

Corrosion of Aluminium in Composite Cements

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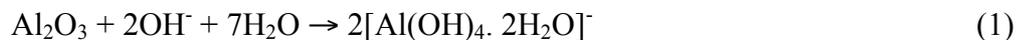
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Introduction

A composite cement is a hydraulic cement composed of Portland cement and one or more inorganic materials that make a substantial contribution to the hydration products [1]. In the UK, composite cements based on the replacement of OPC with high levels of BFS, are used to encapsulate intermediate level wastes (ILW), some of which may contain metals such as aluminium, magnesium and steel.

Cements are used because they are economic, durable and have long-term stability. However, there may be issues regarding the corrosion of some of the metal wastes, which arise from reprocessing and decommissioning, due to the alkaline environment in the cement grouts, aluminium is an example of such waste.

Aluminium is a reactive metal. When it is exposed to air, an oxide layer is formed. This layer generally provides protection to further corrosion, but at high alkalinity this oxide layer breaks down to form soluble aluminium species thus exposing the bare metal (Eq. 1).



The resultant exposed metal then further corrodes (Eq. 2) to produce aluminium hydroxide and also liberate hydrogen gas.



The reactions illustrated in equations (1) and (2) are for corrosion of aluminium in general caustic solutions e.g. NaOH, but in the cement the corrosion products can be different. The product of corrosion is less dense than the metal and hence it occupies more volume. This may lead to stress within cement matrix and possibly leading to cracks.

The aims of this research are to understand the fundamental mechanism and rate of corrosion of the aluminium in different cement systems, to identify the corrosion products at the aluminium/cement grout interface and assess whether the corrosion products have any effects on the cement durability and phases formed in cement. Current work has involved identification of corrosion products using XRD, DSC and SEM. This should lead to better understanding of possible mechanisms of corrosion of aluminium in composite cements.

Experimental

Three cement systems were studied: 100% OPC (as reference material), 7:3 BFS:OPC and 9:1 BFS:OPC. The cement powders were supplied by BNFL plc. Water:powder ratios of 0.33 and 0.37 were used. Table 1 shows the corresponding water:OPC ratios for comparison. High purity aluminium (99.999%) was used throughout this work, and was chosen so that the effect of the cement on the aluminium on its own could be investigated and hence reduce the complication of the chemistry of alloying elements.

Table 1: Corresponding water:OPC ratios for the cement systems

OPC	7:3 BFS:OPC	9:1 BFS:OPC
0.33	1.10	3.30
0.37	1.23	3.70

The cements were mixed in a Hobart mixer followed by a Silverson high shear mixer and then poured into 100ml capacity plastic pots with airtight lids with aluminium rods placed inside. The samples are being cured at 20°C and 40°C in environmental chambers, for times ranging from one day to two years. After curing, the hydration is stopped by immersing in acetone and samples are prepared for XRD, thermal analysis and SEM/EDS.

Results and Discussion

In the pure OPC systems with aluminium, expansion of the pots was observed i.e. bulging in both the lid and base. This expansion occurred rapidly in the first few hours. After a week or so, the amount of expansion decreased. Furthermore, white coloured corrosion products were observed visually on the aluminium encapsulated in OPC. Cracking was also observed within the OPC samples, which may have been due to the expansion of the corrosion products of aluminium. Cracks were only observed with the OPC sample, possibly due to the setting behaviour and higher pH compared to BFS:OPC. OPC sets faster than a BFS:OPC cement, and hence during corrosion, the product expanded and cracks were produced. BFS:OPC has lower pH than OPC, however, corrosion still occurs suggesting that the pH is not low enough for passivation.

The major phase of the corrosion product was found to be aluminium hydroxide as expected. However, unexpectedly, it was found that the aluminium hydroxide was present in the form of bayerite (Fig. 1) and not gibbsite, which is the most common form. Bayerite is metastable and is an intermediate stage between amorphous alumina and monoclinic gibbsite [2]. Formation of bayerite has been reported before as the product of metallic aluminium corrosion [3], but the mechanism is still unclear.

Stratlingite, C_2ASH_8 has also been found in the corrosion product for the cements. The decomposition of stratlingite has been seen to occur at 220°C (Fig. 2), and XRD has confirmed its presence. The formation of stratlingite may have been facilitated by the presence of excess aluminium coming from the metal as amorphous aluminium hydroxide.

Figure 3 show a backscattered electron image of a 9:1 BFS:OPC cement that had been used to encapsulate aluminium. There are many BFS grains and some unreacted cement particles. Furthermore, there are needle-like structures that originally were thought to be ettringite, however, this has not been identified by XRD, so it may be stratlingite which can exist as platey-like form resembling needles.

Cement hydration is largely unaffected with the corrosion of aluminium as most of the standard hydration phases were identified. See table 2.

Table 2: Cement phases identified with XRD and DSC found after 90 days hydration

	OPC	7:3 BFS:OPC	9:1 BFS:OPC
Ettringite	✓	X	X
Monosulfate	X	✓	✓
Portlandite	✓	✓	✓
Calcite	✓	✓	✓
Gehlenite	X	✓	✓

Conclusions

- Aluminium corrodes in BFS:OPC cement even though the pH is lower than OPC.
- Bayerite is the main product of corrosion of aluminium, rather than gibbsite.
- Stratlingite is also part of the corrosion product, most likely formed due to excess aluminium ions present.
- Cement hydration does not appear to have been affected by the corrosion of aluminium as most of the standard phases were identified.

Acknowledgements

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Reference

- [1]. H. F. W. Taylor, 'Cement Chemistry', Academic Press, London, 1990
- [2]. H. D. Ruan, R. L. Frost, J. T. Kloprogge and L. Duong 'Far-infrared spectroscopy of alumina phases' Spectrochim. Acta A, 2002, 58, 265 – 272

- [3]. R. S. Alwitt 'Aluminium – Water Systems' in Oxides and Oxide Films vol. 4 eds. J. W. Diggle and A. K. Vijh, Marcel Dekker, New York, 1976, pp169 - 250

Figures

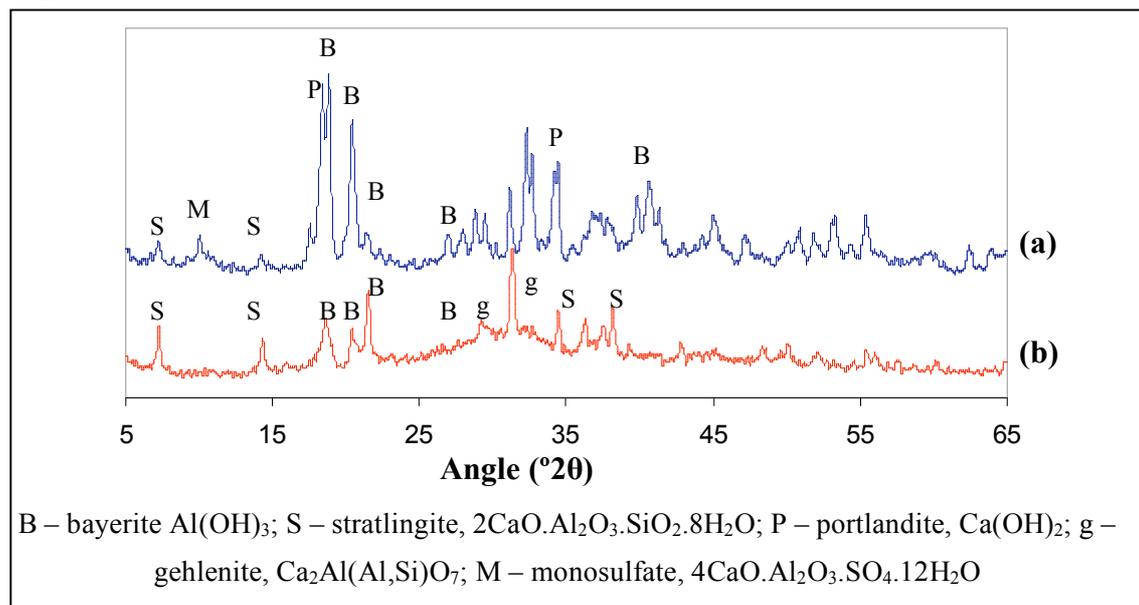


Fig. 1: XRD of (a) OPC, w:s 0.33, 20°C, hydrated for 90 days; (b) 9:1 BFS:OPC, w:s 0.33, 20°C, hydrated for 90 days.

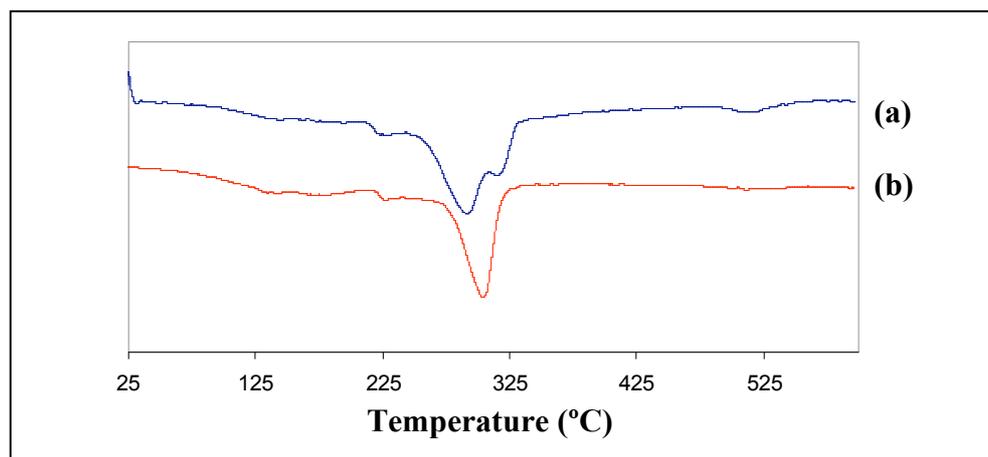


Fig. 2: DSC of (a) OPC, w:s 0.33, 20°C, hydrated for 90 days; (b) 9:1 BFS:OPC, w:s 0.33, 20°C, hydrated for 90 days.

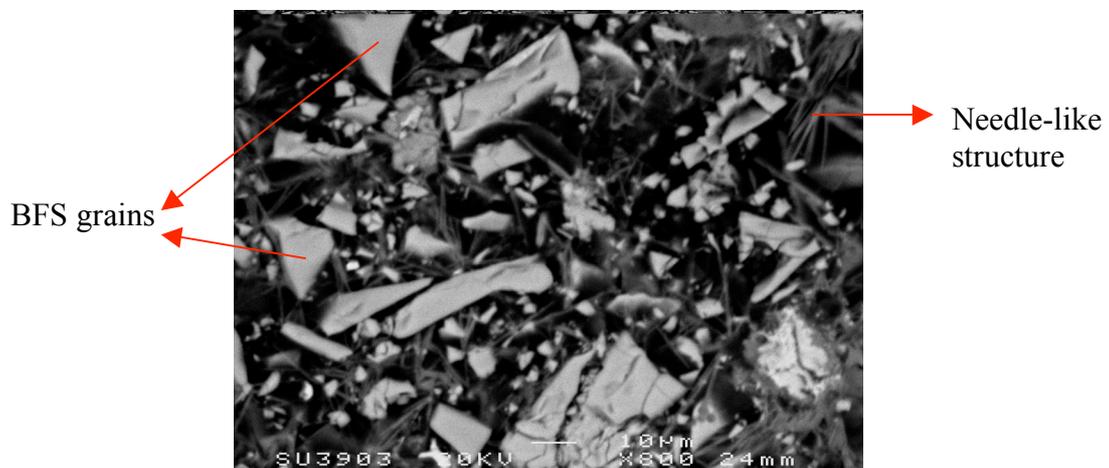


Fig. 3: BEI of 9:1 BFS:OPC interface with aluminium, 0.33, 20°C, 90 days, polished.