



Immobilisation of Fe floc: Part 1, pre-treatment of floc with slaked lime

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ABSTRACT

A series of radioactive iron (Fe^{3+}) hydroxide flocs are produced during reprocessing of nuclear fuel at Sellafield, UK. Before the flocs can be successfully encapsulated in a pulverised fuel ash/ordinary Portland cement composite cement to form a durable cemented wasteform, they need to be pre-treated with slaked lime. This paper reports results after investigating the reaction between a simulant floc and the slaked lime and shows that the floc reacts readily to form an X-ray amorphous hydrated calcium ferrite. Calcite (CaCO_3), formed from carbonation of $\text{Ca}(\text{OH})_2$, appears to contribute to the formation of a crystalline iron hydroxy carbonate phase ($\text{Fe}_6(\text{OH})_{12}(\text{CO}_3)$). This work concludes that pre-treatment allows a pozzolanic reaction to occur between the pulverised fuel ash and the $\text{Ca}(\text{OH})_2$ produced during cement hydration. This increases the quantity of C–S–H formed and increases the compressive strength of the hardened wasteform enough to withstand forces generated during curing and prevent cracking.

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1. Introduction

During re-processing of nuclear fuel by British Nuclear Group (BNG), formerly British Nuclear Fuels Ltd. (BNFL) at the Sellafield reprocessing plant in the UK, a waste stream of radioactive iron hydroxide flocs are produced in the Enhanced Actinide Removal Plant (EARP). Radioactive acidic liquors formed during reprocessing are treated with sodium hydroxide solution, and a range of radioactive iron hydroxide flocs are formed. These are classed in the UK as Intermediate Level Wastes (ILW's) and are aqueous suspensions of an iron hydroxide colloid onto which ions of uranium, plutonium and other actinides are adsorbed, as well as other radioactive species such as caesium. They generally have high viscosity, are shear thinning and are brown in colour. After production in EARP, the flocs are encapsulated in composite cement and, after setting, are stored in an interim overground store prior to final disposal, possibly for longer than 150 years [1].

During development of the cementation process in the 1980s, it was discovered that direct mixing of the flocs with the cement powders produced cemented wasteforms with unacceptably low levels of strength. During curing these wasteforms were unable to withstand shrinkage and cracking was observed which was thought could be due to the release of water caused by the internal exotherm generated during hydration [2]. To overcome this problem, a pre-treatment process was developed where the flocs were mixed with slaked lime and left to age before mixing with the

composite cement powders to give crack-free hardened cement monoliths.

While this empirically determined production process has been successfully used for a number of years at Sellafield, the role that pre-treatment plays in ensuring the formation of a durable wasteform was not fully understood. Initial results investigating this pre-treatment process have previously been reported [3] but this paper provides further information on the chemical and physical interactions that occur between the raw materials and hypothesises as to why the pre-treatment process facilitates a successful cement encapsulation process.

This is the first of two papers reporting fundamental data on the composition and nature of the ill-defined mineralogical phases which are formed, both during pre-treatment and in the subsequent encapsulation of the resulting pre-treated slurry.

2. Review of relevant literature

Very little information detailing the physical and chemical outcomes of treating ferric floc with slaked lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$) has been published, although an extensive amount of commercial development work has been performed in support of the design and operation of EARP. Work recently published by Godfrey et al. [4] and by Caldwell et al. [5] has summarised the encapsulation of an iron floc in cement based on an investigation of ten year old cemented samples of inactive iron hydroxide flocs similar to those studied here.

The generation route of these ILW iron hydroxide flocs has been described by both Hutson [6] and Hildred et al. [7]. The major use

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of these flocs is to remove the alpha emitting radionuclides from the re-processed waste and provide a small reduction in beta and gamma activity. Additions of small amounts of other chemicals, such as nickel ferrocyanide are made to increase the removal of caesium and reduce beta activity. Various forms of liquid ILW liquor are generated during reprocessing operations at Sellafield and all of them contain significant quantities of iron in nitric acid. Sodium hydroxide is added to each of these liquors increasing pH to approximately 10–11 which forms a colloidal iron hydroxide floc which adsorbs the majority of the active material onto the surface of the colloid particles. The resulting floc contains only a few hundred parts per million (ppm) of iron hydroxide, so an ultrafiltration process is used to separate the solids from surplus water. This significantly concentrates the waste and reduces the volume by more than 90% without greatly increasing viscosity, creating a final floc which is thixotropic and contains up to 100 g/l of iron.

The flocs are referred to as radionuclide 'getters', or materials that are added to radioactive effluents to provide sorption of radioactive elements. The EARP flocs are formed *in situ* in the effluent and are subsequently encapsulated in composite cements. The principal reason for using such getters is that the potential for adsorbing active elements directly onto the surface of hydrated cement is poor compared to that of iron or aluminium hydroxides which can be easily incorporated into cement hydrates [8]. Holland and Lee [9] studied the use of various radionuclide getters, including ferric flocs to immobilise radionuclides of radium, caesium and iodine. They concluded that the most appropriate getter in this application was a zeolite and that getter particle size, cement curing temperature and the ratio of water to cement solids (w:s ratio) had little influence on sorption efficiency. Other research has found that by pre-treating the radioactive waste with hexacyanoferrite ions, active caesium and cobalt are bound and leaching of these elements is reduced after encapsulation in cement paste [10]. With regard to the interaction between radioactive elements and the ferric hydroxide floc, Duff et al. [11] stated that uranium (VI) is readily sorbed onto amorphous and crystalline ferric oxides and hydroxides such as hematite and goethite (FeOOH) thus preventing uranium transport.

Iron oxide/hydroxide flocs are widely used in the water processing and treatment industry [12] and naturally occurring amorphous iron oxide flocs have been characterised [13]. Work addressing the shear characteristics of flocs during processing [12], how organic matter reacts with the floc during its removal from drinking water [14], and the uptake of barium and strontium ions into an aqueous solution of hydrous ferric oxide [15] has also been reported.

3. Experimental procedures

3.1. Raw materials

Flocs are produced by BNG in four separate operations during fuel re-processing. To establish processing conditions, simulant flocs containing all of the actual floc constituents excluding the radioactive elements were made. Flocs are prepared by neutralising an acidic (1 M) ferric nitrate solution to pH 9 with 7.2 M sodium hydroxide solution at a constant rate addition of $0.054 \text{ dm}^3 \text{ s}^{-1}$, at 25 °C and an agitation speed of 150 rpm. As in the preparation of the active floc, the required amount of hexacyanoferrate was added after floc formation. The floc studied in our work is the inactive simulant of the most common floc (by volume) produced during re-processing and was supplied by Nexia Solutions after preparation at Sellafield.

The slaked lime was a commercial product called Limbux and was supplied by Buxton Lime Industries Ltd.

3.2. Sample preparation

All floc characterisation experiments were performed on freeze dried samples prepared by freezing the floc in liquid nitrogen for 2 h and then vacuum drying in an Edwards Modulyo –4 K Freeze Dryer operating at a temperature of –48 °C and a vacuum of 5×10^{-2} mBar for 4 days.

To prepare the floc pre-treatment samples, a known mass of floc was placed in three polypots and, whilst continually mixing, 2, 6 and 10 wt% slaked lime, measured as a wt% of wet floc, was added to each sample of floc over a total of 5 min. After the resultant slurries had stood uncovered in the laboratory for 0, 4, 8 and 24 h, they were washed with acetone and filtered through a 0.1 µm filter to remove water. Finally, they were dried under vacuum to produce a powder and then stored in a vacuum desiccator.

To study the affect of pre-treatment on the strength of hardened cement paste, the untreated or pre-treated floc (10 wt% slaked lime for 8 h, mixed as described above) was mixed at ratios of 1:1 for the untreated floc:composite cement powders and 9:8 pre-treated floc:composite cement powders where the PFA:OPC composite cement powders had been pre-blended at a ratio of 5:4. The samples were cast in $50 \times 50 \times 50$ mm steel moulds, sealed in polythene bags and then hydrated for 3 days in an environmental chamber at 20 °C and 95% relative humidity. After this time the samples were demoulded, resealed in the polythene bags and replaced in the environmental chamber for further hydration.

3.3. Sample analysis

The freeze dried samples of floc and the samples of dried pre-treated floc were ground to pass a 63 µm sieve for analysis by Thermogravimetric analysis (TGA), Fourier transform infra-red spectroscopy (FTIR), scanning electron microscopy (SEM)/Energy dispersive spectroscopy (EDS) and Mössbauer Spectroscopy. For TGA, approximately 10 mg of sample was analysed using a Perkin Elmer Pyris 1 Thermogravimetric Analyzer operating with a heating profile of 30–1000 °C at 10 °C/min in flowing nitrogen. For FTIR, 1 wt% of sample mixed with 200 mg of dried potassium bromide was pressed in a pellet and analysed using a Perkin Elmer Spectrum 2000 FTIR Spectrometer. For Mössbauer Spectrometry, samples were analysed using a Wissel Mössbauer Spectrometer with a ^{57}Co source in a rhodium matrix which incorporated the use of a PID temperature controller [16]. The resultant spectra were analysed using the software package RECOIL [17]. For SEM/EDS, samples were adhered to an aluminium microscope stub and after carbon coating were analysed using a Jeol JSM 6400 with a Link ISIS EDS analyser attached.

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

4. Results

4.1. Characterisation of raw materials

Preliminary results characterising the floc have previously been reported [3]. To summarise, the floc was a brown viscous colloid with no odour, exhibited thixotropic characteristics and was largely X-ray amorphous. The suspension was moderately alkaline, with a pH of approximately 9, and contained 16.8 wt% solids. 8.8 wt% of the floc was iron. The freeze dried floc contained no crystalline material and no obvious crystalline particles were discernible by SEM. Further spectroscopic analysis of the floc has now been performed.

FTIR results for the floc (Fig. 1) showed the presence of two major, very broad bands onto which were superimposed several sharp weaker bands. The first, centred at 3410 cm^{-1} , extended between 3700 and 1700 cm^{-1} and was due to the stretching of O–H bonds in water associated with the floc. The second broad band was centred at approximately 500 cm^{-1} and started at approximately 1250 cm^{-1} . However, it was not possible to determine where this band finished because the FTIR equipment used did not measure below 300 cm^{-1} . This band was due to the vibration of Fe–O bonds within the iron hydroxide particles in the floc. The spread of these two bands indicated that the water and iron hydroxide phases present were highly disordered. A band at approximately 1620 cm^{-1} was due to the bending of O–H bonds in water. A very sharp, well defined band at 1385 cm^{-1} could be due to the stretching of B–O bonds. Borate ions are added when producing the floc and were detected by chemical analysis [3]. A few small bands at approximately 600 cm^{-1} could be due to the vibration of S–O bonds from sulphate present in the floc [3]. The very small bands at approximately 2910 and 2850 cm^{-1} were probably due to the presence of oil deposited on the sample during pellet preparation. A small band at approximately 2020 cm^{-1} was due to C≡N stretching in ferrocyanide added to the floc to help precipitate Cs^+ [3].

A plot of the spectra and a table of the results obtained for the freeze dried floc using Mössbauer Spectroscopy are shown in Fig. 2 and Table 1, respectively. Interpretation of the isomer shift (δ) and quadrupole splitting (ΔE_q) were based on work reported by Nishida [18] (Table 2). The redox state of all iron phases present was Fe^{3+} and the spectrum could be resolved into three distinct doublets. The δ and ΔE_q for doublet 1 both indicated the presence of tetrahedral iron, whereas the iron giving rise to doublet 2 was octahedral. The δ of doublet 3 suggested that this iron was octahedral, but the ΔE_q indicated that it could be either tetrahedral or octahedral. However, the latter is more probable because the value of δ has already indicated that the iron is octahedral. The area (A) under doublet 3 showed that the iron responsible for doublet 3 was most prevalent. The values of line width (W+) indicated that the iron giving rise to doublets 1 and 2 was the least and most ordered, respectively.

TGA of the slaked lime showed that the powder contained 91.7 wt% $\text{Ca}(\text{OH})_2$ (CH) with a small amount (2.9 wt%) of calcite (CaCO_3) present. The remaining mass was probably due to ab-

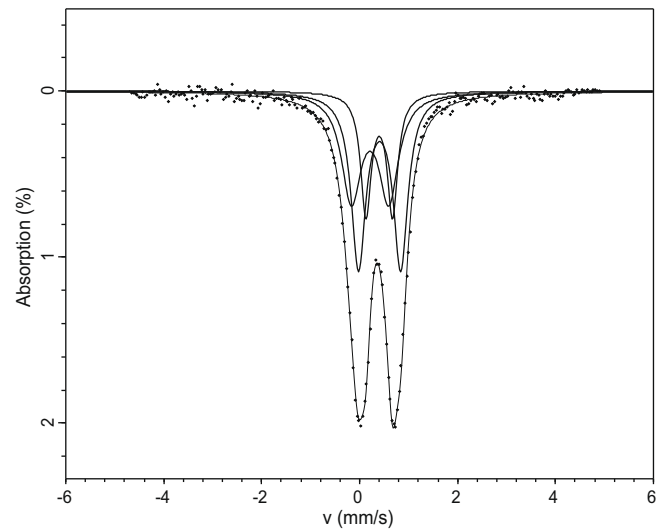


Fig. 2. Mössbauer spectra of freeze dried floc.

Table 1

Values of δ , ΔE_q , A and W+ for Mössbauer spectrum of freeze dried floc.

	δ (mm/s)	ΔE_q (mm/s)	A (%)	W+ (mm/s)	Assignment
Doublet 1	0.21	0.77	35	0.24	Tetrahedral Fe^{3+}
Doublet 2	0.40	0.54	22	0.13	Octahedral Fe^{3+}
Doublet 3	0.41	0.86	43	0.18	Octahedral Fe^{3+}

Notes: δ , isomer shift; ΔE_q , quadrupole splitting; A, absorption area; W+, line width.

Table 2

Summary of δ and ΔE_q for divalent and trivalent iron reported by Nishida [18].

	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	–

Notes: δ , isomer shift; ΔE_q , quadrupole splitting.

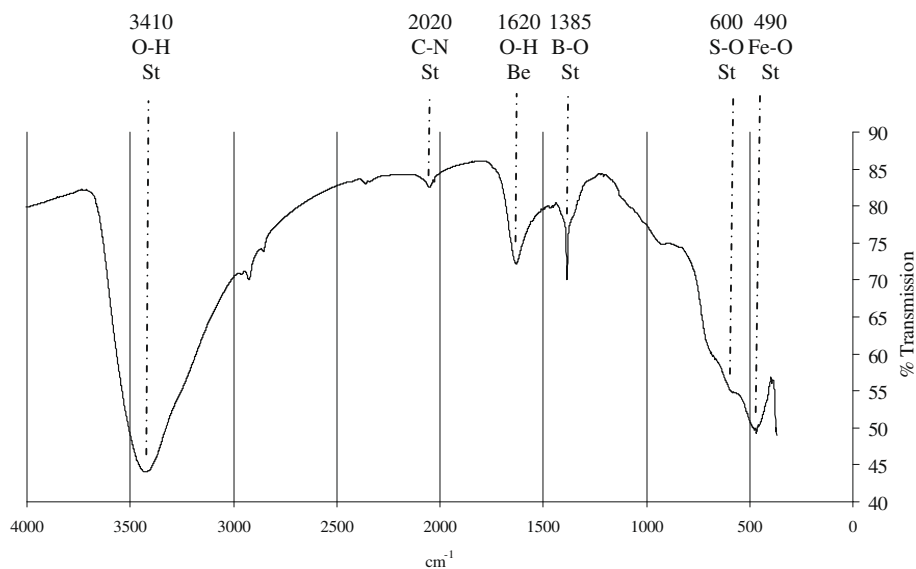


Fig. 1. FTIR trace of freeze dried floc. Note: St, stretching; Be, bending.

sorbed water as the sample was not dried before analysis. When viewed by SEM, the particles appeared somewhat ‘fluffy’ and agglomerated with dimensions between 1 and 30 μm in length.

4.2. Floc pre-treatment

Preliminary XRD, TGA and SEM results have previously been reported [3] and are summarised below.

With 2 wt% slaked lime addition to wet floc, the majority of dried material was amorphous. The only crystalline phase present at 0, 4 and 8 h aging was calcite (CaCO_3), the amount of which increased with aging. At 24 h aging, calcite was still the predominant crystalline phase, but a new phase, the iron ettringite analogue ($\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, card number [38-1480] from the International Centre for Diffraction Data (ICDD), designated Phase X in this paper, was detected. As shown previously [3], a small amount of sulphate is present in the floc. No obvious crystalline material was observed by SEM at all ages and the size of particles varied between >1 and 30 μm . Much particle agglomeration was observed, particularly after 24 h aging. Calcium and iron were the main elements detected by EDS at many spots in all samples.

When 6 wt% slaked lime was added to the wet floc, more crystalline material than at 2 wt% addition was detected, but the majority of the material was again amorphous. At all ages, CH and calcite were detected, and the quantity of the latter generally decreased with aging. Phase X was only detected after immediate mixing and after 4 h aging. Two new phases, Phase Y ($\text{Fe}_6(\text{OH})_{12}(\text{CO}_3)$, ICDD card number [46-98]) and CB ($\text{Ca}_3\text{B}_2\text{O}_6$, ICDD card number [48-1885]) were first detected after 4 h aging with Phase Y predominant. The intensity of the XRD peaks for Phase Y increased with aging. The decrease in calcite content with age and the corresponding increase in intensity of the reflections for Phase Y in the XRD trace suggest that some substitution of carbonate from the calcite into Phase Y may have occurred. No obvious crystalline material was observed by SEM and calcium and iron were the main elements detected by EDS at many spots in all samples.

At the maximum slaked lime addition (10 wt% to wet floc), the majority of the material was still amorphous. Phase Y was the main crystalline phase detected at all ages and the intensity of the XRD reflections for this phase increased with aging. Phase X was only detected after 4 h aging while small amounts of CB were detected at ages over 4 h. Calcite and CH contents generally decreased with

aging. The substitution of carbonate from the calcite into Phase Y is again likely to have occurred. Again, the main elements detected by EDS at many spots on all samples were calcium and iron.

To further characterise the amorphous material produced during pre-treatment, FTIR, and Mössbauer Spectroscopy have been used to analyse the floc pre-treated with 10 wt% slaked lime for 8 h. The FTIR trace (Fig. 3) showed three broad absorption bands centred at 3470, 1405 and 450 cm^{-1} . Superimposed on these were a number of smaller bands. The main band at 3470 cm^{-1} was due to the stretching of O–H bonds in water. Superimposed on this were a number of sharp bands. The band at 3640 cm^{-1} is due to the O–H stretching in CH. The two other bands at 3560 and 3345 cm^{-1} were due to the stretching of O–H bonds in other hydrous phases where the water is ordered, one of which was probably Phase Y. The second main band centred at approximately 1405 cm^{-1} was due to the stretching of C–O bonds, probably in calcite, with the smaller band at 1360 cm^{-1} likely due to the C–O stretching in Phase Y. The third main band centred at 450 cm^{-1} started at approximately 1150 cm^{-1} and finished at approximately 350 cm^{-1} . Within this region were a number of small bands (and possibly more bands at lower frequencies, but this was at the lower limit of detection of the FTIR equipment) which were probably due to the stretching of Fe–O bonds in the floc, the amorphous phase(s) resulting from the reaction between the floc and the slaked lime, and Phase Y. The small band at 1620 cm^{-1} was due to the bending of the O–H bonds in water. Minor bands at 900 and 635 cm^{-1} could be due to the vibration of S–O bonds in the sulphate present in the raw floc. The very small bands at 2910 and 2850 cm^{-1} were probably due to the presence of oil deposited on the sample during pellet preparation. The sharp band at 2030 cm^{-1} was due to C \equiv N stretching in hexacyanoferrite. The borate band detected in the untreated floc was not observed in this sample which indicated that this material is either soluble in the alkaline environment or that it has reacted in some way.

A plot of the Mössbauer spectra (Fig. 4) and a table of the results (Table 3) obtained for the floc pre-treated with 10 wt% slaked lime for 8 h showed a spectrum resolved into two doublets with the redox state of all the iron phases detected being Fe^{3+} . The isomer shift (δ) for doublet 1 suggested that the iron could be either octahedral or tetrahedral but the quadrupole splitting (ΔE_q) indicated it was probably octahedral. The δ and ΔE_q of doublet 2 indicated

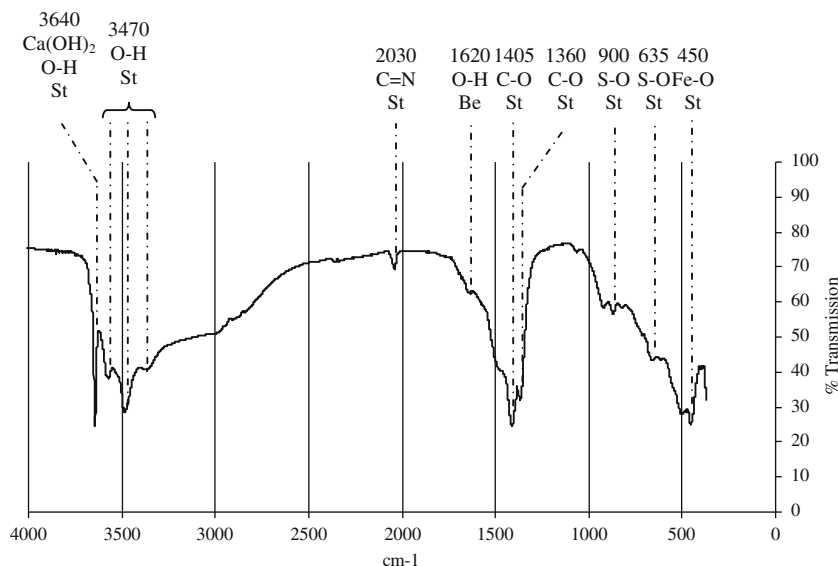


Fig. 3. FTIR trace of floc pre-treated with 10 wt% slaked lime for 8 h. Note: St, stretching; Be, bending.

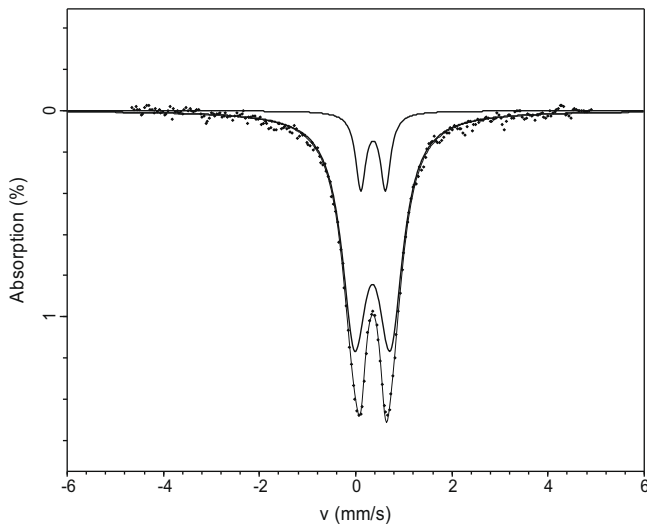


Fig. 4. Mössbauer spectra of floc pre-treated with 10 wt% slaked lime for 8 h.

Table 3

Values of δ , ΔE_q , A and W+ for Mössbauer spectrum of floc pre-treated with 10 wt% slaked lime for 8 h.

	δ (mm/s)	ΔE_q (mm/s)	A (%)	W+ (mm/s)	Assignment
Doublet 1	0.35	0.75	87	0.32	Octahedral Fe ³⁺
Doublet 2	0.36	0.51	13	0.13	Octahedral Fe ³⁺

Notes: δ , isomer shift; ΔE_q , quadrupole splitting; A, absorption area; W+, line width.

the presence of octahedral iron. The iron responsible for doublet 1 was most prevalent (A = 87% area) although the values of linewidth (W+) indicated that the iron in doublet 2 was most ordered.

SEM examination of the floc pre-treated with 2 wt% slaked lime showed that particle appearance, shape and size was similar at all ages. For samples treated with 6 wt% slaked lime, no obvious crystalline material was present in any sample and the particle shape and size was also similar. However, agglomeration appeared to occur earlier than in the samples pre-treated with 2 wt% slaked lime. Some of the material at later aging times appeared to be of a different shape and texture from that seen at earlier ages. This is best illustrated by particle A in Fig. 5, which showed a particle denser in appearance and different from most of the other material.

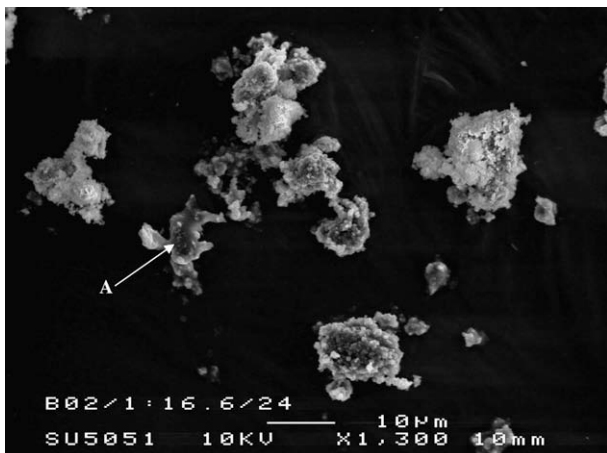


Fig. 5. SEM secondary electron image micrograph of floc pre-treated with 6 wt% slaked lime for 24 h.

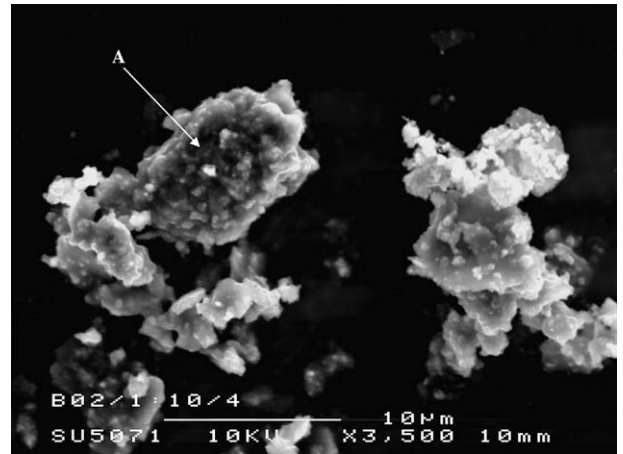


Fig. 6. SEM secondary electron image micrograph of floc pre-treated with 10 wt% slaked lime for 4 h.

The SEM micrographs for the floc pre-treated with 10 wt% slaked lime showed a similar phenomenon at all ages. At 4 h (Fig. 6), and more so after 24 h (Fig. 7) aging, the particle labelled A appeared more dense than most of the other material seen. Agglomeration of particles was still apparent but this reduced as the amount of more uniform material appeared to increase.

Energy dispersive spectroscopy analysis of many spots on all samples of pre-treated floc showed very similar results. The main elements detected at all spots in all samples were calcium, from the slaked lime, and iron from the floc, with only traces of aluminium, silicon, phosphorus and sulphur, also from the floc [3]. Table 4 summarises the EDS results obtained. The distribution of Ca is always associated with that of Fe which indicates a very homogeneous matrix. The average calcium/iron ratio was determined by comparing the height of the calcium peak with that of the iron peak and averaging over the spots analysed. At 2 wt% slaked lime addition the Ca/Fe ratio of the bulk material was approximately 0.3 at all ages and previous results [3] show that all the CH reacted with the floc immediately on mixing. At 6 wt% slaked lime addition, the Ca/Fe ratio at 0 h was 0.64 and increased to approximately 0.85 for the samples aged for 4 h and longer. At 10 wt% slaked lime addition, the Ca/Fe ratio at 0 h was 0.66, which increased to 1.68 by 4 h and 1.85 by 8 h, and the Ca/Fe ratio at 24 h was approximately the same as at 8 h. These results suggest that for 10 wt%

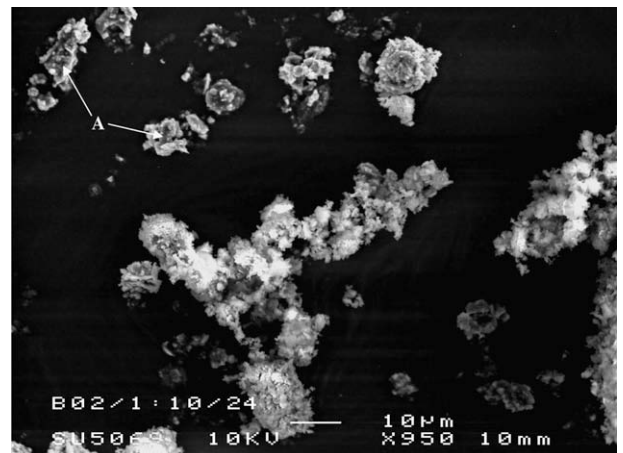


Fig. 7. SEM secondary electron image micrograph of floc pre-treated with 10 wt% slaked lime for 24 h.

Table 4
Summary of EDS analysis of all pre-treatment samples.

Slaked lime addition (wt%)	Age (h)	Number of spots analysed	Main elements detected	Average Ca/Fe ratio ^a
2	0	9	Ca, Fe	0.33
	4	17	Ca, Fe	0.24
	8	14	Ca, Fe	0.38
	24	18	Ca, Fe	0.31
6	0	15	Ca, Fe	0.64
	4	14	Ca, Fe	0.84
	8	16	Ca, Fe	0.87
	24	15	Ca, Fe	0.86
10	0	18	Ca, Fe	0.66
	4	13	Ca, Fe	1.68
	8	15	Ca, Fe	1.85
	24	16	Ca, Fe	1.81

^a Error \pm 10%.

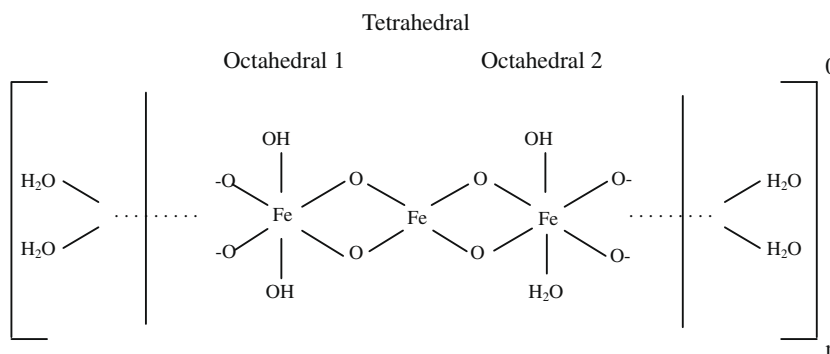


Fig. 8. Speculative arrangement of iron phases in freeze dried floc.

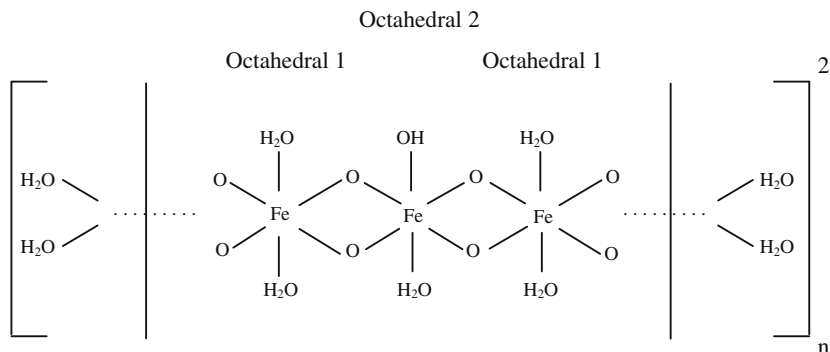


Fig. 9. Speculative arrangement of iron phases in dried floc pre-treated with 10 wt% slaked lime for 8 h.

slaked lime addition to the floc there is an immediate reaction on mixing, which continues at a slower rate between 4 and 8 h after which time the reaction appears complete. Additionally, these results imply that the main reaction product of pre-treatment is an X-ray amorphous hydrated calcium ferrite, the calcium/iron ratio of which varies depending upon quantity of slaked lime added and aging.

By measuring the weight loss between 100 and 500 °C (due mostly to the dehydroxylation of C–S–H) using TGA (Fig. 10 and 11), it is possible to compare the different amounts of amorphous hydrate formed due to pre-treatment. The results for samples hydrated for 7 and 90 days are shown in Fig. 12 and the corresponding values of compressive strength are shown in Table 5. Pre-treating the floc with 10 wt% slaked lime for 8 h before encapsulation created approximately 16% more binder when hydrated

for 7 days which resulted in an increase in average compressive strength of approximately 18%. Similarly, for 90 days hydration, pre-treatment produced approximately 41% more binder which resulted in an increase in average compressive strength of approximately 45%.

5. Discussion

The slaked lime and the floc particles appeared to react rapidly with each other. Mössbauer Spectroscopy showed that changes occurred to the iron environment in the pre-treated floc compared to that of the raw floc as the values of the isomer shift and quadrupole splitting were different. This suggests that new material formed during pre-treatment. Considering that the reactivity of the floc particles was high due to their size and surface charge,

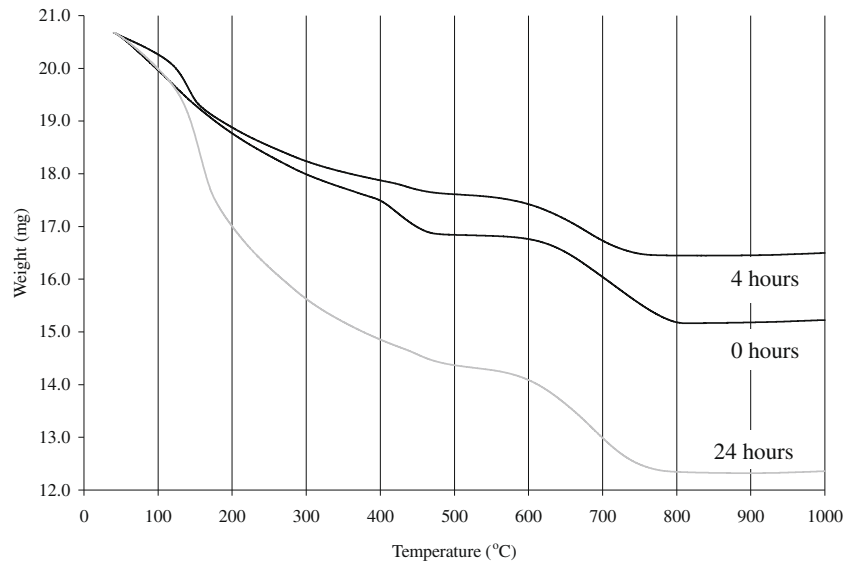


Fig. 10. Normalised TGA traces for floc pre-treated with 10 wt% slaked lime for 0, 4 and 24 h.

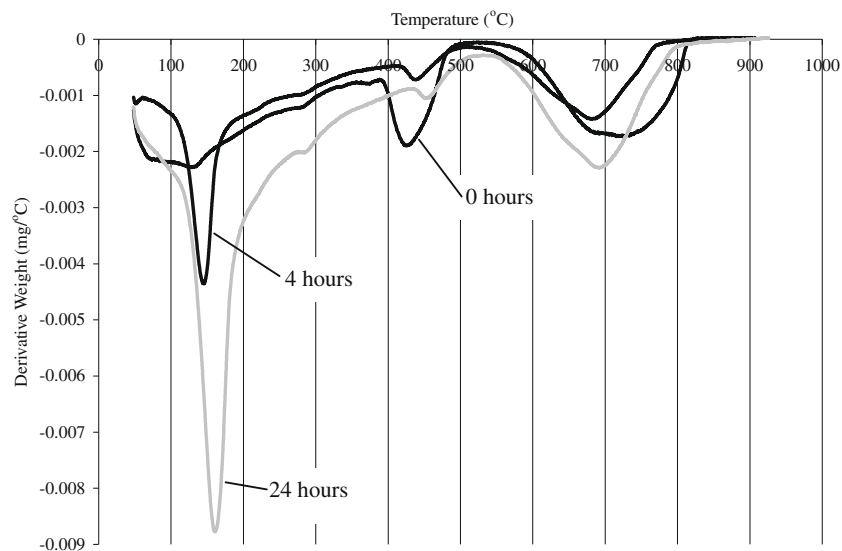


Fig. 11. DTG traces for floc pre-treated with 10 wt% slaked lime for 0, 4 and 24 h.

the formation of a hydrated calcium ferrite was most likely. Such a phase was probably responsible for the slow release of water between 50 and 500 °C during TGA (Figs. 10 and 11). Energy dispersive spectroscopy results suggest that the amount of this material increased with the level of slaked lime addition, so that at lower additions of slaked lime, unreacted floc was likely to remain.

All iron in the untreated floc was trivalent, with Mössbauer Spectroscopy results showing that it was present in one tetrahedral and two octahedral environments. How the differing amounts of water and hydroxyl groups are attached to the iron hydroxide particles will determine the coordination of the iron. One such arrangement is suggested in Fig. 8. FTIR results showed that, even after freeze drying, the flocs contain water which could only be removed by heating. This suggests that the iron phases are hydrated forms of ferric hydroxide.

When 10 wt% slaked lime reacted with the floc for 8 h during pre-treatment, the environment of the ferric iron changed from

one tetrahedral and two octahedral states, to two octahedral states with the hydroxyl and water groups again determining the coordination of the iron. Such an arrangement could be as shown in Fig. 9. TGA results for the pre-treated floc [3] (Figs. 10 and 11) showed that the quantity of CH detected reduced with aging and appeared to reach equilibrium by approximately 8 h, suggesting that by this age, the reaction between the floc and slaked lime was complete. This is in agreement with the EDS results which showed the Ca/Fe ratio equilibrated after approximately 8 h. The only crystalline iron phase detected at this age was Phase Y ($\text{Fe}_6(\text{OH})_{12}(\text{CO}_3)$), although there clearly was an X-ray amorphous hydrated calcium ferrite present. These results suggest that, for this sample (floc treated with 10 wt% slaked lime for 8 h), doublet 1 and 2 in the Mössbauer Spectroscopy results could be due to the X-ray amorphous hydrated calcium ferrite and Phase Y respectively. In this case, the quantity of Phase Y and the hydrated calcium ferrite was in the ratio 13/87.

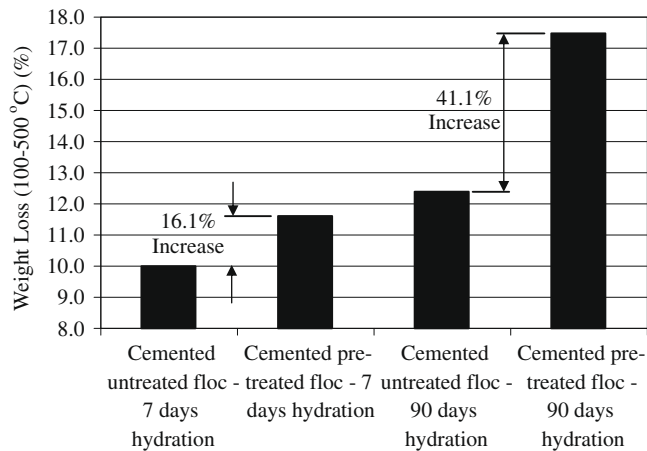


Fig. 12. Weight loss between 100 and 500 °C for cemented untreated and pre-treated floc hydrated for 7 and 90 days.

5.1. Formation of amorphous phases

Only small amounts of crystalline material were detected by XRD in the pre-treated samples, indicating that the majority of the material formed was amorphous making identification of solid phases difficult.

The hydrated calcium ferrite phase detected was ill defined and was likely to have a highly variable composition. Although not determined experimentally, a composition of this material can be estimated. For the sample treated with 10 wt% slaked lime, it was assumed that all reactions were complete by 24 h (the quantity of CH detected by TGA generally had reached equilibrium before that age). If all the floc reacts, the chemical formula of the hydrated calcium ferrite will be $\text{Ca}_x\text{Fe}_y\text{O}_z \cdot n\text{H}_2\text{O}$. Using the TGA and differential thermogravimetric (DTG) curves for this sample (Figs. 10 and 11, respectively) the approximate values of x , y , and n were calculated and the value of z obtained by balancing the charges on the cations.

5.1.1. Calcium content – x

Considering 100 g of wet floc:

16.8 g of this was solid material.

During pre-treatment, 10 g of CH was added to the wet floc (10 wt%).

Total solids content after drying the pre-treated slurry = $10 + 16.8 = 26.8$ g.

Total mass of CH in dried slurry = $10/26.8 \times 100 = 37.3$ wt%.

CH content remaining (from TGA) = 6.8 wt%.

Calcite content (from TGA) = 16.6 wt%. Assuming this has come from CH, this is equivalent to $16.6 \times 74/100$ CH = 12.3 wt% CH

So 'CH' remaining = 6.8 + 12.3 wt%

Therefore %CH used in reaction with floc is $37.3 - 6.8 - 12.3 = 18.2$ wt%

And converting to moles = $18.2/74 = 0.25$ moles Ca or $\text{Ca}(\text{OH})_2$

5.1.2. Iron content – y

Mössbauer Spectroscopy indicated that 87% of the iron in the dried pre-treated slurry was associated with the hydrated calcium ferrite phase. This was difficult to confirm by TGA because the dehydroxylation temperature of Phase Y was superimposed onto that of the hydrated calcium ferrite making deconvolution of these peaks difficult.

Total mass of CH in the dried slurry = 37.3 wt%, so remainder must be floc solids = $100 - 37.3 = 62.7$ wt%.

Iron content in floc solids = $8.8/16.8 \times 100 = 52.4$ wt%.

So amount of iron = $62.7 \times 52.4/100 \times 87/100 = 28.6$ wt%.

And converting to moles = $28.6/56 = 0.52$ moles Fe.

5.1.3. Water content – n

Because 87% of the iron in the dried pre-treated slurry was associated with the hydrated calcium ferrite phase, it was assumed that 87 wt% of all the water in the dried pre-treated slurry was associated with the hydrated calcium ferrite.

Mass of sample (from TGA) = 20.7 mg.

Weight loss due to release of water (50–500 °C, from TGA) = $20.7 - 14.7$ mg = 6.0 mg.

So amount of water in dried pre-treated floc = $6.0/20.7 \times 100 \times 87/100 = 25.2$ wt%.

And converting to moles = $25.2/18 = 1.4$ moles water

Therefore, the approximate composition of the hydrated calcium ferrite phase was $\text{Ca}_{0.25}\text{Fe}_{0.52}\text{O}_{1.03} \cdot 1.4\text{H}_2\text{O}$ which, after recalculation, resulted in approximately $2\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$. The Ca/Fe ratio of this phase was 0.5 which was lower than the value of 1.81 detected for the main matrix by EDS (Table 4). The reason for this discrepancy may be that the crystals of CH and/or calcite

Table 5
Summary of compressive strength test results.

Sample	Maximum load (N)	Compressive strength (MPa)	Average compressive strength (MPa)	Standard deviation	Increase in average strength due to pre-treatment
Cemented untreated floc, 7 days	4940	1.98	1.83	0.13	–
	4435	1.77			
	4350	1.74			
Cemented pre-treated floc, 7 days	5580	2.23	2.16	0.18	18.0
	5738	2.30			
	4905	1.96			
Cemented untreated floc, 90 days	9670	3.87	4.77	1.27	–
	10563	4.23			
	15540	6.22			
Cemented pre-treated floc, 90 days	16880	6.75	6.93	1.09	45.3
	20225	8.09			
	14840	5.94			

detected in the sample by XRD and TGA [3] were very small as none were observed by SEM. The electron beam used for EDS may be large compared to the size of the crystals and so may not only have detected the material in the main matrix, but also the calcium in some intermixed CH and/or calcite. This would increase the Ca/Fe ratio of the main matrix analysed by EDS.

5.2. Formation of crystalline material

The formation of crystalline phases has previously been discussed [3], however, the detection of Phase Y ($\text{Fe}_6(\text{OH})_{12}(\text{CO}_3)$, also known as Green Rust) in samples with slaked lime additions of 6% and above warrants further discussion. Phase Y as formulated contains 4 moles of reduced iron and so may be considered unlikely to form as no obvious reducing agent was present. Reduction of Fe^{3+} could be due to the presence of cyanide arising from the decomposition of the hexacyanoferrite ion in the highly alkaline environment, but this is unlikely as it was chosen for its high stability. Alternatively, the hexacyanoferrite may be oxidised by some of the ferric ions in the floc which are reduced to ferrous ions which may then react with the calcite present to form Phase Y. Additionally, calcium carbonate containing systems have been reported as mildly reducing [19] although it is still not clear what the reductant is. Further, the substitution of some iron in Phase Y with calcium from the slaked lime to form a phase such as $\text{Ca}_4\text{Fe}_2(\text{OH})_{12}(\text{CO}_3)$ may occur. This may take place with little effect on the unit cell, but the extent of such a substitution is dependent on the relative sizes of the iron and calcium ions. A number of similar iron hydroxy carbonate phases with cationic substitutions, such as Wermlandite ($\text{Ca}_2\text{Mg}_{14}(\text{Fe}^{3+}, \text{Al})_4\text{CO}_3(\text{OH})_{42} \cdot 29\text{H}_2\text{O}$), Pyroaurite ($\text{Mg}_6\text{Fe}_2^{3+}\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) and Brugnatellite ($\text{Mg}_6\text{Fe}_2^{3+}\text{CO}_3(\text{OH})_{13} \cdot 4\text{H}_2\text{O}$) have been reported [20].

5.3. Influence of pre-treatment on hardened cement paste

Unless the pre-treatment process is undertaken, a dimensionally stable wasteform may not be produced [2] which may be due to the characteristics of the floc. The high water content of the floc (approximately 85 wt%) produces a composite cement with high water:solids (w:s) ratio (approximately 0.85) which will result in a hardened cement paste with very high porosity and very low strength. Despite the high cement replacement level used (5:4 PFA/OPC), significant temperature rises will still occur in the centre of the 500 l drum containing the cemented floc, with temperatures approximating 80 °C expected [21]. This may lead to free water expansion within the hardening cement paste giving rise to expansive cracking, as the expansion forces may exceed the strength of the matrix during curing. The reaction of PFA in the presence of CH is reported to be slow compared to that of OPC [22], so without pre-treatment, the preferred reaction of the CH produced during the OPC hydration will be with any unreacted floc rather than with the PFA. Pre-treatment with slaked lime will provide CH to react with the floc and will prevent the floc from reacting with the CH produced during the hydration of OPC. This will allow the CH produced by the hydration of the OPC to react with the PFA in the expected pozzolanic reaction and produce more C—S—H binding material likely to prevent cracking due to the expansion of free water.

The increase both in the quantity of C—S—H and the compressive strength due to pre-treatment indicates that the pre-treated cement matrices are stronger and more able to resist forces applied to the microstructure during curing. This suggests that it is the quantity of C—S—H formed in the hardened cement paste that governs the compressive strength of the cemented floc and is responsible for the prevention of crack formation.

6. Conclusions

- The iron floc reacted with slaked lime during the pre-treatment process, to form iron containing phases with different structures to those in the untreated floc.
- The main reaction that occurred during pre-treatment was the formation of an amorphous hydrated calcium ferrite, the quantity of which increased with aging. Its exact composition was difficult to determine but assuming that all the floc had reacted by 24 h and that the amount of CB ($\text{Ca}_3\text{B}_2\text{O}_6$) present was negligible, the approximate composition was $2\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$.
- Several secondary reactions gave rise to crystalline products such as calcite, Phase X ($\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), Phase Y ($\text{Fe}_6(\text{OH})_{12}(\text{CO}_3)$), and low solubility salts such as CB.
- The calcite formed from the carbonation of the CH is likely to have contributed to the formation of Phase Y. How the reduced Fe^{2+} in this phase was formed was not clear but it was possible that it was caused by either a reaction between the ferrocyanide and the iron hydroxide in the floc, the presence of calcium carbonate or by calcium substituting for iron in Phase Y.
- Pre-treatment and the formation of a hydrated calcium ferrite allowed the pozzolanic reaction between the CH produced during the hydration of the OPC and PFA to occur. Approximately 41 wt% more C—S—H was formed in the hardened cement paste after 90 days made with pre-treated floc resulting in a 45% increase in compressive strength. This strength increase was likely to prevent cracking of the hardened cement paste.
- The formation of Phase X, the iron ettringite analogue ($\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), was not unexpected, although the amount of SO_4^{2-} present in the system was low and it might be partially substituted by CO_3^{2-} or other ions present in the floc.

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