

Development of Novel Low pH Cement Systems for Encapsulation of Wastes Containing Aluminium

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Abstract

In this project, a novel binder based on the hydration of magnesium oxide (MgO) and tailored to give a lower pH is being investigated. Initial work has focused on the effect on pH of mixing MgO with a range of pozzolanic materials. Systems yielding promising pH values were studied in more detail and are now being characterized in terms of their setting behaviour, strength development and hydration reactions. Experiments are also being carried out to investigate the interaction of these new binders with aluminium, both in terms of rate of continued corrosion as well as the phases that form by reaction of the binder with aluminium.

Introduction

The considerable amount of historic nuclear waste in the UK vary tremendously in terms of the radioactivity, physical form and chemical nature. The composite cement based on Portland cement and blast furnace slag has a good track record in encapsulation of a range of nuclear wastes. However, the varied nature of nuclear waste means that ideally a toolbox of cementitious binder systems should be available to deal with specific requirements of different types of waste.

Materials and Methods

To determine the effect of cement formulation on pH, blends of MgO with a range of possible pozzolans were prepared. The materials used in the blends were Portland cement (OPC; CEM-I, Lafarge, UK), metakaolin (MK; Metastar 501, IMERYS Minerals Ltd., UK), commercially available magnesium oxide (MgO, MagChem 30, M.A.F. Magnesite B.V., The Netherlands), ground granulated blast furnace slag (GGBFS, Civil and Marine Slag Ltd., UK) and silica fume (SF; Elkem Materials Ltd).

pH evolution with time

Solid sample: the blends were mixed with water and cured in polyethylene bags. Crushing and grinding 1g of each sample and dispersing the fragments in 2g of water. Following 24 h of mixing, the pH was measured by a standard glass pH electrode

Liquid sample: 10g of the solids was mixed with 100g of distilled water, continually agitated by rotation (10 rpm) except when measurements of the pH were taken, allowing the solids to settle before reading the pH.

The setting time was measured with a Vicat apparatus according to BS EN 196-3. The hydration products were studied using a Philips PW1720 powder x-ray diffractometer using Cu K α radiation.

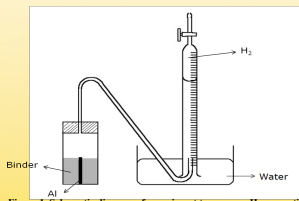


Figure 1. Schematic diagram of experiment to measure H₂ generation

A small strip of aluminium (Al 1050, 6 mm \times 3 mm \times 25 mm) was buried in the binder and allowed to react. The volume of hydrogen escaping from the sample was measured as a function of time using the set-up shown in Figure 1.

Results and Discussion

1 Initial pH trials

The pH values are largely similar for both methods. For all the blends in Figure 2, blends containing OPC gave pH values between 12.5-13. For blends without OPC, the effectiveness in reducing the pH increases as follows: BFS < MK < SF.

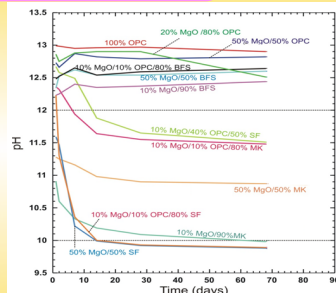


Figure 2. pH versus time in solid samples.

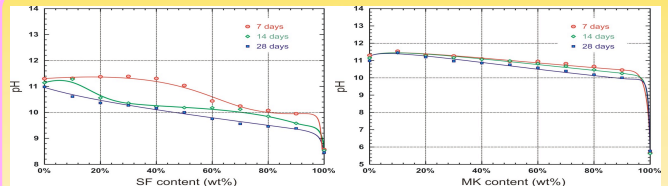


Figure 3: pH versus composition for MgO/SF blends

Figure 4: pH versus composition for MgO/MK blends

Figure 3 and Figure 4 confirm that SF is more effective than MK in reducing pH: a pH \sim 10 requires only 50% SF, whereas for MgO/MK such pH values are only obtainable with 90% MK. Low pH values take 7 to 14 days to form in the MgO-based binder.

2 Physical characteristics of the MgO/SF binders

Sample description	Value (mm)	Water/Solid ratio
100PC	185	0.33
75BFS/25PC	184	0.35
50MgO/50SF	183	1.3
20MgO/80SF	185	1.6

Figure 5. Consistency (by flow table)

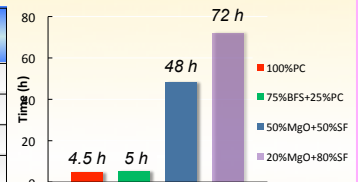


Figure 6. Final setting time

For MgO/SF binders, much more water is needed to give similar flow properties with BFS/PC binders; the high water content poses a real challenge in strength development and as shown in Figure 6, this leads to long setting times.

3 Early results from corrosion tests

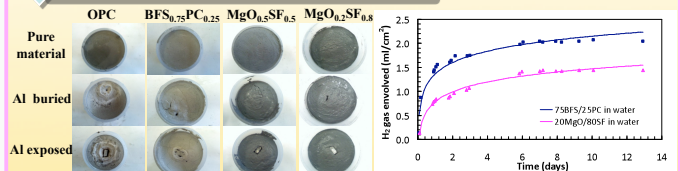


Figure 7. Al in binder systems at 1 day

Figure 8. H₂ generation during corrosion testing of Al

The holes and cracks shown in Figure 7 are caused by the release of hydrogen which is generated during the corrosion. The amounts of hydrogen generated as a function of time in the reference binder and in a blend of 20MgO/80SF are compared in Figure 8. The initial rate of hydrogen evolution in the MgO/SF binder is significantly reduced but after 48 hours, the H₂ generation almost stopped in both binders.

Conclusion

- MgO/SF binder offer lower pH than PC, PC/BFS binder
- Less H₂ when Al is encapsulated in MgO/SF binder
- Al corrosion finishes in two days for wet test systems
- Issues with setting and water content for MgO/SF binder

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