International Workshop on Innovation in Low-carbon Cement & Concrete Technology
21-24 September 2016, University College London, U.K.
Paper number 18

DEVELOPMENT OF CALCIUM SULFOALUMINATE CEMENT COMPOSITES FOR NUCLEAR WASTE ENCAPSULATION

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ABSTRACT: In the UK, nuclear wastes are usually ‘cemented’ before disposal so that harmful radionuclides can be physically and chemically contained. In this process, conventional Portland cement is blended with high levels of relatively inert mineral additions, mostly to reduce the high heat evolution in large pours. Calcium sulfoaluminate cement (CSAC) has recently attracted interest in various applications due to its lower pH and ability to bind significant quantities of water compared with conventional Portland cement. Such qualities are particularly suited to the encapsulation of legacy wastes such as aluminium and uranium, which would otherwise corrode if embedded within a Portland cement environment. While some early trials have demonstrated

good potential of CSAC, the rapid reaction rate (and associated heat generation) is still restricting its use. In this paper, common mineral additions such as ground granulated blastfurnace slag (GGBS), pulverised fuel ash (PFA) and limestone powder (LSP) were incorporated at very high replacement levels (up to 75%) in an attempt to dilute the cement matrix and hence reduce the heat of hydration. Studies of compressive strength, heat of hydration and aluminium corrosion revealed that these CSAC composites demonstrate excellent potential for aluminium waste encapsulation.
Keywords: Calcium sulfoaluminate cement, composites, nuclear waste encapsulation, corrosion, aluminium

INTRODUCTION

The UK nuclear industry currently utilises composite blends of Portland cement (PC) with up to 90% of ground granulated blastfurnace slag (ggbs) for the encapsulation of low and intermediate level nuclear wastes. In this process, the wastes are directly mixed with cement and cured in large stainless steel drums before being transported to a storage facility for monitoring. Such a high replacement of Portland cement is necessary in order to reduce the high heat of hydration in large volume pours. While PC-based matrices have been successfully utilised for the encapsulation of various waste streams, the high pH environment (usually around 12.5 – 13) coupled with freely available moisture, will cause the corrosion of certain waste metals such as aluminium. Since aluminium is only passive between pH 4 – 8.5, the use of an alternative low-pH cement system could serve to reduce/inhibit the corrosion. Calcium sulfoaluminate cement (CSAC) has been recognised as one such alternative. Not only does CSAC have a reduced pH (usually around 10.5 – 12), it also has an excellent water binding capability due to the formation of its main hydration product, ettringite. To maximise ettringite formation, calcium sulfate (usually in the form of gypsum or anhydrite) is added. When gypsum is added, the following main reaction occurs:

$$C_4A_3\$ + 2C\$H_2 + 34H \rightarrow \underset{\text{ettringite}}{C_3A \cdot 3C\$ \cdot 32H} + \underset{\text{gibbsite}}{2AH_3} \qquad (1)$$

Unfortunately, however, the industry remains sceptical of this material as the rapid nature of the hydration reaction will cause excessive heat generation in large volume pours. This research aimed to bridge the gap in the literature by developing ‘CSAC composites’ through the high-volume replacement of CSAC powder with mineral additions. In this paper, the effect of adding common mineral additions to a reference CSAC has been evaluated and discussed.

MATERIALS AND METHODS

In a previous study by the authors, a CSAC ‘reference’ sample was developed in which a suitable type and quantity of calcium sulfate was determined(1). Trials revealed that if gypsum is used as a source of additional sulfate, a lower pH can be maintained (compared with the less reactive anhydrite). This reference formulation (C0) was then blended with GGBS, pulverised fuel ash (PFA) and limestone powder (LSP) at two levels – 50 and 75%. To meet the requirements for workability, the w/s ratio was adjusted to achieve a mini slump of 85 ± 5 mm (as recommended by the UK nuclear industry). 25 x 25 x 25 mm cube samples were cast and tested for compressive strength. Heat of hydration was studied using a TAM Air isothermal conduction calorimeter. Al corrosion rates were continuously monitored using a novel quantitative test facility developed at for this project (based on polarisation resistance measurement) (2). All samples were cured in sealed conditions at a temperature of 40°C to simulate industrial conditions.

RESULTS AND DISCUSSION

Water demand and initial pH of CSAC composites

The results of the mini slump tests are shown in Table 1. It can be seen that the addition of PFA and GGBS to C0 served to increase the water demand slightly while LSP served to reduce the water demand. Measurements of the fresh paste pH revealed that the composites maintained a pH value of ~10.5 (similar to C0).

Compressive strength of CSAC composites

The compressive strength results for the CSAC composites are presented in Figure 1. Overall, strengths were significantly reduced compared with C0; however, the minimum strength criterion (> 4 MPa after 7 days) was met with all composites. Regression of strength at later ages was noted in all samples. It is possible that this is an effect of curing at elevated temperature which may have caused delayed reactions to occur after rapid formation of the initial ettringite 'skeleton'. Studies are ongoing to elucidate the causes of this.

Table 4. *Outcome of mini slump tests*

Key	Addition %	w/s
C0 (CSAC/gypsum 85:15)	-	0.43
PFA/C0	50	0.48
GGBS/C0	50	0.49
LSP/C0	50	0.41
PFA/C0	75	0.49
GGBS/C0	75	0.48
LSP/C0	75	0.42

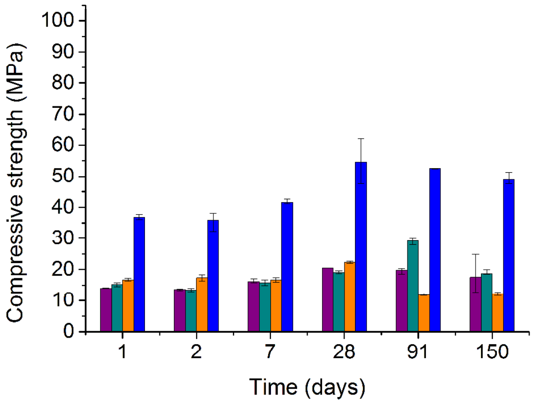

Figure 1 (a) CSAC with 50% mineral additions

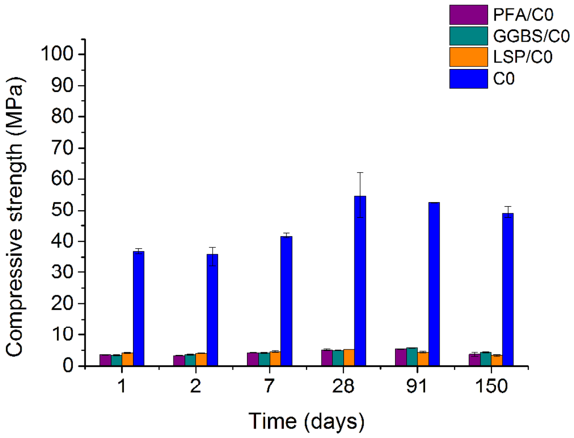

Figure 1 (b) CSAC with 75% mineral additions

Heat of hydration of CSAC composites

The results from isothermal conduction calorimetry for the CSAC composites are presented in Figure 2. As expected, the heat output of the CSAC reference was significantly reduced by using high levels of mineral additions. At very high levels (75%), the total heat output was lower than the GGBS/PC 9:1 reference system. This demonstrates a potential advantage of using latent hydraulic or pozzolanic additions with low pH cements. The lack of hydroxyl ions compared with a highly alkaline PC-based system ensures that PFA or GGBS behave mostly as fillers which may be advantageous in reducing the exothermic reaction.

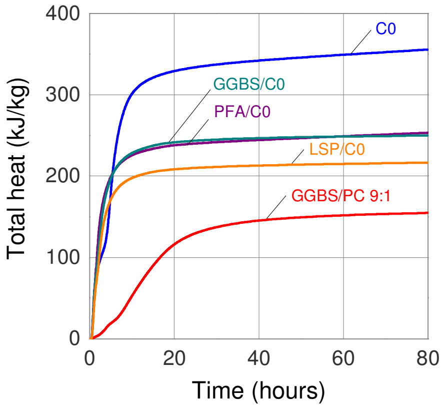

Figure 2 (a) Total heat output with 50% mineral additions

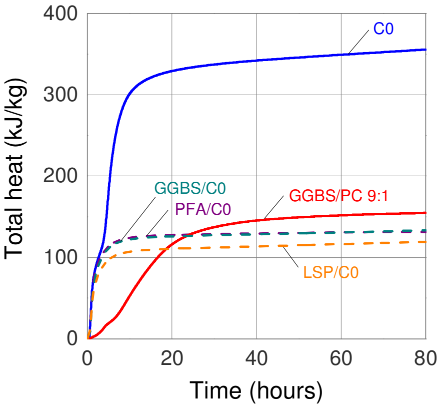

Figure 2 (b) Total heat output with 75% mineral additions

Corrosion of Al in CSAC composites

Quantitative corrosion rate measurements revealed that the corrosion of embedded Al was practically non-existent in the CSAC composites. As can be seen from Figure 3, the corrosion of Al in all CSAC composites was minimal, appearing as a tiny 'spike' in each plot. Interestingly, the corrosion rates were slightly higher with 75% additions which is likely due to the higher effective free water in these highly diluted cement systems.

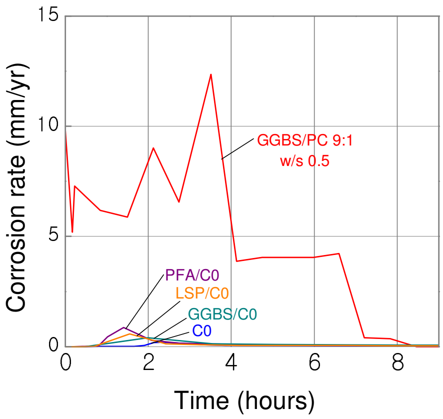

Figure 3 (a) Corrosion of Al in CSAC with 50% mineral additions

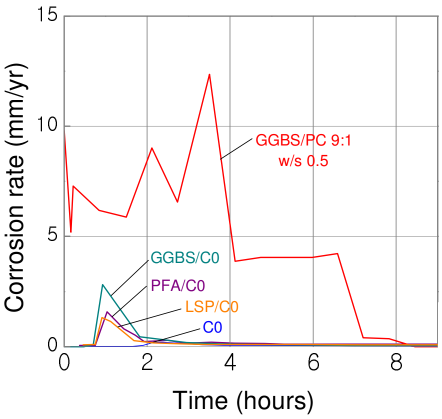

Figure 3 (b) Corrosion of Al in CSAC with 75% mineral additions

CONCLUSIONS

A significant reduction in the heat output of CSAC was successfully achieved by using high-volume mineral additions, namely PFA, GGBS and LSP. Compared with the reference PC system, a significant reduction in Al corrosion was achieved using the newly developed CSAC composites. This could be attributed mostly to the low initial pH (around 10.5). While further optimisation of the formulations are necessary, this study demonstrates that CSAC composites can be highly diluted while still meeting strict performance criteria.

AKNOWLEDGEMENT

Thanks are given to the Department for Employment and Learning (DEL) Northern Ireland for funding C. McCague in his PhD project. The authors are grateful to Hanson Cement (CSAC), and Saint-Gobain (gypsum) for supplying the materials in this study. The facilities provided to C. McCague as a visiting research student in the Department of Civil, Environmental and Geomatic Engineering at University College London is also gratefully acknowledged.

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