calcium sulfate is usually specified by calculating the stoichiometric quantity of gypsum or anhydrite required for maximum ettringite formation based on the following equations:

$$\underset{\text{ye'elimite}}{C_4A_3\overline{S}} + \underset{\text{gypsum}}{2C\overline{S}H_2} + \underset{\text{water}}{34H} \rightarrow \underset{\text{ettringite}}{C_3A{\cdot}3C\overline{S}{\cdot}32H} + \underset{\text{gibbsite}}{2AH_3} \quad (1)$$

$$\underset{\text{ye'elimite}}{C_4A_3\overline{S}} + \underset{\text{anhydrite}}{2C\overline{S}} + \underset{\text{water}}{38H} \rightarrow \underset{\text{ettringite}}{C_3A{\cdot}3C\overline{S}{\cdot}32H} + \underset{\text{gibbsite}}{2AH_3} \quad (2)$$

While reactions 1 and 2 can give reasonable estimates of the additional gypsum or anhydrite quantities required, this 'full hydration' approach relies on the assumption that full consumption of the solid and liquid reactants will occur. Furthermore, equation 2 indicates that a w/b ratio as high as 0.78 may be necessary to complete hydration in a fully sulfated system. In terms of workability, such high w/b ratios would not be practical (w/b ratios of less than 0.5 are usually specified in structural concretes). Therefore, in order to achieve good hydration of the cement component in CSA concretes, the ye'elimite content of the CSA clinker would have to be very low to reduce the chemical water demand. With varying compositions available for modern CSA clinkers e.g. ye'elimite-rich or belite-rich, it is apparent that using equations 1 and 2 will not be optimised for all cases.

A new methodology for formulating CSA cement pastes is considered necessary to account for the lower-than-theoretical w/b ratios that are commonly specified for CSA concretes. When the traditional methodology is used for high-ye'elimite CSA cements, i.e. by considering full stoichiometric quantities, a significant amount of unhydrated ye'elimite and calcium sulfate would remain in the concrete which has the potential to affect mechanical performance and durability. For the new approach, a simple algorithm was devised [3] to calculate the required calcium sulfate content based on the following inputs:

1. Target w/b ratio anticipated for the CSA concrete mix;
2. Calcium sulfate type (gypsum or anhydrite);
3. Ye'elimite mass (%) in the CSA cement clinker.

Unlike the traditional approach, the algorithm outputs the mass (%) of calcium sulfate (gypsum or anhydrite) required to react with ye'elimite and the mixing water only. When devising the algorithm, close attention was given to the calcium sulfate type. For example, if gypsum is specified as the input, the mass of the two molecules of bound water in gypsum is taken into account when calculating the mass of water required for an 'equivalent' mix containing anhydrite. Often in the literature when the effect of different calcium sulfates on CSA pastes is examined, only a fixed mass of gypsum is compared with a fixed mass of anhydrite [4-6]. However, when the bound water in gypsum is taken into account, the actual sulfate available for reaction (1) becomes significantly less than the sulfate available in equation (2) and is therefore not a true comparison.

3. MATERIALS AND METHODS

The CSA cement chosen for this study was high-ye'elimite Type III CSA having a Blaine specific surface area of 421 m^2/kg (obtained from Hanson Cement). A Rietveld analysis carried out on the CSA cement clinker revealed that the main crystalline phases consisted of ye'elimite at 77.2% followed by belite (14.3%), perovskite (5.7%), mayerite (1.6%) and periclase (1.2%). Synthetic anhydrite was obtained from Francis Flower and the gypsum was supplied by Saint-Gobain Formula.

A summary of the mix proportions for the CSA cement paste formulations investigated in this work is shown in Table 1.

Table 1. Summary of CSA paste formulations investigated

MIX ID	CSA clinker/%	Gypsum /%	Anhydrite/ %	w/b
1	77	23	-	0.41
2	81	-	19	0.48
3	70	30	-	0.41
4	74	-	26	0.48

Mixes 1 and 2 were calculated using the new methodology whereas mixes 3 and 4 were calculated using the theoretical ‘full hydration’ methodology. The mix proportions were designed using a ‘base’ w/b ratio of 0.41 which was considered to be practical for construction purposes (determined through mini slump trials). In order to have a correct chemical comparison, the calculations (for both methodologies) have taken into account that gypsum has two molecules of bound water, hence higher water contents in Mixes 2 and 4.

Specimens were prepared by using standard mixing techniques for cement pastes with all powders dry-blended beforehand. All samples were wrapped in wet hessian cloth, sealed in zip-lock polythene bags and cured at 20 °C. The compressive strength of the hardened cement pastes was determined at regular intervals by crushing 25 mm cement paste cubes. Tests for water absorption [7] and air permeability were carried out at 2 months; while carbonation [8] and chloride resistance [9] were assessed at 2.5 months.

4. RESULTS AND DISCUSSION

The main findings from the experimental programme are summarised in Table 2. From the mini slump results shown, it is apparent that the water demand in the mixes containing anhydrite is higher compared with those containing gypsum. The faster dissolution rate of gypsum led to reduced setting times compared with anhydrite. These findings are in line with previous studies comparing the effects of different calcium sulfate types [10,11].

It is interesting to observe the effects of the new calculation methodology when comparing the results from mechanical and durability related tests. In terms of compressive strength, the mix proportions derived using the new methodology (i.e. Mix 1 and 2) show a clear superiority at days 3, 7 and 28 compared to those mixes derived using the theoretical 'full hydration’ approach (Mix 3 and Mix 4). The strength for most mixes increased gradually within the 28-day period except for Mix 1 and Mix 3, both of which show a slight decrease in strength at 28 days. As expected, the mixes containing the less-reactive anhydrite had lower early strengths compared with those containing gypsum which is similar to what was observed in a previous study [4].

For water absorption (Figure 1) and air permeability (Figure 2), similar improvements were observed with the mixes formulated using the new methodology. This suggests that improved hydration is possible using the new ‘target w/b’ approach. On the other hand, in terms of carbonation and chloride penetration, significant improvements were not observed. It is anticipated that further monitoring of these samples over a longer period will determine whether any significant differences are evident. The testing carried out in this work has also demonstrated that improved durability may be achieved when anhydrite is specified over gypsum as the calcium sufate source. This is likely attributed to the slow and steady hydration mechanism when the less-reactive anhydrite is present which contributes to a more refined microstructure and hence a decrease in permeability.

Table 2. Summary of main results

	New ‘target w/b’ methodology		‘Full hydration’ methodology	
	Mix 1 Gypsum (23%)	**Mix 2 Anhydrite (19%)**	**Mix 3 Gypsum (30%)**	**Mix 4 Anhydrite (26%)**
w/b ratio	0.41	0.48	0.41	0.48
Mini slump (mm)	54	82	48	94
Setting time				
Initial	1 h 48 min	4 h 05 min	2 h 05 min	3 h 35 min
Final	2 h 58 min	12 h 38 min	3 h 20 min	5 h 20 min
Compressive Strength (MPa)				
Day 1	40.55	3.51	35.33	15.62
Day 3	56.21	36.47	45.7	22.99
Day 7	57.89	50.22	49.92	24.1
Day 28	51.94	58.33	49.58	24.73
Air permeability coefficient (m^2)	2.76×10^{-14}	7.00×10^{-15}	8.75×10^{-14}	-
Weight of Water absorbed ($kg.m^{-2}$)	12.36	4.98	23.6	8.18
Carbonation depth (mm)	4.84	3.27	4.9	4.11
Chloride penetration depth (mm)	16.51	8.48	12.35	7.31

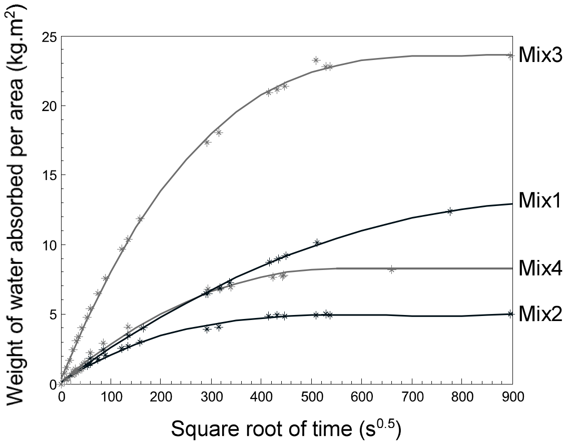

Figure 1. Water absorption of hardened CSA cement pastes after 2 months.

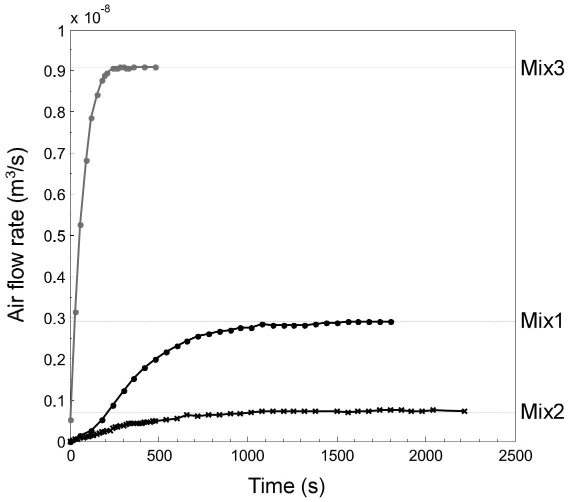

Figure 2. Air permeability of hardened CSA cement pastes after 2 months. (Note: data for Mix 4 is not given as the apparatus was in need of repair at the time).

5. CONCLUSIONS

The results in this paper emphasise the fact that careful consideration must be given to both the type and quantity of calcium sulfate in order to correctly specify CSA cement for concrete applications. To achieve the best performance, it is possible that an optimum calcium sulfate content must be determined by taking account of the target w/b ratio rather than using calcium sulfate contents based on the common 'full hydration' method.

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REFERENCES

[1] Gartner E. and Hirao H, 2015. A review of alternative approaches to the reduction of CO2 emissions associated with the manufacture of the binder phase in concrete, Cem. and Concr. Res., 78A:126-142.

[2] Zhang L. and Glasser FP, 1999. New Concretes Based on Calcium Sulfoaluminate Cement. In *Modern Concrete Materials: Binders, Additions and Admixtures*, Dundee, Thomas Telford.

[3] Murdaymootoo K. and Hui J, 2016. Effects of gypsum and anhydrite on the durability properties of calcium sulfoaluminate cement, Undergraduate Dissertation, In *Department of Civil, Geomatic & Environmental Engineering*, University College London, London, U. K.

[4] Péra J, Ambroise J, Holard E, Beauvent G, 2003. Influence of the type of calcium sulfate on the properties of calcium sulfoaluminate cement. In *Proceedings of the 11th International Congress on the Chemistry of Cement*, Durban, South Africa.

[5] Péra J. and Ambroise J, 2004. New applications of calcium sulfoaluminate cement, Cem. and Concr. Res., 34(4): 671-676.

[6] Winnefeld F. and Barlag S, 2010. Calorimetric and thermogravimetric study on the influence of calcium sulfate on the hydration of ye'elimite, J. Therm. Anal. Calorim., 101(3): 949-957

[7] CEN, 2002. Products and systems for the protection and repair of concrete structures. Test methods. Determination of resistance of capillary absorption (EN 13057:2002). London, U.K.

[8] BSI, 2013. Testing hardened concrete. Determination of the potential carbonation resistance of concrete. Accelerated carbonation method (BS 1881-210:2013). London, U.K.

[9] CEN, 2015. Testing hardened concrete. Determination of the chloride resistance of concrete, unidirectional diffusion (EN 12390-11:2015). Brussels, Belgium.

[10] McCague C, 2015. Development of novel composite cement systems for the encapsulation of aluminium from nuclear wastes, PhD thesis. In *School of Planning, Architecture and Civil Engineering*, The Queen's University of Belfast, Belfast, Northern Ireland.

[11] McCague C, 2014. Effect of calcium sulfates on the early hydration of calcium sulfoaluminate cement and the stability of embedded aluminium, In *Proceedings of the 2nd International Symposium on Cement-based Materials for Nuclear Wastes*, Avignon, France.