CHARACTERISATION OF CORROSION OF NUCLEAR METAL WASTES ENCAPSULATED IN MAGNESIUM SILICATE HYDRATE (MSH) CEMENT.

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ABSTRACT

A novel low pH magnesium silicate hydrate cement system for encapsulating nuclear industry wastes has been developed using blends of MgO, silica fume (SF), MgCO₃ and sand. Aluminium and Magnox swarf were encapsulated in both this new system and in a BFS/PC control system used in the nuclear industry. The interaction of the optimised mortar with the metal strips has been investigated, both in terms of rate of continued corrosion as well as the phases that form by reaction of the binder with different metal strips. Magnox swarf was better bound into the BFS/PC system than MgO/SF system whereas Al 1050 metal strips were bound better into the MgO/SF samples than into the BFS/PC reference mortar. No H₂ generation was recorded when aluminium or magnox were encapsulated in the new binder, which is substantially better than what can be achieved with the reference system. Hence, the newly developed binder could potentially encapsulate mixtures of reactive metals better than the existing solution.

INTRODUCTION

Nuclear wastes are mainly produced in nuclear power stations and are generated from the processing and associated production of nuclear fuel. There is a considerable amount of intermediate level legacy nuclear waste in the UK which varies in terms of physical form and chemical composition. The inhomogeneous nature of these wastes is a major challenge to formulate reliable and robust systems for waste encapsulation¹.

Encapsulation in cements has been shown to be a viable option for some of the wastes and a good record of treatment and containment for a range of wastes has been accrued over the years². Composite cements based on the partial replacement of ordinary Portland cement (OPC) with blastfurnace slag (BFS) or pulverised fuel ash (PFA) are commonly used in the UK, but research into potential alternatives has evaluated the potential for waste encapsulation using calcium aluminate cement, magnesium phosphate cement, calcium phosphate cement, calcium sulpho-aluminate cement, alkali-activated systems and geo-polymers³.

Aluminium and Magnox, a magnesium alloy, are the main metal wastes in the legacy intermediate level radioactive waste (ILW) stream in the UK. They arise from the de-cladding of nuclear fuel and components of the fuel rods. In the legacy waste stream, accrued during past operations, these metals have not been separated. This poses a challenge for treatment since the requirements for passivation of corrosion of these metals are very different. A moderate pH (pH 4-10) is advantageous for amphoteric aluminium because both high pH and low pH cause corrosion⁴. Additionally, at high pH the corrosion also generates H₂ through:

In sharp contrast, passivation of magnesium requires a high pH⁴ as the solubility of magnesium hydroxide decreases with pH.

Considering that aluminium may still be passive for pH values up to 10 and that magnesium hydroxide could remain stable down to pH 9, it was decided to design cements whose pore water

pH would be in the range of pH 9-10. An expected further advantage of this approach is that a much wider range of metals shows low corrosion and/or mobility in this pH range⁴. Hence, such a binder could potentially have much wider application than in legacy waste encapsulation, which would enhance the commercial viability of the product. Earlier work has shown that the reaction between magnesium oxide (MgO) and silica fume (SF) yields magnesium-silicate-hydrate gel (MSH), and that this cement has a good strength and a pH in the desired range⁵. It was shown also that partial substitution of MgO with magnesium carbonate (MgCO₃) allows buffering the initial pH of the system around pH 10 and that addition of sand to produce a mortar rather than a neat cement improves the dimensional stability⁶.

In this work the corrosion of metal wastes in the optimised M-S-H binder will be compared to the corrosion in one of the current industry standard cements (OPC/PFA). A first set of measurements details the hydrogen gas generation over time. This is followed by a characterisation of the interaction products that form using X-ray diffraction and scanning electron microscopy observation of sections showing the metal-cement interface.

EXPERIMENTAL

The raw materials used were Portland cement (PC; CEM II, Lafarge, UK), a commercially available magnesium oxide (MgO, MagChem 30, M.A.F. Magnesite B.V.), ground granulated blast furnace slag (BFS, Civil and Marine Slag Ltd., UK), silica fume (SF; Elkem Materials Ltd), magnesium carbonate (MgCO₃, Fisher, UK) and sand (RH110, Sibelco, UK). Metal wastes used are a high purity Al alloy (Al 1050) and magnox swarf.

Experiments were completed using a control composite cement consisting of 25 wt% OPC and 75 wt% BFS and a water to solids ratio of 0.33, and a M-S-H cement formulation containing 20 wt% MgO, 5wt% MgCO₃, 25 wt% SF and 50 wt% sand. The water to solids ratio was 0.35 and 1% of hexametaphosphate was added to improve the rheology of the cement. To establish that the binder systems used have sufficient strength for handling and storage, the unconfined compressive strength (UCS) of the samples was determined using a standard compression tester (Zwick/Roell). The load rate used was 300 kPa/s and the maximum load applied to the blocks was recorded. The interaction between metals and the binders was studied by encapsulating small strips of metal (25 mm × 6 mm × 3 mm) in the cement systems. The volume of H₂ generated from the samples was determined using the experimental setup shown in Figure 1.

Figure 1. Schematic diagram of the set-up used to measure the hydrogen generation

X-ray diffraction (PW 1700 with Cu K α radiation, Philips, The Netherlands) was used to identify the crystalline phases formed on the metal surface after 28 days of encapsulation. The variation of the chemical composition near the metal-binder interface was analysed by energy dispersive elemental analysis in a scanning electron microscope (JEOL-JSM-840A, Jeol, Japan). Samples were polished to a 1 μ m surface finish, dried and gold coated before being examined.

RESULTS AND DISCUSSION

The development of the compressive strength of both types of binders is shown in Figure 2. The 28 day compressive strength of both mixes is similar and above 60 MPa, which is much higher than the strength required for nuclear waste encapsulation (>5 MPa)⁷. After 90 days curing, the optimised MgO/SF mix offers a higher compressive strength than PC/BFS mix of around 80 MPa. The continued strength gain also indicates full reaction of the cement requires more than 28 days.

Figure 2. Compressive strength as a function of curing time for the reference and MgO/SF binders.

The volumes of hydrogen gas generated over time when aluminium is encapsulated in the two cements are compared in Figure 3. The initial rate of hydrogen evolution in the reference binder is extremely high, but this is followed by a marked slower rate of hydrogen evolution indicating that some form of passivating reaction layer may form. In the MgO/SF system, no H_2 evolution was detected during the test period. In a similar formulation without $MgCO_3$, the initial pH was found to be higher and hydrogen gas evolution was observed⁶. Therefore the suppression of corrosion in the current, optimized, binder is attributed to the buffering capacity of the magnesium carbonate.

As shown Figure 4, after 28 days of encapsulation, the Al strip in the reference binder (25% PC/ 75% BFS) has corroded significantly, whereas the surface of the Al strip embedded in the MgO/SF system shows no signs of surface attack. Moreover, the Al strip was found to be firmly bound to the binder.

Higher magnification images of the interface in both systems are shown in Figure 4. There is a clear reaction layer of up to 1 mm between the OPC/BFS cement and the Al strip, which also contains many large pores due to early virulent hydrogen evolution. In contrast, the interface between Al and MgO/SF is clean and devoid of clear reaction layers. The results of the electron probe micro-analysis, see Table 1, confirms this interpretation as the Al content near the interface is elevated in the OPC/BFS system whereas hardly any Al can be detected near the interface in the MgO/SF system.

Figure 3. Hydrogen gas evolution versus time for aluminium encapsulation in a PC/BFS reference blend and in an MgO/SF binder.

Figure 4. Al sample after 28 days encapsulation in (a) PC/BFS, (b) MgO/SF

Figure 5. Interface between Al and the binder for (a) PC/BFS and (b) MgO-SF

Table 1. Electron probe micro-analysis results (wt%). Locations are indicated in the micrographs.

		O	Na	Mg	Al	Si	K	Ca
Al + PC-BFS								
Al								
	Spectrum 3	7.58			85.33	6.96		0.12
Al / PC-BFS interface								
	Spectrum 2	57.26	1.30	2.31	10.41	8.36	0.94	19.39
	Spectrum 4	58.57	1.46	1.80	10.61	7.73	1.19	18.65
PC-BFS matrix								
	Spectrum 1	51.70	0.84	3.49	4.59	11.96	1.03	26.33
	Spectrum 5	50.59	0.87	3.61	4.82	13.15	1.03	25.93
Al + MgO-SF								
Al								
	Spectrum 1	9.75			83.41	6.85		
Al/MgO-SF interface								
	Spectrum 2	53.29	0.27	11.25	0.89	34.30		
MgO-SF matrix								
	Spectrum 3	56.02		17.30	0	26.68		

The Al bars were then removed to allow examining the interface by XRD. The XRD patterns are presented in Figure 6 and show that the surface of the aluminium, which was encapsulated in BFS/PC system, consists mainly of $\text{Al}(\text{OH})_3$. The aluminium removed from the optimized MgO/SF has hardly changed from normal aluminium with very weak peaks due to hydroxide products. This confirms again that there is hardly any corrosion of the Al bar when it is encapsulated in the MgO -SF binder.

Figure 6. X-ray diffraction patterns of the surface of the aluminium removed from the binder after 28 days for OPC/BFS and the MgO/SF binder. Peaks have been labelled with Al for aluminium and B for Bayerite ($\text{Al}(\text{OH})_3$).

Experiments with magnox swarf did not yield hydrogen generation at a level detectably by the simple set-up used for either binder, and as shown in Figure 7, the magnox swarf is bound into the binders quite well with no large gaps appearing for either binder consistent with the absence of hydrogen gas evolution at the level detectable with the set-up used. Higher magnification images obtained by scanning electron microscopy are shown in Figure 8. There is a limited interaction zone surrounding the magnox swarf in the OPC/BFS binder, which is confirmed by an elevated Mg content in the binder within $200\text{ }\mu\text{m}$ of the interface, see Table 2. The measurement in the bulk binder, spectrum 3, shows only 4.15 wt% Mg, which is consistent with what would be expected from the raw material data. Hence, encapsulation of magnox swarf in the reference binder does not lead to problems consistent with the successful industrial practice.

Surrounding the magnox in the MgO/SF binder, a gap has appeared. It is not entirely clear whether this is due to cracking during handling or whether the crack existed before the sample was prepared. A further change is that there is now a region with higher Mg and lower Si content (spectrum 2 and 4) suggesting that some magnesium from the magnox has diffused into the matrix. However, since magnesium is already a major component of the binder, this should not affect phase formation too much as it could merely lead to some brucite ($\text{Mg}(\text{OH})_2$) formation in addition to M-S-H gel. Moreover, for this binder also the extent of the interaction layer is limited ($< 200\text{ }\mu\text{m}$).

(a)

(b)

Figure 7. Magnox swarf sample encapsulated in (a) PC/BFS, (b) MgO/SF

(a)

(b)

Figure 8. Interfaces between magnox swarf (Mg) and binders for (a) OPC/BFS and (b) MgO/SF

Table 2. Electron probe micro-analysis results (wt%). Locations are indicated in the micrographs.

		O	Na	Mg	Al	Si	K	Ca
Mg + PC-BFS								
Magnox interface	Spectrum 2	4.57		94.71	0.72			
	Spectrum 1	51.44		43.68	0.95	1.82	0.19	1.91
	Spectrum 4	58.07		24.99	1.48	3.65	0.29	11.10
PC-BFS matrix								
	Spectrum 3	49.40	0.85	4.15	4.62	13.60	0.78	11.10
Mg + MgO/SF								
Magnox interface	Spectrum 1	9.83		90.06				0.11
	Spectrum 2	56.43	0.34	20.01		22.35	0.40	0.48
	Spectrum 4	56.07	0.27	18.91		24.12	0.26	0.38
MgO-SF matrix								
	Spectrum 5	54.87		13.96		30.61	0.23	0.33

CONCLUSIONS

The compressive strength of both the MgO/SF binder and of the OPC/BFS binder after 28 days is higher than the required strength for nuclear waste encapsulation. The strength of MgO/SF system is similar to the control sample after 28 days curing but higher after 90 days, which suggest continued reaction after 28 days in the MgO/SF system.

No H₂ gas has been detected when Al is encapsulated in the MgO/SF binder, which can be explained by the lowering of the initial pH by substitution of MgO with MgCO₃. The surface of the Al strip embedded in the optimized MgO/SF system is clear and shows hardly any hydroxides and the Al strip was found to be firmly bound to the binder. In contrast Al encapsulated in the OPC/BFS reference binder corrodes badly leading to pore formation and a large interaction zone elevated in Al.

When magnox swarf is encapsulated in the binders, no H₂ gas generation was detected for either system. Based on the observation that reaction layers do form in either system, the sensitivity of the simple set-up was probably too low to detect its formation. Layers with enhanced Mg levels were found for both binders but these are limited to approximately 200 µm.

These results indicate that the newly proposed MgO/SF binder could potentially encapsulate mixtures magnox swarf and aluminium without extensive corrosion, which is better than what can be achieved with the current reference system.

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