Journal of Nuclear Materials 393 (2009) 92–101

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Immobilisation of Fe floc: Part 2, encapsulation of floc in composite cement

N.C. Collier [a,*], N.B. Milestone [a], J. Hill [b], I.H. Godfrey [c]

[a] *Immobilisation Science Laboratory, Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK*
[b] *AMECNNC Ltd., The Renaissance Centre, 601 Faraday Street, Birchwood Park, Birchwood, Cheshire WA3 6GN, UK*
[c] *Nexia Solutions, Sellafield, Seascale, Cumbria CA20 1PG, UK*

ARTICLE INFO

Article history:
Received 27 August 2008
Accepted 18 May 2009

ABSTRACT

Radioactive iron (Fe^{3+}) hydroxide flocs are produced during reprocessing of nuclear fuel at Sellafield, UK. The flocs must be pre-treated with slaked lime before encapsulation in a pulverised fuel ash/ordinary Portland cement composite cement to produce a crack-free wasteform. This paper reports results obtained after investigating the fate of the iron in the floc during cementation. Results indicate that the iron in the floc reacts by substituting into and adsorbing onto the C–S–H phase formed during hydration. Additionally, a small quantity is substituted into a crystalline katoite phase, $Ca_3AlFe(SiO_4)(OH)_8$. These substitutions are significant because the iron in the floc is rendered chemically immobilised within the cement rather than simply being physically encapsulated. No new phases are formed after twelve years cement hydration and examination of the twelve year old sample indicates that the durability of the wasteform appears to be high.

1. Introduction

The generation and subsequent encapsulation processing route of iron hydroxide flocs by British Nuclear Group (BNG) at the nuclear fuel reprocessing plant at Sellafield in the UK has previously been explained [1]. Acidic liquors produced in the Enhanced Actinide Removal Plant (EARP) contain very small but significant amounts of radioactivity. Ferric nitrate is added to these liquors and the resultant solutions are treated with sodium hydroxide solution to precipitate colloidal iron flocs onto which active species such as uranium, plutonium and other actinides, as well as radioactive caesium, are adsorbed. These are classed in the UK as intermediate level wastes (ILWs). After production in EARP, the flocs are partially dewatered by filtration, pre-treated with slaked lime ($Ca(OH)_2$, CH (using cement chemist's notation where C=CaO, H=H_2O, A=Al_2O_3, S=SiO_2)) and encapsulated in a Pulverised Fuel Ash (PFA)/ordinary Portland cement (OPC) composite cement. After setting, the hardened wasteforms are stored temporarily in an interim overground store awaiting final disposal.

Because the iron hydroxide particles have radionuclides adsorbed, the manner in which they are held in the hydrating cement is of prime importance and any interaction between the iron hydroxide in the pre-treated floc and the hydrating cement needs to be understood. The interaction of the floc with $Ca(OH)_2$ during pre-treatment has been reported [2] and initial results investigating the subsequent cement encapsulation process have previously been reported [1]. However, this paper provides a more in-depth analysis of the chemical and physical interactions between the cement and an inactive floc of the same composition as one of the active flocs produced at Sellafield. This is the second of two papers describing the nature and composition of the mineralogical phases formed during the pre-treatment process and in the subsequent encapsulation of the resultant pre-treated slurry.

2. Review of relevant literature

Despite general literature reporting the physical and chemical interactions between radioactive wastes and cement systems, little literature exists in the public domain that specifically addresses the physical and chemical outcomes of cement encapsulated ferric floc. However, an extensive amount of commercial development work has been performed in support of the design and operation of EARP within British Nuclear Fuels Ltd (BNFL). Work published by Godfrey et al. [3] and Caldwell et al. [4] summarises an investigation into the compositional and physical characteristics of a ten year old sample of cemented inactive iron hydroxide floc, similar to that investigated in this paper. Our paper addresses in detail the fate of the iron in the floc and for the first time identifies how this iron is bound into the hardened cement paste.

After being ultra-filtered, the ferric flocs still contain approximately 85 wt% water [5,6] so even though no additional water is used during mixing of the composite cement, the hardened matrix is very porous which may affect the long term durability of the wasteform. The colloidal nature of the floc means that considerable water is bound to the floc particles and is unavailable to contribute

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[*] Corresponding author. Tel.: +44 114 222 5504; fax: +44 114 222 5943.
E-mail address: n.collier@sheffield.ac.uk (N.C. Collier).

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doi:10.1016/j.jnucmat.2009.05.010

to workability. This is in line with comments by Godfrey [6] who stated that despite the high water:solids (w/s) ratio, the floc/composite cement paste was highly viscous.

It has been generally accepted in the UK that a cement based medium is the most suitable encapsulant for immobilising radioactive ILW [7–12] as the hydrated cement provides a dense, low permeability matrix able to retain radionuclides by a combination of high pH, surface sorption and lattice incorporation. OPC alone is unsuitable for immobilisation of nuclear waste because the high heat of hydration may cause internal stresses and cracking in the matrix during curing, affecting the integrity of the waste product during storage, transport and disposal. The exotherm generated during the hydration of OPC has been postulated to perhaps crystallise the C–S–H, and reduce the surface area available for adsorption or produce steam during hydration which could cause increased voidage, drying shrinkage and possible radionuclide release [8]. However, no evidence of this has been found in the hardened blended cements used for processing ILW at BNFL. By replacing some of the OPC with a secondary cementitious material such as PFA, a reduction in the heat of hydration is indeed obtained; in a 500 l drum with a similar formulation to that studied in this research, temperatures of approximately 80 °C have been reported, significantly less than that when using OPC [6,13,14]. The addition of PFA also improves the rheological properties of the paste [8,9].

Even though the level of radioactivity of the wastes being encapsulated is relatively low, possible radiological effects on the encapsulating hardened cement have to be considered. Glasser [7] has reported that while ionising radiation had little impact on dry cement it did cause radiolysis of the water within the hydrating cement paste. Palmer and Fairhall [15] reported similar results when they examined two cemented ILWs. They found that irradiation with gamma rays had virtually no effect on hardened cement strength, and concluded that physical and chemical effects modify the wasteform properties much more than radiation effects. Wilding [8] observed no loss of stability due to radiation, but stated that spalling and gas pressurization could occur. Richardson et al. [16] also showed that the microstructure and degree of hydration were not significantly altered by exposure to gamma radiation, aside from the formation of an ettringite phase in the irradiated samples. This may be caused by the radiolysis of water to form a hydroxide radical which may interact with sulphides to produce sulphates which in turn may lead to the formation of ettringite-type phases.

The durability of cemented ILW is of importance within the nuclear industry due to the long lifetime requirement of the final wasteform. Pore structure has a major influence on the leaching characteristics of a hardened cement paste. Brodersen and Nilsson [17] pointed out that the addition of PFA to a cement paste often produced a less permeable hardened material which could reduce hygroscopic water uptake in hardened cement and reduce transport of gases and water vapour through hardened cement. Zamorani [18], when summarising the important points concerned with leaching of radioactive wastes encapsulated in hardened cement paste, stated that when all the soluble CH had dissolved in the leach water, the C–S–H decomposed to restore the equilibrium, and reduced the pH of the solution, increasing the solubility of the active elements. He concluded that degradation of hardened cement paste depended on physical factors (porosity, compressive strength and density) as well as leachant factors (pH, flow rate, temperature and water chemical composition).

Glasser [11,19] and Atkins and Glasser [20] have provided reviews on the interactions between wastes and the hardened cement matrix in which they are encapsulated. The alkalis present in the cement clinker and the later formation of CH, give rise to a highly alkaline pore solution [21] which keeps the solubility of many metal hydroxides low which in turn restricts their transport through the hardened cemented wasteform [19] and controls which hydroxides can enter solution [22]. The pozzolanic reaction which occurs in hydrating PFA/OPC cement reduces the pH through the removal of CH. Dhir [23], quoting work by Diamond, stated that the pore solution extracted from a hardened PFA/OPC concrete showed only a very small reduction in pH from 13.75 to 13.55 when compared to that of using only OPC. Concerning the addition of ferric hydroxide to cement, Taylor and Newbury [24] have stated that the low solubility of iron in the alkali pore solution reduces its migration in a hardened cement paste whilst Glasser [10] has stated that ferric hydroxides retard the setting of cement matrices.

It is generally reported that a reducing pore solution in a hardened cement paste lowers the solubility of many encapsulated waste ions [10,11,19,22]. Cements are normally produced under oxidising conditions but may contain traces of chemically reduced iron (Fe^{2+}) and manganese (Mn^{2+}). These have low electroactivity and are insoluble at high pH so OPC itself offers a low reducing potential. Blending OPC with other cementitious materials such as PFA creates only a slightly reducing environment because the significant amounts of carbon and chemically reduced iron (magnetite (Fe_3O_4)) it contains are chemically too inactive [4].

Over the past 20 years, considerable research has addressed how impurities can be incorporated into the cement hydrates C–S–H, ettringite and monosulphate. All these phases have been found to accommodate a variety of anionic and cationic substitutions [19]. While C–S–H accounts for at least 60 wt% of all hydration products in OPC and PFA/OPC hardened cement pastes [21], Glasser [11] stated that waste ions are more likely to be sorbed onto the surface of C–S–H than substituted into the C–S–H structure. From their work in hydrating pure alite to form C–S–H, Richardson and Groves [25] reported that Al^{3+} and Fe^{3+} were substituted into tetrahedrally coordinated sites. They also stated that the appearance of anionic groups such as OH^-, SO_4^{2-} and $CO_3{}^{2-}$ within C–S–H was likely to be caused by intermixing of other hydration products with C–S–H during the hydration of the cement. Similarly, Taylor [26] has stated that Al^{3+} ions, rather than being substituted into C–S–H, are present in monosulphate which is mixed within the C–S–H as it forms. He felt that any Mg^{2+}, Fe^{3+} and SO_4^{2-} ions detected in the C–S–H were in intermixed regions of hydration products. Gougar et al. [27] has reported that C–S–H isolates waste ions through various mechanisms including sorption, substitution at interlayer sites and admixing with other phases present in the hydrated cement.

In ettringite, the SO_4^{2-} ions located within the channels between the columns of hexagonal prisms can be readily replaced with other anionic groups where complete or partial replacement may occur. Ettringite contains Al and can also contain Fe or both, and phases can also form where other cations replace some of the Ca^{2+} or Al^{3+}. Thus the scope for ionic substitution in the ettringite structure is large. Monosulphate is similar to ettringite in terms of the replacement of Al^{3+} ions with Fe^{3+} or Cr^{3+} ions and in terms of the anionic groups that it contains. The structure comprises main layers containing calcium and aluminium with interlayers containing the SO_4^{2-} and OH^- groups [28]. These SO_4^{2-} groups have been reported to be replaced by OH^-, CO_3^{2-} and Cl^- ions [21].

3. Experimental procedures

3.1. Raw materials

Four flocs are produced by BNG during re-processing and in order to allow processing conditions to be established, they have made a substantial quantity of simulant material which contains all of the actual floc ingredients apart from the radioactive species. The iron hydroxide floc studied here was the inactive simulant of

Table 1
Oxide composition of OPC and PFA calculated after elemental composition had been determined by ICP/OES, and Bogue cement phase composition.

OPC		PFA	
Composition	Quantity (wt%)	Composition	Quantity (wt%)
CaO	64.58	CaO	1.44
SiO_2	20.96	SiO_2	48.64
Al_2O_3	5.24	Al_2O_3	25.88
Fe_2O_3	2.61	Fe_2O_3	7.57
MgO	2.09	MgO	1.42
SO_3	2.46	SO_3	1.20
K_2O	0.59	K_2O	2.83
Na_2O	0.28	Na_2O	1.91
Chloride[a]	0.05	TiO_2	0.92
Insoluble Residue	0.27	LOI	4.16
Total	99.13	Total	95.97
C_3S	51.0		
C_2S	20.8		
C_3A	9.8		
C_4AF	10.0		

[a] Determined by a colorimetric method.

the most common floc (by volume) produced during re-processing. The simulant floc was supplied by Nexia Solutions and initial characterisation has previously been reported [1]. The method of floc preparation is described in part 1 of this paper [2]. To summarise, the floc was a brown viscous aqueous colloidal suspension which had no odour, exhibited thixotropic characteristics and the solids were largely X-ray amorphous. It had a pH of approximately 9 and contained 16.8 wt% solids, 8.8 wt% of which was iron. After freeze drying, the floc solids contained no crystalline material and no obvious crystalline particles were discernible by SEM. After pre-treatment of the floc with 10 wt% slaked lime for 8 h, the main phase formed was an X-ray amorphous hydrated calcium ferrite with an approximate composition of $2CaO{\cdot}2Fe_2O_3{\cdot}12H_2O$. Small amounts of calcite, $Ca_6Fe_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$, $Fe_6(OH)_{12}(CO_3)$ and $Ca_3B_2O_6$ were also detected.

The OPC was supplied by Castle Cement Ltd and the PFA by Ash Resources Ltd, both to an original BNFL specification in terms of fineness and composition. The elemental composition of both powders was determined using inductively coupled plasma/optical emission spectroscopy (ICP/OES) performed at The University of Sheffield. The resultant calculated oxide compositions of both powders and the resultant calculated cement phase composition are shown in Table 1.

3.2. Sample preparation

All samples were mixed in batches of 3 kg of wet cement paste. 10 wt% $Ca(OH)_2$ was added to a known mass of floc in a Hobart Planetary A12 Mixer during continual mixing over a 5 min period and the resultant slurry stood uncovered for 8 h. After this time, the required mass of pre-blended cement powders (a PFA:OPC ratio of 5:4 and a pre-treated floc to composite cement powders ratio of 9:8) was mixed into the slurry (5 min powder addition and 15 min further mixing) during continual mixing. The resultant paste was placed in 50 ml polypots which were vibrated to remove air voids and then sealed and stored in an environmental chamber controlled at 20 °C and 95% relative humidity. Floc-free reference samples were also made at the same w/s ratios and in the same manner as above.

To replicate a radioactive floc encapsulated in the same hardened composite cement paste, an iron hydroxide floc doped with cerium as simulant was made to the same molar ratios as the floc supplied by Nexia Solutions and both untreated and pre-treated samples were encapsulated in cement using the same method as above. These cements were hydrated at 40 °C and 95% RH for 28 days to accelerate the hydration of the cement. To make the doped floc, 188.80 g of $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in 250 ml distilled water. 7.75 g $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in this solution and, whilst stirring, a 1 M solution of NaOH was gradually added until the pH reached approximately 11 and the solution flocculated. The final suspension was left to settle for 24 h after which time the clear supernatant was decanted. The remaining solution was then washed with distilled water, left to settle for 24 h and the clear supernatant removed by decantation. This washing, settling and decantation process was repeated for a total of five times. The residue was then dried in an oven at 60 °C until the mass equilibrated. The remaining solids were then mixed for 24 h with distilled water at the same water:solids weight ratio as the inactive floc and mixed to form the same cement paste as with the floc supplied by Nexia Solutions.

A twelve year old sample of cemented pre-treated floc, made with the same composite cement and slaked lime powders and to the same mixing ratios as that being studied in this research, was obtained from Nexia Solutions. This sample had the Nexia Solutions identification code IDM/93/12 and was used to analyse for any changes in composition, microstructure and physical properties that may occur between 720 days and 12 years hydration.

3.3. Sample analysis

To arrest hydration, the cement samples were removed from their polypots at the desired age and lightly crushed by hand, if necessary using a percussion mortar, 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. The resultant samples were then subsequently stored in sealed glass jars.

To prepare samples for analysis by Thermogravimetric Analysis (TGA), Fourier Transform Infra-Red Spectroscopy (FTIR) and Mössbauer Spectroscopy, the dried samples were crushed by hand and ground to pass a 63 μm sieve. For TGA, approximately 10 mg of sample was heated in an alumina sample pan in a Perkin Elmer Pyris 1 Thermogravimetric Analyzer heating from 30 to 1000 °C at 10 °C/min in a flowing nitrogen atmosphere. FTIR analysis was performed using a Perkin Elmer Spectrum 2000 FTIR Spectrometer and analysis by Mössbauer Spectroscopy used a Wissel Mössbauer Spectrometer with a ^{57}Co source in a rhodium matrix and the software package RECOIL [29].

Pieces of dried sample approximating 6 × 6 × 6 mm were set in epoxy resin, hand ground and polished for analysis by Scanning Electron Microscopy (SEM). After carbon coating, the samples were examined using backscattered electron imaging (BEI) in a Jeol JSM 6400 electron microscope fitted with a Link ISIS EDS Analyser to allow analysis by Energy Dispersive Spectroscopy (EDS).

For analysis by Mercury Intrusion Porosimetry (MIP), pieces of dried sample approximately 3 × 3 × 3 mm and with a combined weight of approximately 0.6 g were prepared. Samples were then analysed using a Micromeritics Poresizer 9320 MIP machine.

For accelerated leach testing, pieces of hardened cement approximately 2 × 2 × 2 mm with a combined sample weight of 2.00 +/− 0.01 g were prepared. The design of the leach testing experiment complied with BS 2071 (1989) [30] and, while not a standard test, did provide accelerated results. Elemental composition of the resultant leachate was determined using inductively coupled plasma/optical emission spectroscopy (ICP/OES).

4. Results

From previous work [1], the main crystalline phase detected after pre-treatment of the floc with 10 wt% lime for 8 h and encapsulation of the resultant slurry in the same PFA/OPC composite cement used in this work was an iron substituted katoite, $C_3(A,F)SH_4$, which formed after 2 days cement hydration.

4.1. Thermal analysis

Fig. 1 shows the derivative thermogravimetric (DTG) traces for the cemented pre-treated floc hydrated for 7, 90 and 720 days at 20 °C. The biggest peak in all samples was the broad peak between approximately 50 and 550 °C which was due to the release of water from C–S–H. Superimposed onto this C–S–H peak were other smaller peaks. After 7 days hydration the main peak due to the highest rate of water loss from C–S–H was at approximately 120 °C. Peaks for CH and calcite were also detected at approximately 440 and 650 °C respectively. A small peak at approximately 140 °C may be due to the highest rate of water loss from a C–S–H substituted with reactive iron from the floc. To ease identification of this peak, it is referred to as Fe C–S–H in this paper. For the 90 day sample, peaks attributed to C–S–H, Fe C–S–H, hydrogarnet (C_3AH_6) and calcite ($CaCO_3$) were detected, although the latter was much reduced compared to that at 7 days. C_3AH_6 was not detected by XRD, but the hydrogarnet type phase $C_3(A,F)SH_4$ was identified and will release water at approximately the same temperature as C_3AH_6 (approximately 320 °C). After 720 days hydration, the C–S–H peak shifted to a slightly lower temperature (approximately 100 °C) which may have been due to variations in sample mass. Peaks for Fe C–S–H and $C_3(A,F)SH_4$ were also present, as was a very minor calcite peak. The amount of calcite detected reduced with aging indicating its consumption as hydration progressed. Small peaks at approximately 900 °C in all samples could be due to the release of oxygen from hematite (Fe_2O_3) present in the PFA.

As hydration time increased, the size of the Fe C–S–H DTG peak increased compared to that of the peak for the highest rate of water loss from C–S–H, suggesting that more iron may be substituting into the C–S–H. The CH peak was not detected in the 90 and 720 day samples, probably because of its consumption in the pozzolanic reaction with PFA. The intensity of the small peak at approximately 300 °C attributed to water loss from $C_3(A,F)SH_4$ generally appeared to increase with hydration time. The small sharp peaks on the 90 day trace at approximately 200, 510 and 650 °C and at 160 and 550 °C on the 720 day trace were instrumental artefacts.

4.2. Spectroscopic analysis

FTIR and Mössbauer Spectroscopy were used in an attempt to characterise the amorphous material in the cemented floc and to attempt to determine if iron in the floc was reacting with any of the cement hydration products.

The FTIR traces for cemented pre-treated floc hydrated for 7, 90 and 720 days (Fig. 2) were very similar. Three main bands, centred at 3460, 970 and 450 cm^{-1}, were due to the vibration of O–H bonds in water, Si–O bonds and Fe–O bonds respectively. The band at 1620 cm^{-1} was due to the bending of O–H bonds in water whereas the sharp peak at 3640 cm^{-1} was due the vibration of O–H bonds in CH which disappeared on extended hydration. This is in line with XRD results previously reported [1]. The Si–O band at 970 cm^{-1} was due to C–S–H while the small shoulder at 865 cm^{-1} on the lower frequency side of this band could have been due to the stretching of Si–O bonds in the aluminosilicate glass present in un-reacted PFA. The Fe–O band was due to the presence of iron oxide-hydroxide phases. A well defined doublet between 1380 and 1480 cm^{-1} showed the presence of calcite (1400 cm^{-1}) whereas the band at 1460 cm^{-1} could be due to $Fe_6(OH)_{12}(CO_3)$ (referred to as Phase Y) which was the main crystalline phase detected during both pre-treatment and cementation of this sample [1]. Previous work has shown that the raw floc contains hexacyanoferrate and after cementation the phase monosulphate ($3C_3A{\cdot}CaSO_4{\cdot}H_{12}$, AFm) is formed [1]. These two phases have been detected in these samples as a weak band at 2020 cm^{-1} due to the vibration of C≡N bonds present in hexacyanoferrate in the raw floc whilst weak bands at 1080 and 700 cm^{-1} could be due to the vibration of S–O bonds in monosulphate. The very small bands at approximately 2910 and 2850 cm^{-1} were probably due to contamination of the samples by oil during sample preparation whilst the small band at approximately 2300 cm^{-1} in the 720 day trace was an instrumental artefact.

The floc free reference cement and cemented pre-treated floc hydrated for 90 days at 20 °C were analysed by Mössbauer Spectroscopy. Hematite and magnetite were the only iron bearing phases detected in the former (the spectrum was resolved into two doublets, one having values of isomer shift (δ) and quadruple splitting (ΔE_q) of 0.90 and 2.36 mm/s respectively, and the other having values of δ and ΔE_q of 0.3 and 0.73 respectively). Results for the latter are shown in Fig. 3 and Table 2 and because this

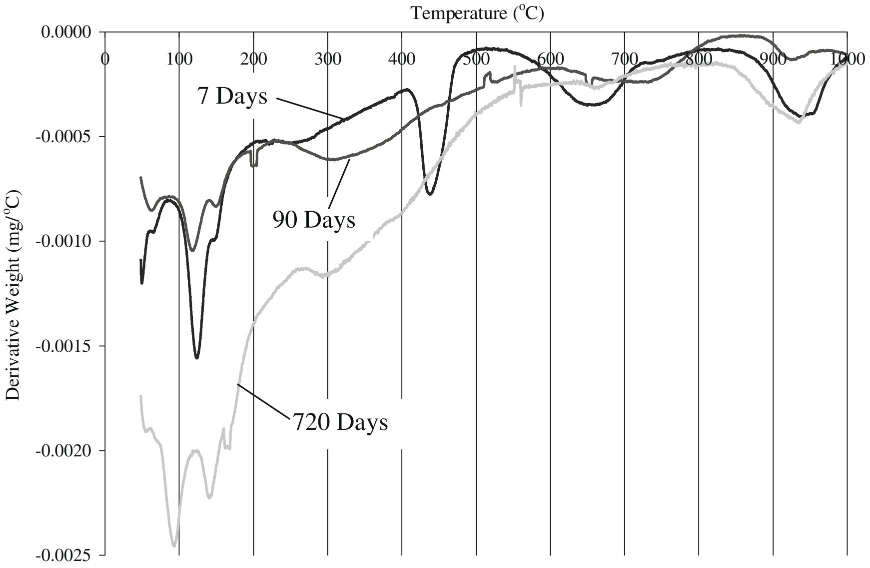

Fig. 1. DTG curves for cemented floc hydrated for 7, 90 and 720 days at 20 °C.

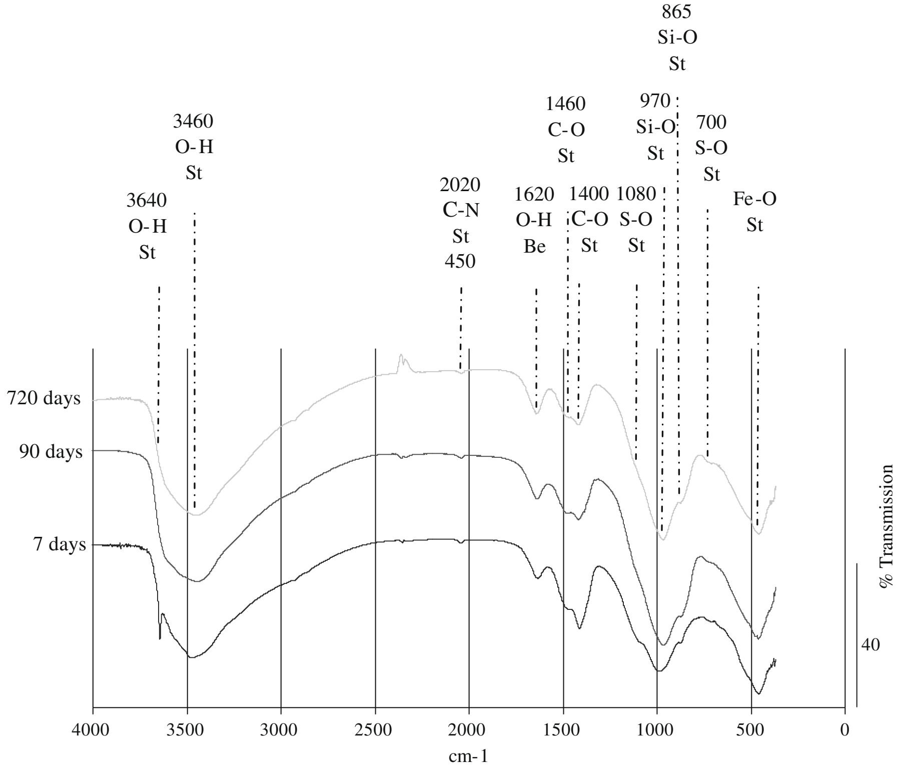

Fig. 2. FTIR trace of cemented pre-treated floc hydrated for 7, 90 and 720 days at 20 °C. St = Stretching, Be = Bending.

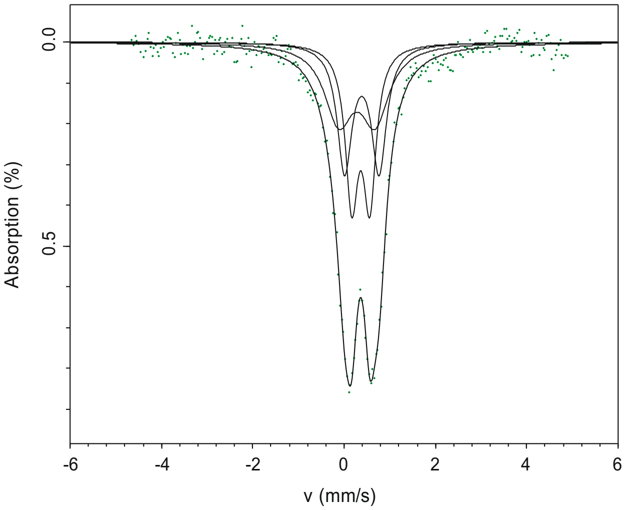

Fig. 3. Mössbauer spectrum for cemented pre-treated floc hydrated for 90 days at 20 °C.

sample was run at a low velocity range, the sextets for hematite and magnetite [31] were not resolved. All iron detected was Fe^{3+} and the spectrum resolved into three doublets. Results reported by Nishida [32] (Table 3) were used to interpret the spectra. The values of δ and ΔE_q for doublet 1 both indicated the presence of octahedral Fe^{3+} whilst the lowest value of line width (w+) indicated that this iron bearing phase was most ordered of all material. The combination of δ and ΔE_q results for doublet 2 indicated the presence of octahedral Fe^{3+}, whereas the combination of δ and ΔE_q of doublet 3 suggested tetrahedral Fe^{3+}. Doublet 3 had the highest value of w+ which indicated that this iron bearing phase was the least ordered of all material.

The values of δ and ΔE_q for the iron in the cemented pre-treated floc were markedly different from those detected in the floc free reference cement indicating that the three forms of iron detected in the former were due to the presence of iron phases formed from the floc. Our results for doublet 1 (Table 2) were similar to results reported by Faucon et al. [33] where the iron had substituted for non-labile calcium in the structure of the C–S–H. For doublets 2 and 3, the values of ΔE_q, and to a lesser extent the values of δ, were similar to those reported by Faucon et al. for iron in $C_3(A,F)SH_4$ and for the substitution of iron for labile calcium on the surface of the C–S–H respectively. The lower value of w+ in doublet 2 indicated a more crystalline material.

4.3. Electron microscopy

Analysis of particle shape and size, and the distribution of elements within the microstructure of the cemented floc was performed using backscattered electron imaging (BEI) and EDS on polished surfaces of the cemented floc. Fig. 4 shows a BEI micrograph and EDS results for cemented pre-treated floc hydrated for 90 days. Spot analysis at many points in the main binding matrix of the sample, marked X, showed that calcium, silicon and iron were detected. This suggests that the main matrix is C–S–H into which iron from the floc is incorporated. This was supported by the element maps (Fig. 4) which showed that calcium, silicon and iron were widely dispersed in the matrix and that iron was pervasive throughout the cement microstructure. As expected, only aluminium and silicon were detected in the cenospheres of the aluminosilicate PFA glass or as mullite ($Al_6Si_2O_{13}$).

4.4. Leach testing

Accelerated leach testing was performed to simulate ground water leaching of the cement in an underground repository and was performed on the cemented pre-treated floc which had been

Table 2
Values of δ, ΔE_q, A and $w+$ for Mössbauer spectrum for cemented pre-treated floc hydrated for 90 days at 20 °C, and reference data.

	δ (mm/s)	ΔE_q (mm/s)	A (%)	$w+$ (mm/s)	Assignment
Doublet 1	0.36	0.39	33	0.16	Octahedral Fe^{3+}
Doublet 2	0.38	0.75	32	0.20	Octahedral Fe^{3+}
Doublet 3	0.28	0.80	36	0.38	Tetrahedral Fe^{3+}
Replacement of labile Ca in C–S–H with Fe, and Fe in $C_3(A,F)SH_4$[a]	0.39	0.86			
Replacement of non-labile Ca in C–S–H with Fe[a]	0.31	0.39			

Note: δ – isomer shift, ΔE_q – quadrupole splitting, A – absorption area, $w+$ – line width.
[a] [32].

Table 3
Summary of δ and ΔE_q for divalent and trivalent iron reported by Nishida [32].

	δ (mm/s)	ΔE_q (mm/s)
Fe^{3+} tetrahedral	0.20–0.32	0.7–1.0
Fe^{3+} octahedral	0.35–0.55	0.3–0.9
Fe^{2+} tetrahedral	<1.0	–
Fe^{2+} octahedral	>1.0	–

Note: δ – isomer shift, ΔE_q – quadrupole splitting.

hydrated for 720 days at 20 °C. The test was also carried out on the cemented pre-treated cerium doped iron hydroxide floc hydrated for 28 days at 40 °C. A summary of the ICP/OES elemental analysis results of all leachates is shown in Table 4.

The quantity of elements leached from the cemented pre-treated floc was very low with calcium the highest; up to 1.50 mg/g of sample was leached, which is equivalent to only 0.15 wt% of the sample. The leaching of calcium affects the long term durability of the wasteform, so this small quantity indicated that the cement was very stable. The aluminium and silicon levels leached were slightly lower than that of calcium while the amount of iron leached was significantly lower indicating that the iron was very strongly bound in the sample.

In the younger cemented pre-treated iron hydroxide floc doped with cerium, very little of the cerium was leached (<3.75 μg/g of sample) and it remained strongly adsorbed to the cemented floc. The higher level of calcium leached (7.18 mg/g of sample) is probably due to the young age of the sample (28 days) but very little iron was leached (<0.75 μg/g of sample). Overall, the results showed that both the iron and the cerium were more tightly bound into the cement microstructure than aluminium, calcium or silicon.

4.5. Porosity analysis

MIP was used to determine the porosity and size of pores in the cement as this affects the permeability of soluble ions through the hardened matrix. These tests were carried out on samples of cemented pre-treated floc that had been hydrated for 28 and 90 days at 20 °C (Table 5). The total porosity and majority pore size of the 90 day sample was approximately 3% and 50% lower respectively than the sample hydrated for 28 days caused by C–S–H forming in the large pores previously occupied by water.

Fig. 5 shows the MIP plot for cemented pre-treated floc hydrated for 28 and 90 days at 20 °C where pore diameter (D) has been plotted on a log scale against $dV/d\log D$ and where V is the volume. Both traces showed that most of the pore diameters lay within the size range 0.01–1.0 μm with a very small number of pores up to 100 μm in diameter. In the 28 day sample there were two pore populations, the majority with a diameter of approximately 0.08 μm and a second smaller number of larger pores approximately 0.18 μm in diameter. The trace for the 90 day samples was similar but the majority pore diameter had reduced to approximately 0.04 μm with much fewer larger pores of approximately 0.13 μm in diameter.

4.6. Analysis of long term aged cemented floc

Analysis of a twelve year old cemented floc supplied by Nexia Solutions (sample identifier IDM/93/12) showed that it was generally amorphous with the main phase being poorly crystalline C–S–H, but small quantities of crystalline $C_3(A,F)SH_4$, quartz, calcite, CH, and hematite were also detected. EDS showed that the distribution of calcium, silicon and iron in this sample was uniform and closely inter-related. Very small amounts of aluminium, calcium and silicon (0.26, 0.36 and 2.66 mg/g of sample respectively) were leached from the cement and even a smaller amount of iron (<7.5 μg/g of sample).

5. Discussion

5.1. Cementation of the waste

5.1.1. Amorphous cement hydration products

All cemented samples studied were largely amorphous and, because of the high water content of the floc, the proportion of solid material to pore space was low giving rise to a porous matrix.

It is clear that iron from the floc has reacted with the C–S–H with a small amount incorporated into crystalline $C_3(A,F)SH_4$. This is contrary to that reported by Caldwell et al. [4] and Godfrey et al. [3] who suggested that the iron from the floc was not chemically incorporated into the C–S–H, but was microencapsulated. In our work, DTG showed that there were two steps in the rate of water loss from C–S–H in the cemented pre-treated floc, one at a temperature normally associated with that of hydrated OPC, and a second at a slightly higher temperature. This suggests that two forms of C–S–H are present. If iron from the floc had substituted in the C–S–H it is likely to lead to crosslinking of the silicate chains causing water to be bound more tightly into the C–S–H requiring a higher temperature to release it from the structure. EDS showed that after cementation, iron from the floc was pervasive and was always intimately associated with calcium and silicon. The colloidal iron hydroxide in the floc may react with the cement hydration products due to its small particle size and high surface charge, characteristics typical of a colloidal suspension. Mössbauer spectroscopy results confirm that iron from the floc has adsorbed onto and substituted into the C–S–H during hydration of the cement. Further adsorption of the iron onto OH^- groups on the surface of the C–S–H may also have occurred with the positively charged floc particles attaching to the OH^- groups on the surface of the C–S–H [21,35]. Replacement of silicon with iron in the chains of silicate tetrahedra may also have occurred [25] but was not detected experimentally.

Pre-treatment of the floc with slaked lime before encapsulation in cement also can affect how the iron in the floc reacts with the C–S–H. Thermal analysis of the cemented untreated and pre-treated floc hydrated for 90 days (Fig. 6) showed that pre-treatment gave rise to a small DTG peak at approximately 150 °C, already attributed to the presence of an Fe C–S–H. Such peaks were not observed in the un-treated cemented floc. Similar results were found for the samples hydrated for 7 and 720 days. This suggests that after pre-treatment, the iron from the floc can be more readily incorporated into

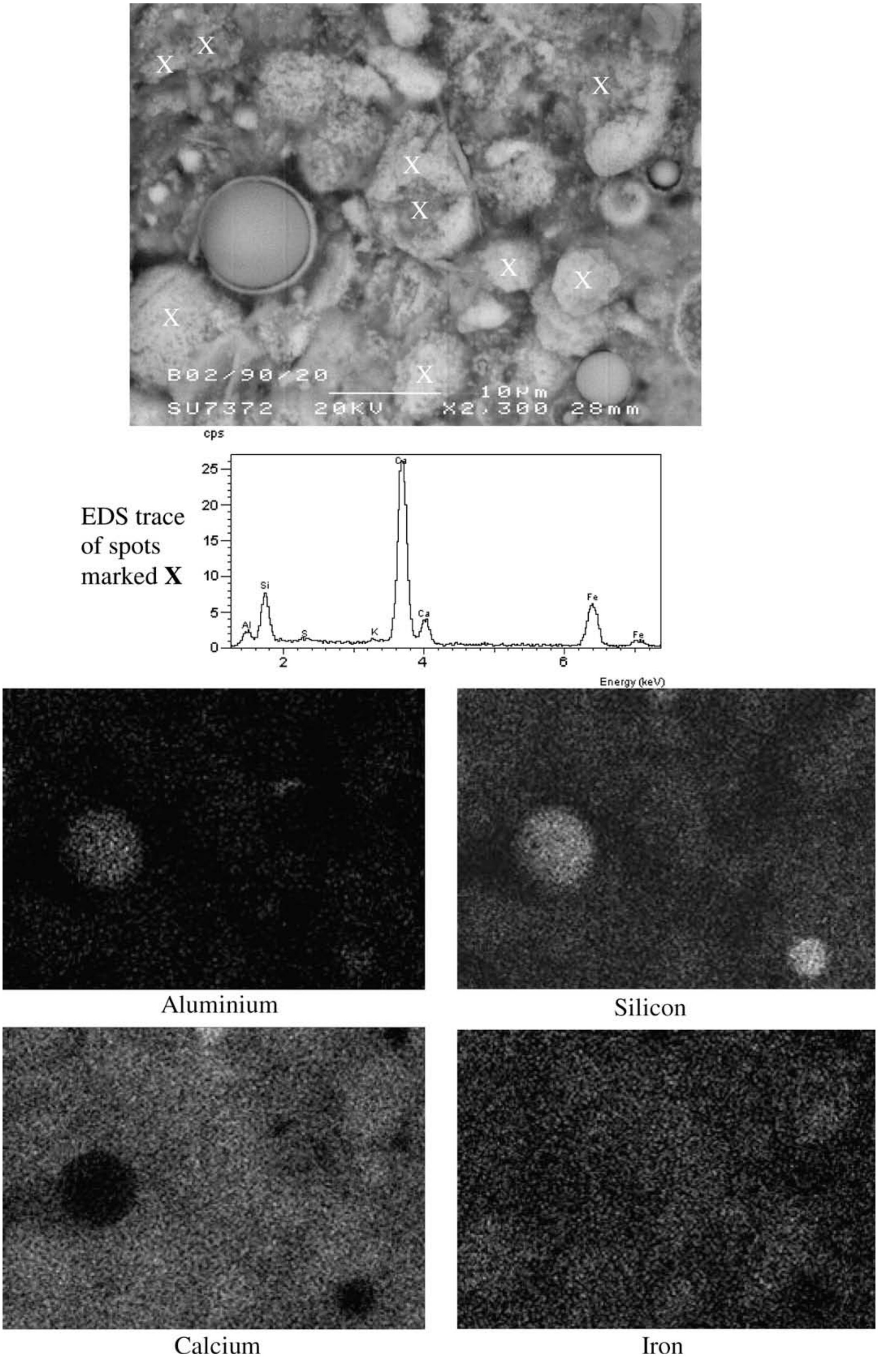

Fig. 4. SEM BEI micrograph, EDS trace and element maps of polished surface of cemented pre-treated floc hydrated for 90 days at 20 °C.

the C–S–H during hydration of the composite cement due to the more highly alkaline environment created by the slaked lime during pre-treatment. Additionally, the main reaction product of pre-treatment (an X-ray amorphous calcium ferrite phase [2]) may be more reactive and lead to more incorporation of iron into the C–S–H.

5.1.2. Crystalline cement hydration products

The katoite type phase, $C_3(A,F)SH_4$, was the main crystalline phase formed in the cemented pre-treated floc and contained iron from the floc in a trivalent octahedral state. $C_3(A,F)SH_4$ forms after approximately 7 days hydration, and the XRD peaks became more

Table 4
Summary of leach tests.

Sample	Quantity of elements detected				
	(mg/g of sample)			(μg/g of sample)	
	Al	Ca	Si	Fe	Ce
Cemented pre-treated floc[a]	0.80	1.50	1.22	<7.5	–
Cemented pre-treated cerium doped floc[b]	1.01	7.18	0.29	<0.75	<3.75

Note: Detection error: Al, Ca, Si, Fe ± 5%, Ce ± 25%.
[a] Hydrated for 720 days at 20 °C.
[b] Hydrated for 28 days at 40 °C.

Table 5
Summary of MIP tests.

Sample	Total porosity (%)	Majority pore size (μm)
Cemented pre-treated floc, 28 days	51	0.08
Cemented pre-treated floc, 90 days	48	0.05

Note: All samples hydrated at 20 °C.

intense. At hydration times of 90 days and longer, the intensity of the XRD peaks was high indicating significant amounts of a well ordered material. This is of interest because hydrogarnet phases observed in hydrated OPC and composite cements are not typically very crystalline [21] and can usually only be synthesised hydrothermally [35], so the formation of such a phase in a cement hydrated at 20 °C was surprising, but may be due to the high reactivity of the floc particles. Katoite type phases are generally stable [21] and $C_3(A,F)SH_4$ has been reported to be chemically inert during leaching of the hardened cement paste in which it is contained [34]. Caldwell et al. [4] and Godfrey et al. [3] also found a similar katoite phase in their ten year old samples of cemented iron hydroxide floc, but the exact composition was not reported.

Many of the PFA cenospheres in the cemented floc were encased in C–S–H which corresponds well with work reported by Williams et al. [36] who stated that CH is deposited onto the cenospheres of PFA and forms nucleation sites for C–S–H growth. This happens more with the cemented pre-treated floc than with the floc free cement suggesting that the floc may increase the reactivity of the PFA. The amount of CH detected in the cemented pre-treated floc reduced with hydration time and was not present after 90 days hydration, indicating that the small amount of CH remaining after floc pre-treatment reacts with the PFA. This is in line with the results of Caldwell et al. [4] who reported the absence of CH in a 10 year old sample of cemented pre-treated floc.

5.2. The cemented wasteform

The high water content of the floc (approximately 85 wt%) produced a wasteform with very high porosity (approximately 50%) where the majority pore size and total porosity reduced with time as the larger capillary pores were replaced by more C–S–H with smaller gel water pores between the C–S–H. This was also observed by SEM where the microstructure of cemented pre-treated floc appeared to contain more C–S–H and be less porous after 90 days than after 28 days. Such high porosity will tend to produce a more open microstructure which, in turn, will adversely influence the durability of the hardened wasteform.

5.2.1. Durability

Analysis of the 12 year old sample of cemented pre-treated floc supplied by Nexia Solutions (IDM/93/12) gave results very similar to those of the cemented pre-treated floc hydrated for up to 720 days in terms of composition, microstructural characteristics, association of iron, calcium and silicon, and leaching performance, which indicates that little change has occurred between 720 days and 12 years hydration. The XRD and TGA results reported by Caldwell et al. [4] and Godfrey et al. [3] for IDM/93/12 were also very similar to those obtained here for the composition of the samples hydrated for 720 days, although these researchers did not identify the exact composition of crystalline and amorphous material. Very small XRD reflections were present for anhydrous cement phases which indicates that anhydrous cement particles still remained in IDM/93/12, even after 10 years hydration. The porosity of IDM/93/12 varied between 48% and 52% which was very similar to the results obtained for the cemented floc hydrated for 28 and 90 days. This indicates that any changes that occur in the porosity of the wasteform between 28 days and 12 years hydration were very small.

The durability of a cemented wasteform can be described in terms of intrinsic and extrinsic stability (stability in a closed and open system respectively). The intrinsic stability of cemented wasteforms is reported to be good [19]. In our work, no new phases were formed between 90 and 720 days hydration with very similar results for IDM/93/12 which suggests that addition of a ferric floc makes no change to the intrinsic durability of the hardened cement paste and there is no reason to suggest that this would not continue for a longer period of storage. Accelerated leach testing showed that very small amounts of iron and cerium (as a non-active stimulant) were leached over 24 h, which indicated that these elements were strongly chemically bound within the microstructure. Results for leaching of IDM/93/12 were similar to that of

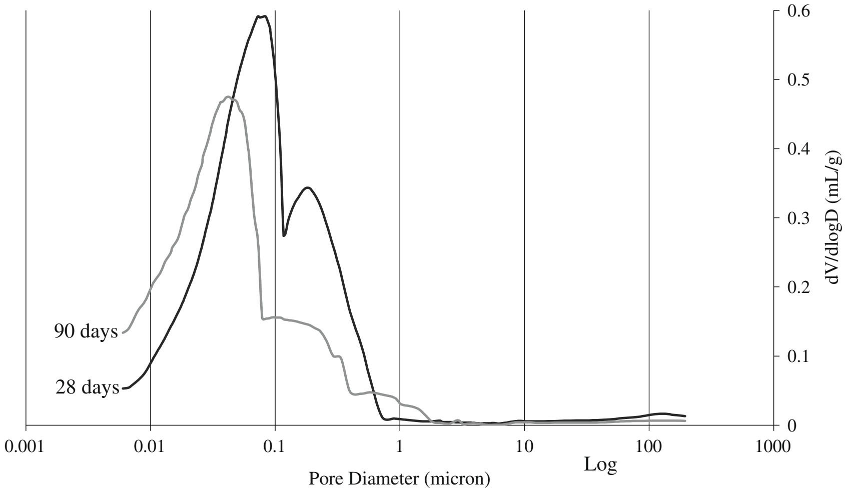

Fig. 5. MIP traces of cemented floc hydrated for 28 and 90 days at 20 °C.

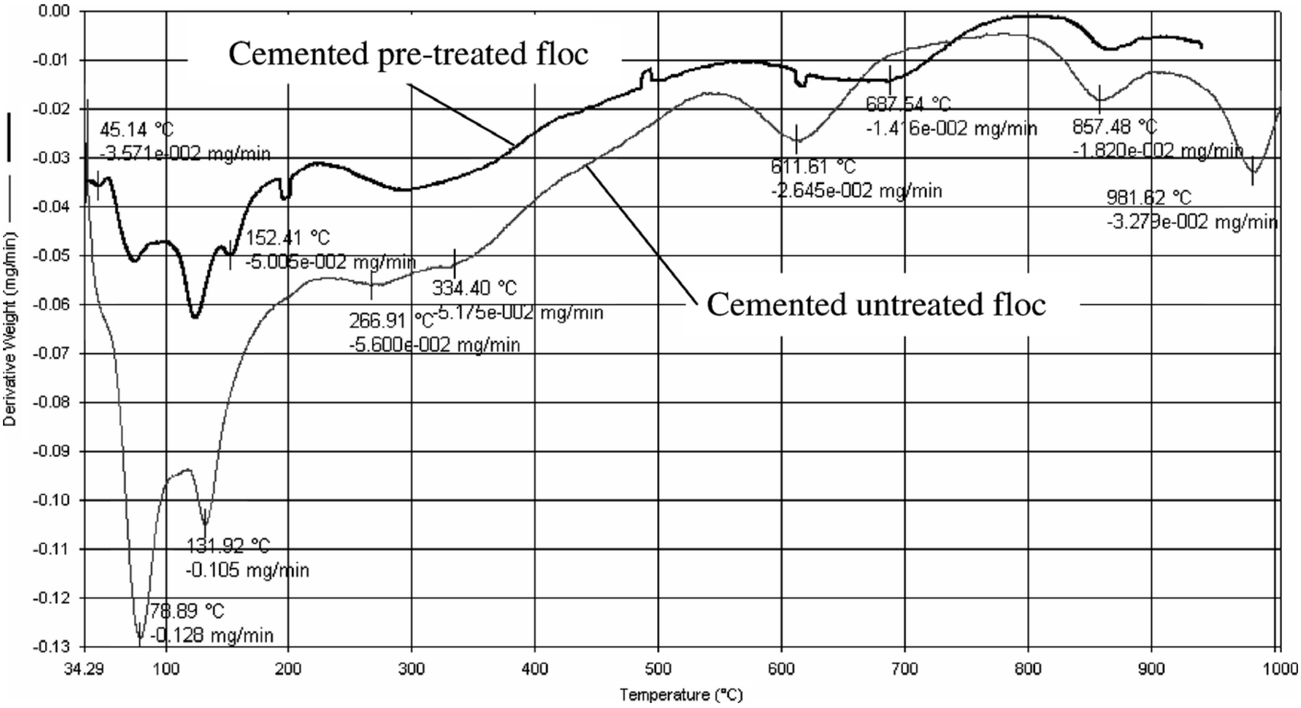

Fig. 6. DTG curves for cemented untreated floc and cemented pre-treated floc both hydrated for 90 days at 20 °C.

the cemented pre-treated floc hydrated for 720 days. The leach test used here is considerably more aggressive to the hardened cement paste than any leaching by groundwater in a repository. The temperature of the water in the leach test (approximately 75 °C) is higher than any groundwater in a repository, fresh water was continually passed over the hardened cement paste, whereas in a repository water flow would be low compared to the volume of the wasteform, and the pH of any groundwater is likely to be alkaline due to conditioning of the backfill in the repository. Therefore, the extrinsic durability of the wasteform in an underground repository is likely to be higher than that in performing these leach tests.

Apart from leach testing the cemented floc doped with cerium as a simulant radionuclide, no experimental work was performed to address the fate of the radionuclides attached to the surface of the floc particles. Nevertheless, this requires discussion. Reaction of the radionuclide bearing floc particles with the C–S–H will change the charge on the floc surface which may result in the release of the radionuclides from the floc. In this case the radionuclides will be physically, rather than chemically, immobilised in the cement matrix as their potential for sorbing directly into the cement matrix is generally low [7]. This release into the cement pore solution may make them more leachable than the iron chemically bound to the C–S–H. Leach test results confirm that this may be the case as a slightly higher amount of cerium than iron was leached from the cerium doped cemented floc. However, the different radionuclides attached to the floc may directly ion exchange with the negative sites created in the C–S–H by iron substitution and so be held chemically.

6. Conclusions

- Pre-treated ferric floc can be incorporated into a PFA/OPC cement to give a porous matrix in which the iron is strongly held. The normal hydration products of C–S–H and CH were formed.
- Mössbauer spectroscopy showed the formation of several distinct phases which contained iron from the floc. These were a crystalline iron substituted katoite, $C_3(A,F)SH_4$, confirmed by XRD, and an iron substituted C–S–H. EDS showed iron was intimately mixed with the hydration products suggesting adsorption on the C–S–H. TGA indicated two types of C–S–H suggesting iron substitution within the silicate chains providing cross linking and a more stable hydrate which decomposed at a higher temperature.
- Small amounts of CH were detected at early ages which reduced with time. This occurred faster with the cemented pre-treated floc than in a floc free cement suggesting that the floc accelerated the pozzolanic reaction with the PFA.
- Results compare well with those of previously reported 12 year old samples. Soxhlet leach testing confirmed that the use of the cemented pre-treated floc as a durable wasteform was high as very little cerium, used as an actinide stimulant, was leached.

Acknowledgements

The authors thank Dr Sue Forder at Sheffield Hallam University for analysing samples using Mössbauer Spectroscopy and the subsequent analysis of results. Thanks are also due to Professor John Sharp of the Immobilisation Science Laboratory for useful discussions and to the Nuclear Decommissioning Authority (NDA) and the Engineering and Physical Sciences Research Council (EPSRC) as joint financial sponsors of this research.

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