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The encapsulation of $Mg(OH)_2$ sludge in composite cement

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A B S T R A C T

A range of magnesium hydroxide waste sludges arising from the re-processing of nuclear fuel exist in the UK and require safe long-term disposal. Similar wastes undergo a cementation process in order to immobilise radioactive material prior to disposal. Simulant magnesium hydroxide sludges have been prepared and their subsequent interactions with composite cement systems based on the partial replacement of ordinary Portland cement with blastfurnace slag and pulverised fuel ash have been studied. This work has concluded that there was little reaction between the sludge and any of the composite cements during hydration. Apart from a small quantity of a hydrotalcite-type phase containing magnesium from the sludge, the main phases detected were C–S–H and unreacted brucite. This indicates that the magnesium in the sludges is encapsulated by the cement, rather than being immobilised or chemically bound within the hardened matrix.

1. Introduction

Magnox nuclear fuel reactors have been operating in the UK since the early 1960's and use fuel rods consisting of natural uranium fuel encased in Magnox cladding. The fuel rod cladding is a magnesium alloy, containing small amounts of aluminium and other metals. During operations at the Sellafield nuclear fuel reprocessing plant, the spent fuel rod assemblies are removed from the reactors and are transferred to ponds and stored under water for up to one year to reduce temperature. When cool the Magnox casings are removed and the uranium fuel rods go through further processing operations but the Magnox swarf is kept in the ponds in temporary storage. Throughout this storage process, the ponds are maintained at a pH above 10.5 to minimise corrosion of the Magnox metal. However, over the past 40 years of storage some corrosion has occurred [1] leaving a range of magnesium hydroxide-based sludges, with varying solids contents and processing characteristics, classified as Intermediate Level Wastes (ILW) which require immobilisation for long term storage. Most ILW produced in the UK is immobilised in cementitious systems and kept in an interim storage above ground prior to final disposal, possibly in an underground repository. The cementing systems used by the nuclear industry are composite cements based on the partial replacement of ordinary Portland cement (OPC) with secondary cementitious materials (SCMs) such as blastfurnace slag (BFS) and pulverised fuel ash (PFA).

It has been accepted in the UK that cementitious systems based on OPC are suitable encapsulants for ILW [2–7]. The characteristics that make them suitable are:

a) The high pH of the pore solution (>12.3) precipitates many active waste species, and inhibits their migration through the hardened matrix.
b) C–S–H (standard cement nomenclature used where $CaO = C$, $SiO_2 = S$, $H_2O = H$), the main phase formed during hydration of the cement, has a very high surface area providing sites onto which radionuclides can sorb.
c) Many different wastes can be incorporated in the hardened cement paste.
d) The final cemented wasteform has a high level of durability.
e) The pores in the hardened cement paste are very small which restricts the migration of larger active elements and lowers liquid and gas permeability.
f) There is little or no degradation of the hardened cement matrix due to irradiation by the waste.
g) Cements are readily available and relatively inexpensive.
h) UK ILWs are often wet making them compatible with cementitious systems.

Neat OPC is unsuitable for these applications because the heat of hydration is high and may cause internal stresses and cracking of the matrix, which could lead to the release of radioactive material. The exotherm generated during the hydration of OPC could also raise the temperature sufficiently to produce steam and crystallise the C–S–H to, reducing the surface area for adsorption leading to possible radionuclide release [3]. Replacing some of the OPC with BFS (ratios between 4 and

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9:1 are common) or PFA lowers both the heat of hydration and the permeability of the matrix [8,9] which is desirable in both casting larger cement structures where internal cracking is detrimental [10,11] and in the immobilisation of waste where the containment of toxic or radioactive material is paramount [12]. A coarse BFS is usually chosen over the finer ground granulated blastfurnace slag (GGBS) because the larger particle size makes it less reactive and lowers the heat of hydration. Using such high replacement levels however, means that the amount of $Ca(OH)_2$ produced by the OPC hydration is sufficient to only activate small quantities of BFS.

Research on waste immobilisation over the past 30 years has mostly focussed on the incorporation of inactive and radioactive material into the cement hydrates C–S–H, ettringite and monosulphate, which can accommodate a variety of anionic and cationic substitutions in stable phases [13]. Much of this work has focussed on incorporation into C–S–H, which accounts for at least 60 wt.% of the hydration products in hardened cement pastes [14]. The high porosity of C–S–H leads to high surface area so sorption of waste ions onto the surface of C–S–H is more likely than substitution into the C–S–H structure [6] although Richardson and Groves [15] following hydration of pure C_3S, reported that Al^{3+} and Fe^{3+} ions substitute into tetrahedrally coordinated sites of the C–S–H. Gougar et al. [16] have reported that C–S–H immobilises waste ions through various mechanisms including sorption, substitution at interlayer sites and integration with other phases present in the hydrated cement. Ettringite ($C_3A.3CaSO_4.H_{32}$) has a columnar structure of hexagonal prisms [14] where the SO_4^{2-} ions are located within the column channels and can be replaced with other anionic groups. The aluminium in ettringite can be substituted for iron or other trivalent ions, and other cations can replace some of the Ca^{2+}, for example where silicon ions substitute for aluminium in thaumasite ($Ca_3Si(OH)_6(SO_4)(CO_3).12H_2O$). Monosulphate ($3C_3A.CaSO_4.H_{12}$) has a lamellar hexagonal structure with excellent cleavage and is similar to ettringite in terms of the cationic replacement of Al^{3+} ions with Fe^{3+} or Cr^{3+} and the anionic group replacement with oxyanions.

Magnesium hydroxide (brucite, $Mg(OH)_2$) has low solubility (0.0009 g/100 ml), making it relatively unreactive, and is less soluble than magnesium carbonate (magnesite, $MgCO_3$). When present in hydrating cement, magnesium ions exchange for calcium ions within the structure of C–S–H phases [16] to form magnesium–silicate–hydrate material (M–S–H), but such substitutions are difficult to detect without the use of advanced experimental techniques. Most work investigating the immobilisation of Magnox waste in cementitious systems is commercially sensitive, but some information is available in the open literature. When analysing corroded Magnox swarf encapsulated in BFS/OPC composite cement, Caldwell *et al.* [17] found that the magnesium ions from the corrosion product did not substitute into any crystalline cement hydrates. They also found no evidence of M–S–H phases and surmised that the hydrating cement was acting as a micro-encapsulant to the corroded swarf. Rather than investigating the products formed from chemical interactions between corroded Magnox swarf and encapsulating cement paste, Fairhall and Palmer [18] focussed on Magnox swarf corrosion characteristics during encapsulation. They concluded that Magnox swarf can be successfully encapsulated in BFS/OPC systems and that the Magnox swarf corrosion was governed by temperature and water availability, and that by measuring corrosion, product lifetime can be predicted.

This paper reports investigations into the encapsulation of a $Mg(OH)_2$ sludge simulant in 9:1 and 4:1 BFS/OPC and 5:4 PFA/OPC systems.

2. Experimental

2.1. Materials

The $Mg(OH)_2$ powder was supplied by National Nuclear Laboratory (NNL) (formally Nexia Solutions Ltd) from Intermag Company Limited, with the trade name Hydromag. It contained 80.8 wt.% $Mg(OH)_2$ and 8.5 wt.% $MgCO_3$ (the remainder was due to absorbed water). The OPC, BFS and PFA were also obtained from NNL and originally supplied by Castle Cement Ltd, Scunthorpe and Ash Resources Ltd respectively, all to an original British Nuclear Fuels Ltd (BNFL) specification in terms of fineness and composition. The elemental compositions were determined using inductively coupled plasma/optical emission spectroscopy (ICP/OES) and are shown in Table 1.

2.2. Mixing and curing

A magnesium hydroxide sludge simulant was made by adding 30 wt.% Hydromag powder to distilled water over a period of 2 min in a Hobart Planetary Mixer A12 set at speed 1. After scraping any unmixed solids from the paddle and the sides of the bowl into the resultant slurry, mixing was continued for a further 8 min after which time the resultant slurry was transferred to a Silverson L4RT high shear mixer for a further 20 min. A further sludge was made by using 0.01 M sodium hydroxide solution instead of distilled water in order to determine if sludge pH had any influence on the properties of hardened cement samples. The resultant sludges were stored in air-tight containers.

All samples were mixed in batches of approximately 1 kg of wet cement paste at a sludge to composite cement powders ratio of 1:1. The required mass of cement powders was pre-blended in a figure of eight mixer for 5 min at three composite cement ratios: 9:1 and 4:1 BFS:OPC and 5:4 PFA:OPC. A known mass of Hydromag sludge (or water, if making sludge-free samples), made up previously with either distilled water or sodium hydroxide solution, was placed into a dry mixing bowl in a Hobart Planetary Mixer A12 and with the mixer set at speed 1, the blended cement powder was added over a 2 min period. The mixer was stopped after a further 2 min and any unmixed solids scraped from the sides of the mixing bowl and the paddle into the bowl. Mixing was then continued to give a total powder addition plus mixing time of 10 min. The paste was placed in 50 ml polypots which were placed on a vibrating table for 3 min to remove air voids. These pots were then sealed and stored in an environmental chamber set at 20 °C and 95% relative humidity. For compressive strength measurement, the freshly mixed cement paste was placed into pre-oiled 50 × 50 × 50 mm steel moulds. These moulds were then sealed in zip lock plastic bags and stored in the same curing conditions as the samples in the polypots. The cubes were demoulded after 48 h and replaced into the plastic bags inside the environmental chamber. Samples were hydrated for 7, 28 and 90 days.

Table 1
Oxide composition of powders and cement phase composition.

OPC		BFS		PFA	
Composition	Quantity (wt.%)	Composition	Quantity (wt.%)	Composition	Quantity (wt.%)
CaO	64.58	CaO	42.1	CaO	1.44
SiO_2	20.96	SiO_2	34.5	SiO_2	48.64
Al_2O_3	5.24	Al_2O_3	13.74	Al_2O_3	25.88
Fe_2O_3	2.61	Fe_2O_3	0.97	Fe_2O_3	7.57
MgO	2.09	MgO	7.29	MgO	1.42
SO_3	2.46	SO_3	–	SO_3	1.20
K_2O	0.59	K_2O	0.49	K_2O	2.83
Na_2O	0.28	Na_2O	0.22	Na_2O	1.91
TiO_2	–	TiO_2	–	TiO_2	0.92
Chloride[a]	0.05	Chloride[a]	0.02	LOI (H_2O, C and CO_2)	4.16
Insoluble residue	0.27	Insoluble residue	–	Total[b]	95.97
Total	99.13	Total	99.33		
C_3S	51.0				
C_2S	20.8				
C_3A	9.8				
C_4AF	10.0				

[a] Determined by a colorimetric method.

[b] Omits oxides of B, P, Mn, Sr, Li, Cr and Cl.

2.3. Sample analysis

Hydration was arrested by removing the samples from their polypots and lightly crushing by hand, using a percussion mortar if necessary, to a particle size of approximately 8 × 8 × 8 mm. These particles were then immersed in acetone for 7 days before drying in a vacuum desiccator (1×10^{-2} mBar) for 3 days to remove the acetone. Subsequently, the samples were stored in sealed glass jars.

For analysis by X-ray diffraction (XRD) and thermogravimetric analysis (TGA), the hardened cement paste was crushed and ground in an agate mortar to pass a 63 μm sieve. XRD spectra were obtained using a Siemens D500 diffractometer operating at 2°/min and a step size of 0.02° between 5–65° 2θ whereas for TGA a Perkin Elmer Pyris 1 Thermogravimetric Analyzer programmed with a heating profile of 30–1000 °C at 10 °C/min in a flowing atmosphere of nitrogen was used.

For examination by scanning electronic microscopy (SEM), particles of hardened cement paste were set in epoxy resin and hand ground and polished. After carbon coating, they were examined in backscattered electron imaging (BEI) mode and the elemental composition and distribution was analysed using electron dispersive spectroscopy (EDS). The microscope used was a Jeol JSM 6400 with a Link ISIS EDS Analyser attached.

For measurement of total porosity, a piece of sample approximately 10 × 10 × 20 mm was prepared from a sample where hydration had not been arrested. This was immersed in water and kept at 60 °C overnight to re-saturate any surface pores. After cooling, any surface water was removed using a damp cloth. The sample was weighed and then placed in an oven held at 105 °C overnight to remove free water. After cooling, the sample was re-weighed and the loss in weight compared with the original weight of the sample to determine wt.% porosity.

For compressive strength measurement, the cubes of hardened cement paste were removed from the environmental chamber at the desired age and a Hounsfield Model H100KS Compressive Strength Testing Machine was used to test samples in triplicate.

The degree of slag reaction was measured for all samples by using the TET preferential dissolution method devised by Goguel [19] which is similar to that reported by Escalante-Garcia et al. [20] and Luke and Glasser [21]. This method uses a solution of ethylenediamine tetra-acetic acid (EDTA), tetramethyl ammonium hydroxide (TMAOH) and triethanolamine (TEA) to dissolve anhydrous and hydrated cement phases and leave unreacted slag. To make up 500 ml of TET solution, 56 ml of TMAOH 25% solution, 13.15 g of EDTA and 29.8 g of TEA were placed in a 500 ml volumetric flask and distilled water added to make up to 500 ml. The resulting solution was then titrated with TMAOH to pH 12.6. Approximately 100 mg of the composite cement (after crushing and grinding to pass a 63 μm and drying overnight to constant weight at 105 °C) was added to approximately 50 ml of TET solution and mixed on a roller for 30 min. The solution was then passed through a 0.1 μm filter, washed with distilled water and dried overnight to constant weight at 105 °C. Knowing the weight of the filter, and having previously measured the quantity of slag removed by the TET solution in a control experiment performed solely on the slag, the amount of reacted slag was then calculated and normalised to the amount of slag in the anhydrous composite cement powder.

3. Results and discussion

3.1. Sludge

In order to determine if carbonation occurred during mixing, sludges made with water and sodium hydroxide solution were dried overnight at 105 °C to constant weight and analysed by TGA. The results were compared with those for the Hydromag powder and are shown in Table 2. Upon mixing the powder with either the distilled water or the sodium hydroxide solution, there was an increase in the quantity of brucite detected and a concomitant decrease of magnesite, with most change being seen on mixing with the sodium hydroxide solution. This is caused by the difference in solubilities of brucite and magnesite. The solubility of magnesite (0.01 g/100 ml) is more than an order of magnitude greater than that of brucite (0.0009 g/100 ml) [22] so any magnesite present in the Hydromag will dissolve during mixing and precipitate as brucite. The pH of the sodium hydroxide solution as mixed was 12 whereas the distilled water had a pH of 7, but when the Hydromag powder was added to both, the pH of the resultant sludges immediately after mixing were 10.44 and 10.23 respectively. This suggests that it is the Hydromag powder that has the most influence on the pH of the resultant sludge rather than the mixing fluid used. The equilibrium pH for saturated $Mg(OH)_2$ is around 10.5 based on K_{sp}.

Table 2
Content of hydromag powder and dried sludges.

Mix	$Mg(OH)_2$ (wt.%)	$MgCO_3$ (wt.%)
Powder	80.8	8.5
Sludge (distilled water)	83.8	6.7
Sludge (sodium hydroxide solution)	86.0	5.7

3.2. Cemented sludges

The pH of the three composite cement pastes made with both forms of sludge was measured immediately after mixing (Table 3). Those sludges made with the sodium hydroxide were approximately half a pH unit higher than those made with the water. As the ratio of OPC to BFS or PFA increased, the pH also increased. During the early hydration of OPC, hydroxides of potassium and sodium are released into solution, and $Ca(OH)_2$ is formed from the hydration of the calcium silicates [14]. This produces a pore solution approximating pH 13.5. BFS and PFA will react with $Ca(OH)_2$ to produce additional C–S–H but with a stoichiometry different to that formed from the hydration of OPC and reduces the pore

Table 3
pH of sludge cement pastes.

Cement paste	pH
9:1 BFS/OPC, distilled water	12.17
Sodium hydroxide solution	12.80
4:1 BFS/OPC, distilled water	12.38
Sodium hydroxide solution	12.97
5:4 PFA/OPC, distilled water	12.62
Sodium hydroxide solution	13.21

Table 4
Summary of all phases detected in all samples.

Mix	Mix solution	Main phases		Other minor phases							
		C–S–H	B	M	H	G	P	C	E	Q	Mu
9:1 BFS/OPC	Water[a]	✓				✓	✓				
	Water	✓	✓	✓	✓	✓					
	NaOH	✓	✓	✓	✓	✓					
4:1 BFS/OPC	Water[a]	✓				✓	✓	✓	✓		
	Water	✓	✓	✓	✓	✓	✓	✓			
	NaOH	✓	✓	✓	✓	✓	✓	✓			
5:4 PFA/OPC	Water[a]	✓					✓	✓	✓	✓	✓
	Water	✓	✓	✓	✓		✓	✓	✓	✓	✓
	NaOH	✓	✓	✓	✓		✓	✓	✓	✓	✓

Alite (Ca_3SiO_5) and belite (Ca_2SiO_4) omitted.
B — brucite ($Mg(OH)_2$), M — magnesite ($MgCO_3$), H — hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$), G — gehlenite ($Ca_2Al_2SiO_7$), P — Portlandite ($Ca(OH)_2$), C — calcite ($CaCO_3$), E — ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3.26H_2O$), Q — quartz ($SiO_2$), Mu — mullite ($Al_6Si_2O_{13}$).

[a] Sludge free samples.

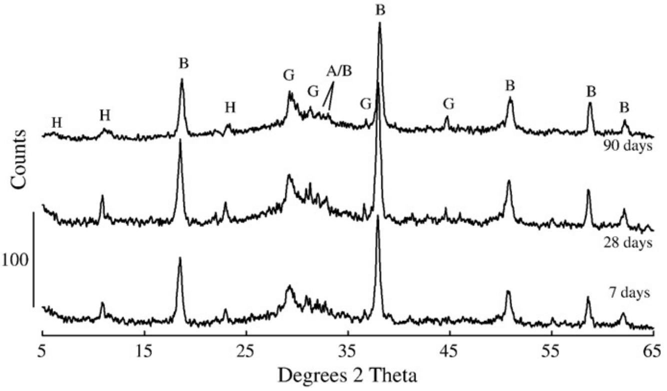

Fig. 1. XRD traces for cemented sludge samples made with distilled water and 9:1 BFS/OPC after hydration for 7, 28 and 90 days. Notes: 1) B — brucite ($Mg(OH)_2$), H — hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$), G — gehlenite ($Ca_2Al_2SiO_7$), A — alite ($Ca_3SiO_5$), B — belite ($Ca_2SiO_4$).

water pH [23,24], but these reactions are slower than the similar reactions occurring to the OPC [14]. Therefore, the higher the quantity of OPC, the higher the pH of the paste pore water. As the pH of the sludges made with either sodium hydroxide solution or water were so similar, the pH of the cemented sludge will be influenced mostly by the reaction between the cement powder and mixing fluid.

3.2.1. Phase composition

Table 4 summarises the composition of all sludge free and cemented sludges hydrated for all ages. Fig. 1 shows the XRD traces for the cemented sludges made with 9:1 BFS/OPC and the distilled water-based sludge after 7, 28 and 90 days hydration.

The main phase present in all samples was C–S–H which arises primarily from the hydration of the OPC, and secondarily from the activation of the BFS with hydroxides formed during the hydration of the OPC [25], or from the pozzolanic reaction between the PFA and the Portlandite produced from the hydration of the OPC. Brucite was the main crystalline phase detected in all cemented sludge samples which indicated that most, if not all, of the brucite in the Hydromag did not react during cement hydration, probably due to its low solubility.

The low count rate observed when analysing samples by XRD and the presence of an amorphous hump at approximately 30° 2θ indicated that only small quantities of other crystalline phases were present in all samples. The main crystalline phase detected in all sludge free samples containing BFS, was gehlenite, but small quantities of Portlandite, calcite and ettringite were detected (the latter two phases were only detected in the 4:1 BFS/OPC system), increasing as the quantity of OPC used increased. All PFA/OPC cemented sludge samples contained similar crystalline phases to those in the BFS/OPC samples with the exception of gehlenite, which was only present in the BFS and small quantities of quartz and mullite from the PFA.

For all cemented sludge samples, small quantities of magnesite and a hydrotalcite-type phase ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$) were detected, with the former present in the original Hydromag. The d-spacings of the hydrotalcite-type phase did not exactly match those reported for pure hydrotalcite but the positions and pattern of the reflections for the phase detected were sufficient to indicate that this phase was similar in composition to hydrotalcite.

For each of the three different composite cement formulations, the phases detected in the samples made with the distilled water-based sludge were the same as those detected in the samples made with the sodium hydroxide-based sludge. Additionally, hydration time had no influence on the type of phases detected.

TGA was used as a technique complimentary to XRD to confirm the presence of crystalline material and to detect amorphous phases. Fig. 2 shows the DTG curves of the 4:1 BFS/OPC hardened cement paste made with the distilled water-based sludge after hydration for 7, 28 and 90 days. Using TGA/DTG, small amounts of Portlandite and calcite, undetected by XRD, were found in all 4:1 BFS/OPC and 5:4 PFA/OPC samples. As can be seen from the example in Fig. 2, the size of the dehydroxylation peak for Brucite (~ 400 °C) [22] was very large. The only other significant peak in all samples was that for the dehydration of C–S–H which occurs between approximately 50 and 550 °C [14]. The small peak at approximately 150 °C was due to the removal of physisorbed water from the hydrotalcite-type phase detected [26].

TGA was used to measure the amount of binding material (mostly C–S–H) formed in all samples by measuring the weight loss between 50 °C and the point at which brucite began to lose water (approximately 300 °C). This allowed comparison with the preferential dissolution experiments, the results of which indicated the amount of slag reaction (mostly forming C–S–H) in each system. C–S–H loses water up to approximately 550 °C, so by measuring up to approximately 300 °C, some of the weight loss due to C–S–H was disregarded. However, most weight loss from C–S–H occurs before approximately 300 °C, so

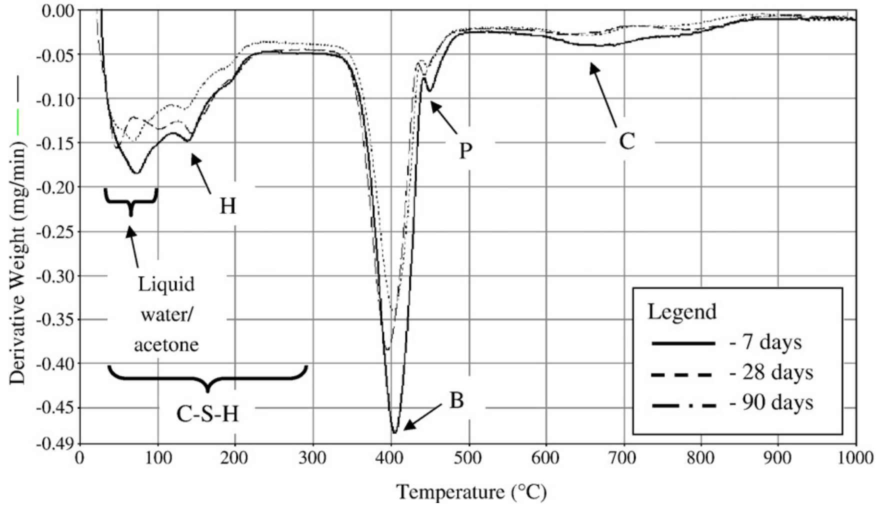

Fig. 2. DTG traces for cemented sludge samples made with distilled water and 4:1 BFS/OPC after hydration for 7, 28 and 90 days. Notes: 1) C–S–H — calcium silicate hydrate, B — brucite ($Mg(OH)_2$), H — hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$), P — Portlandite ($Ca(OH)_2$), C — calcite ($CaCO_3$). 2) Weight losses are from the dehyoxylation of brucite and Portlandite, the dehydration of C–S–H and the decarbonation of calcite. Weight loss from hydrotalcite is due to both dehydroxylation and dehydration. Weight loss from acetone and water is due to decomposition.

Table 5
Summary of weight loss between 50 and approximately 300 °C in all samples of cemented sludge hydrated for 28 and 90 days.

	Sludge mixing fluid	9:1 BFS/OPC		4:1 BFS/OPC		5:4 PFA/OPC	
		28 days	90 days	28 days	90 days	28 days	90 days
Weight loss (%)	Water	6.0	6.4	7.2	7.5	7.6	8.5
	NaOH	6.3	7.3	8.1	8.89	8.5	9.7
Increase in weight loss (%)[a]		5.6	13.2	12.5	19.1	11.5	14.3

[a] Due to using sodium hydroxide solution rather than water as the sludge mixing fluid.

disregarding temperatures above 300 °C compensated for the superimposition of other peaks (for brucite and Portlandite) on to the C–S–H peak. Therefore, comparative quantitative results for C–S–H and trends in weight loss could be investigated. These results are shown in Table 5.

From the above results it is obvious that there is little reaction of the sludge, be it made with distilled water or sodium hydroxide solution, with any of the cement pastes in which it is encapsulated. Only a small amount of magnesium containing hydration product, a hydrotalcite-type phase, was detected and much unreacted brucite was evident. The XRD reflections of the hydrotalcite-type phase suggest that its stoichiometry is slightly altered to that of hydrotalcite, and influenced by the presence of Mg^{2+} and OH^- ions in the sludge. The pH of the sludge had no discernible influence on the type of phases detected in the hardened cement pastes, despite the effect of pH upon other physical and chemical properties.

3.2.2. Microstructural characteristics

Figs. 3, 4 and 5 show SEM BEI micrographs and associated EDS images for the distilled water-based cemented sludges made with the three different cement formulations after hydration for 90 days. For each cement formulation, it was seen that the magnesium was pervasive in all cement microstructures with its location not particularly associated with any other elements. If any substitution of magnesium into C–S–H had occurred then a band of magnesium, similar to that of the hydration rims of C–S–H seen around the particles of BFS labelled A and B in Figs. 3 and 4 respectively, would be present. Similar associations between calcium, silicon and magnesium would also be seen in the PFA/OPC microstructure in Fig. 5. Because of its low concentration, the hydrotalcite-type phase identified by XRD and TGA could not be identified by SEM/EDS in any of the hardened cement pastes.

3.2.3. Slag reaction

The preferential dissolution results for all the BFS cemented sludge samples made with both sludges and hydrated for 90 days are shown

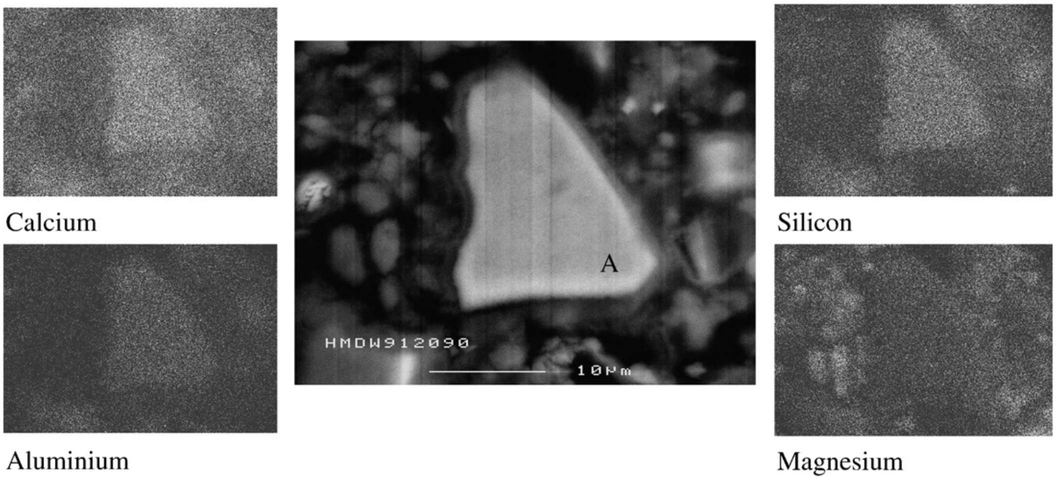

Fig. 3. SEM BEI micrograph and EDS images of cemented sludge made with distilled water and 9:1 BFS/OPC after hydration for 90 days.

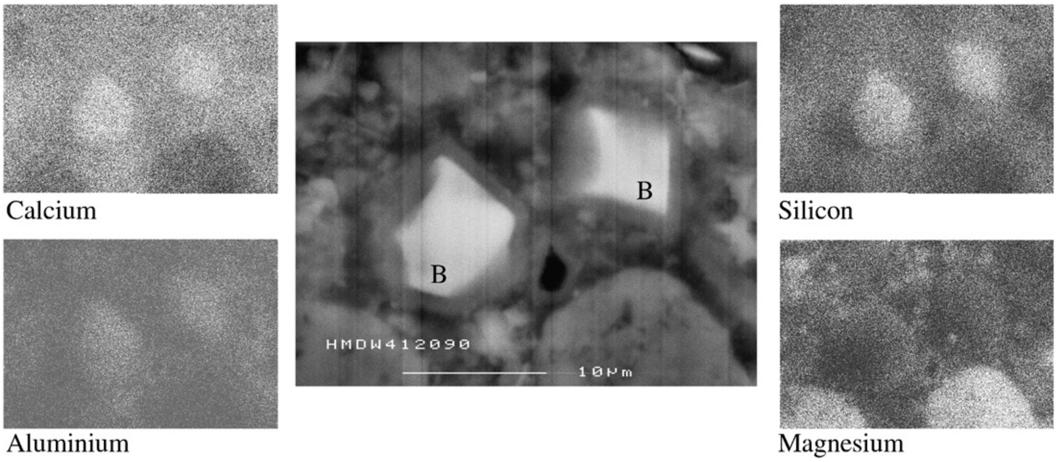

Fig. 4. SEM BEI micrograph and EDS images of cemented sludge made with distilled water and 4:1 BFS/OPC after hydration for 90 days.

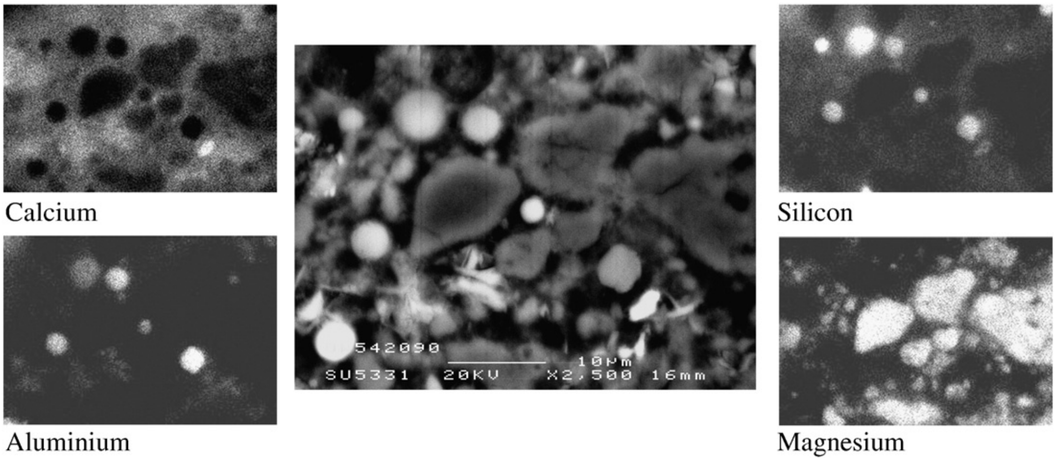

Fig. 5. SEM BEI micrograph and EDS images of cemented sludge made with distilled water and 5:4 PFA/OPC after hydration for 90 days.

in Fig. 6. These results show that considerable unreacted slag remained (up to >88 wt.%), even after 90 days hydration. In all cases, more slag reacted in the 4:1 system than in the 9:1 system. When the sodium hydroxide-based sludge was encapsulated rather than the water-based sludge, an increase in slag reaction of 19.1% in the 9:1 system and 33.0% in the 4:1 system was found. Despite the pH of the two sludges being very similar (pH 10.23 and 10.44 with distilled water and sodium hydroxide solution respectively), the influence upon slag reaction is high. This suggests that either the chemistry, and the slight increase in pH, of the sludge has a significant influence on the amount of slag reacting, or that much of the NaOH is consumed during the slag reaction causing more slag to react.

Assuming that all the slag that reacted formed C–S–H, and that all of the weight loss between 50 and approximately 300 °C was due to water loss from hydration products, particularly C–S–H, a direct comparison of the increase in amount of hydration products formed due to mixing with the sodium hydroxide-based sludge rather than the water-based sludge can be made. Both sets of results for the 9:1 and 4:1 BFS/OPC systems are shown in Fig. 6. For both systems, there is an increase in C–S–H formed using the sodium hydroxide-based sludge, although the weight loss results for both systems calculated from TGA is less than the difference in reacted slag. This was primarily because the weight loss from C–S–H between approximately 300 and 550 °C was not included because of the superimposition of peaks other than that of the C–S–H.

The same preferential dissolution experiment was performed on the PFA/OPC samples but the samples gained rather than lost weight during the test which suggests that some of the hydration product formed was not dissolved during the test. This hydration product may be the C–S–H formed from the pozzolanic reaction of the PFA.

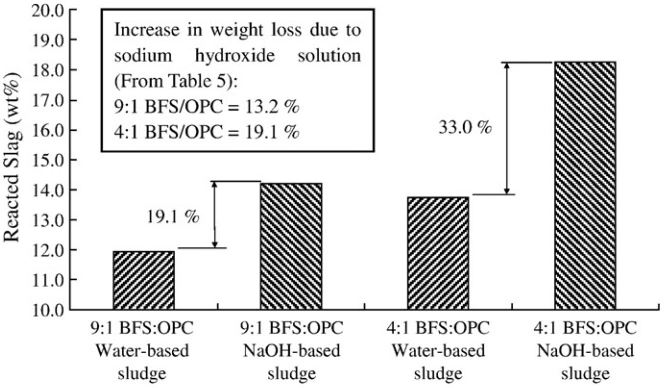

Fig. 6. Quantity of slag reacted in BFS/OPC systems hydrated for 90 days.

3.2.4. Physical properties

The porosity and compressive strength of 28 and 90 day samples of each cement formulation made with both sludges are shown in Fig. 7. The porosity of each cement formulation generally reduced with hydration time whilst the inverse was true of their compressive strengths. This was due to more C–S–H forming with time, filling the pore space previously occupied by water and binding the microstructure together in a more cohesive solid. The 4:1 BFS/OPC samples

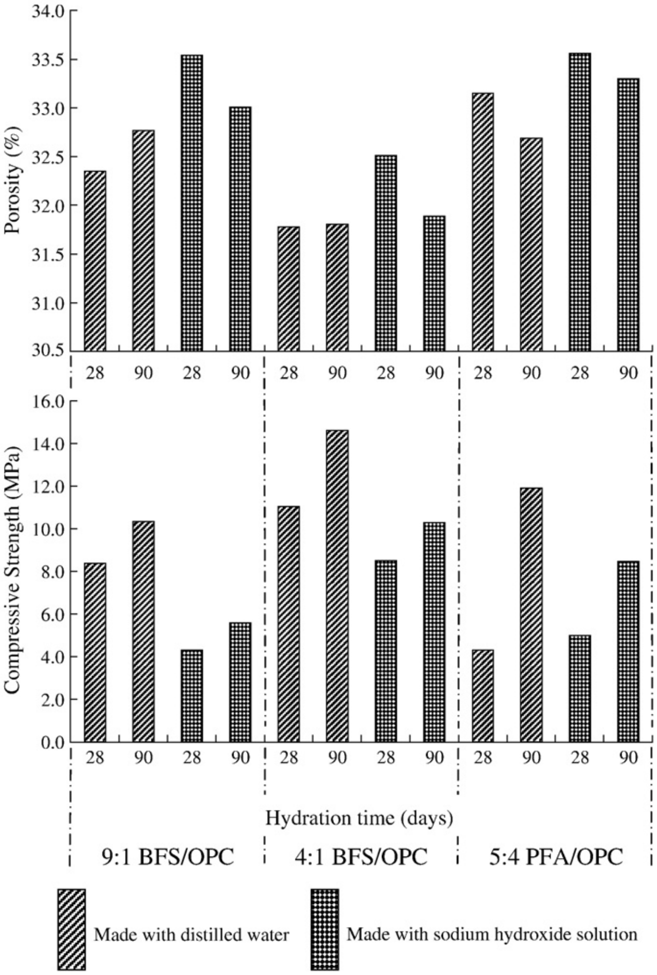

Fig. 7. Porosity and compressive strength results for cemented sludges made with 9:1 and 4:1 BFS/OPC and 5:4 PFA/OPC.

exhibited lower porosity and higher compressive strength at all ages than those made with the 9:1 ratio. Despite the presence of more OPC in the PFA composite cement samples, their porosity was higher and the compressive strength lower at all ages than the 4:1 BFS/OPC samples. This suggests that in these samples, the PFA was less reactive than the BFS, in line with other researchers who have suggested that PFA is less reactive and slower to react than other pozzolanic materials [27,28].

The preferential dissolution results show that the amount of BFS reaction in the sludges made with sodium hydroxide solution was higher than in those made with distilled water, with more binding hydrates (mostly C–S–H) formed as a result. This agrees with results obtained by other researchers who have reported that the reactivity of secondary cementitious materials such as these can be increased by mixing with alkaline activators [29–31]. This activation increases the quantity of C–S–H formed which should reduce the porosity of the hardened cement microstructure and cause a subsequent increase in compressive strength. However, the porosity and compressive strength results obtained in this work showed otherwise (Fig. 7) where the porosity was higher and the compressive strength lower for the samples made with the sodium hydroxide-based sludge than that made with distilled water. This suggests a different type of C–S–H, with perhaps a different stoichiometry, is formed with alkaline activation.

4. Further discussion

4.1. Immobilisation potential

Because of the lack of reaction between sludge and cement during hydration, and the resultant lack of chemically bound magnesium, it is apparent that the solids in the sludge studied are encapsulated within, or surrounded by, the hydrating cement, rather than being chemically bound or immobilised within the cement. Despite the detrimental effect that the sodium hydroxide-based sludge had on the porosity and compressive strength of the resultant hardened cement paste compared to that of the distilled water-based sludge, these two physical properties of a wasteform do not have high importance for a wasteform producer [3,8]. However, the increase in C–S–H caused by the increased reaction of the BFS is very desirable. More C–S–H means that more waste ions can be bound to the hardened cement matrix, so in this case the sodium hydroxide based sludges will produce wasteforms capable of taking a higher waste loading.

The results presented in this paper indicate that the magnesium in the sludge does not react with the C–S–H during cement hydration. However, C–S–H is capable of binding many other ions, such as aluminium and iron, both into the structure of C–S–H and by adsorption onto the surface of the C–S–H [15,16,32]. Our work in this paper has focussed on the encapsulation of a very pure brucite-based sludge, but, in reality, most industrial magnesium-based sludges resulting from reprocessing of nuclear fuel will contain many other waste ions, including aluminium and iron [33]. In these cases even though the magnesium in the sludge would be encapsulated in the hardened cement paste, any aluminium and iron are likely to be immobilised.

Even though the hardened cement paste made at a BFS/OPC ratio of 4:1 did not have the highest OPC content, this formulation produced the wasteform with the best physical properties, with the quantity of reacted slag and compressive strength highest and the porosity lowest of all formulations of hardened cement paste.

5. Conclusions

- There was little reaction of the sludge solids with any of the cement formulations during the hydration period studied. Much unreacted brucite remaining from the sludges, was detected in all cemented samples. A small quantity of a hydrotalcite-type phase, likely to contain magnesium from the sludge, was detected in all cemented sludge samples. The stoichiometry of this hydrotalcite-type phase is slightly different to that of hydrotalcite reported in the literature, and is likely to be influenced by the quantity of Mg^{2+} and OH^{-} ions present.
- There appeared to be no incorporation of magnesium from the sludge in the C–S–H formed during cement hydration. The sludge solids were encapsulated, or surrounded by the hydrating cement, rather than being immobilised, or chemically bound within the hardened cement structure.
- The 4:1 BFS/OPC formulation produced the wasteform with the best properties in terms of quantity of slag reaction, compressive strength and porosity.
- An alkaline sludge made with sodium hydroxide solution rather than distilled water increased the reaction of both BFS and PFA during sludge cementation which increased the amount of C–S–H formed. Despite this there was an increase in porosity and a decrease in compressive strength of all hardened cement pastes upon alkaline activation.
- The pH of the mixing fluid had little influence on the pH of the resultant sludge. Upon mixing the powder with the mixing fluid during sludge preparation, the brucite content increased and magnesite content decreased. The pH of all formulations of cement paste was governed mostly by the quantity of OPC used.

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