

Encapsulation of Iron Hydroxide Floc in Composite Cement

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Background

The Enhanced Actinide Removal Plant (EARP) at Sellafield treats liquid effluent generated during reprocessing by co-precipitating uranium, plutonium and other actinides, as well as some other radioactive species, with iron as iron hydroxide flocs. In the UK, these flocs are classed as Intermediate Level Waste (ILW), with the preferred method of disposal being encapsulation in cementitious systems [1]. A composite cement based on the partial replacement of ordinary Portland cement (OPC) with pulverised fuel ash (PFA) is used. This provides advantages over using neat OPC including reduced permeability and lower heat of hydration [2-4]. Despite extensive use in the water processing industry, there is little literature on encapsulating iron hydroxide compounds in cementitious systems. It has however, been reported that ferric hydroxides retard the setting of cement [5].

Introduction

This project investigates the composition of a simulated floc, and determines how it interacts with the composite cement during encapsulation and storage. The project falls into three parts:

1. Characterisation of the raw materials. To understand the physical nature and chemical composition of the floc.
2. Floc pre-treatment before encapsulation. An empirical approach has shown that the floc can be successfully cemented, producing a dimensionally stable wasteform, after pre-treating it with calcium hydroxide, but the processes involved are not fully understood.
3. Floc encapsulation studies in a PFA/OPC composite cement system. Studies are being made of the pre-treated floc/cement system with a particular emphasis on its durability and microstructural development to understand the interaction between the floc and the composite cement.

Experimental

The simulant floc studied is called Bulks 02, was prepared in 2002 and represents the majority of the flocs produced at Sellafield. The floc has been characterised according to its appearance, water content, pH, crystalline phases present (XRD), particle size and shape (SEM) and elemental composition (EDS and chemical analysis).

To investigate the pre-treatment process, the weight ratio of calcium hydroxide added to the floc was varied and the resultant slurry stood for various lengths of time. This was then washed with acetone, micro filtered and the resultant powder analysed using XRD, SEM(EDS), and TGA.

Mimicking the industrial process, floc cement samples were mixed and are curing for times ranging from 1 to 1440 days. Floc free samples of OPC and PFA/OPC, made at the same water:solids ratio as the floc cement samples, are also curing to act as references. Acetone quenching was used to stop the hydration of the samples prior to analysis using XRD, SEM/EDS, TGA, DSC and MIP.

Results

Floc Characterisation

Bulks 02 was moderately alkaline, at pH 8.65, and contained 16.8% solids. Results from XRD showed that, when freeze dried, the floc was largely amorphous, with no obvious crystalline phases present. A five year old sample, however, showed the presence of hematite (Fe_2O_3) and iron oxide hydroxide hydrate ($\text{Fe}_5\text{O}_7(\text{OH}) \cdot 4\text{H}_2\text{O}$).

Floc Pre-Treatment

2% calcium hydroxide addition initially resulted in the formation of an amorphous product containing small amounts of calcite from initial carbonation. However, after 24 hours standing, a phase formed that appears to be iron substituted ettringite, $\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, because the peaks do not exactly match those of pure ettringite.

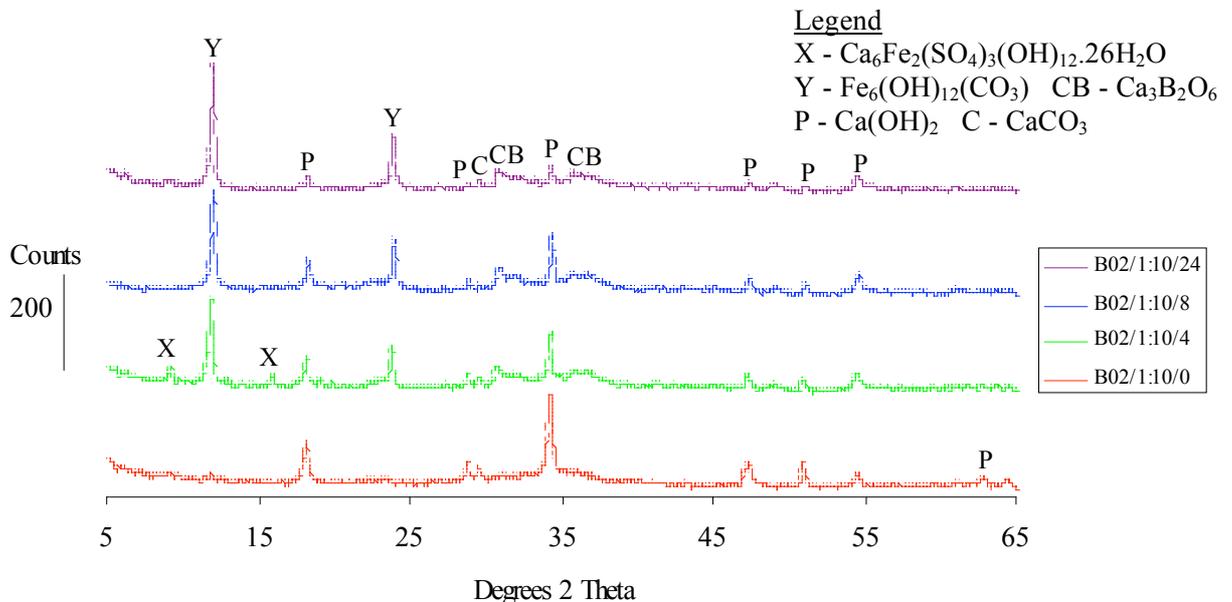


Fig 1. XRD trace of Bulks 02 treated with 10% calcium hydroxide for standing times of 0, 4, 8 and 24 hours

With 6% calcium hydroxide addition the same calcium ferrite sulphate phase formed after only 4 hours standing but then had disappeared after 8 hours. An iron hydroxide carbonate phase, $\text{Fe}_6(\text{OH})_{12}(\text{CO}_3)$, and calcium borate phase, $\text{Ca}_3\text{B}_2\text{O}_6$, were detected after 4 hours. The amount of both of these phases increased with standing time. After 4 hours standing, the calcium hydroxide had virtually disappeared.

The results for 10% calcium hydroxide addition (Fig. 1) were similar to those for 6% addition, except that a small amount of calcium hydroxide was detected, even after 24 hours standing. In addition to this, the results from XRD suggested that the amount of each phase formed was higher at 10% than at 6% addition. As shown in Fig.2, no obvious crystalline particles were apparent in the SEI SEM images, and the EDS trace indicated that calcium and iron were the principal elements detected, suggesting that the major phase formed is an X-ray amorphous calcium-ferrite phase.

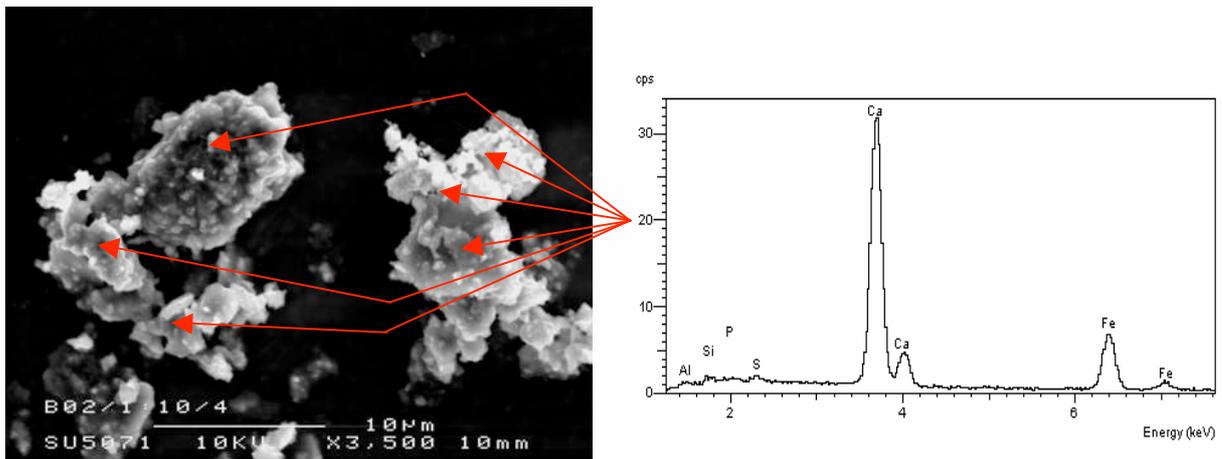


Fig 2. SEM micrograph and EDS trace of Bulks 02 treated with 10% calcium hydroxide for a standing time of 4 hours

Floc Encapsulation

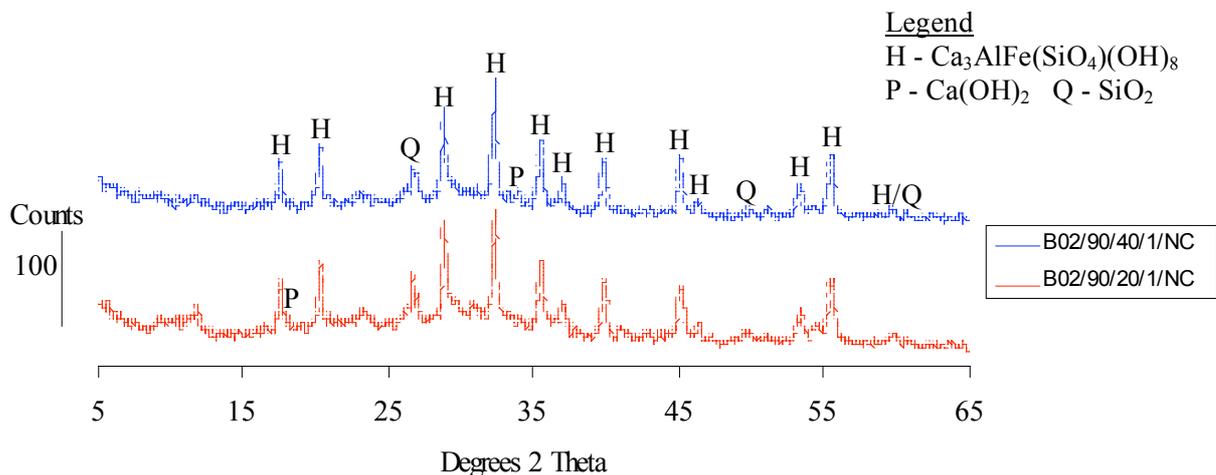


Fig 3. XRD trace of pre-treated Bulks02 cement hydrated for 90 days at 20 and 40°C

XRD results to date show that the main crystalline phases formed after 90 days hydration of the floc free samples were monosulphate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$), calcium hydroxide and C-S-H gel. The main crystalline phase formed in both untreated and pre-treated Bulks 02 cement samples appeared to be iron substituted siliated katoite ($\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$) (Fig.3). Other crystalline phases detected were calcium hydroxide and quartz. The hydration temperature did not affect the quantity or types of phases present. SEM SEI micrographs of a fracture surface of the Bulks 02 cement sample showed a generally featureless matrix with very few crystalline particles (Fig.4).

Discussion and Conclusions

The simulated floc has been shown to be an amorphous colloidal suspension, to be moderately alkaline and to have high water content. Pre-treating the floc has been determined as a suitable regime for crack prevention in floc cements. During mixing in pre-treatment, some of the calcium hydroxide carbonates immediately, presumably as it dissolves in the floc suspension and is exposed to air during mixing.

The pre-treatment process may prevent cracking of the floc cement for two reasons. Firstly, the untreated floc readily takes up calcium hydroxide although no major crystalline phases form. This suggests that, without pre-treatment, the preferred reaction of the calcium hydroxide produced by the hydration of the OPC, is with the iron floc rather than the PFA. If this is the case, the amount of pozzolanically produced C-S-H that can be formed is reduced, also reducing the strength. PFA is reported to be relatively unreactive and slow to react when compared to OPC [6] and so may be less reactive than the iron floc. Secondly, after pre-treating the floc, a small amount of calcium hydroxide remains, and, during hydration of the composite cement, its presence will increase the early formation and amount of pozzolanically produced C-S-H. This should make a stronger cement, which is less likely to crack during processing. However, as the amount of this residual calcium hydroxide is small, the phases formed during pre-treatment may also aid in producing a stronger cemented wasteform. The crystalline phases formed during pre-treatment were not detected after cementation, indicating that these phases are reactive and could react with the cement during hydration, as could the X-ray amorphous calcium-ferrite phase.

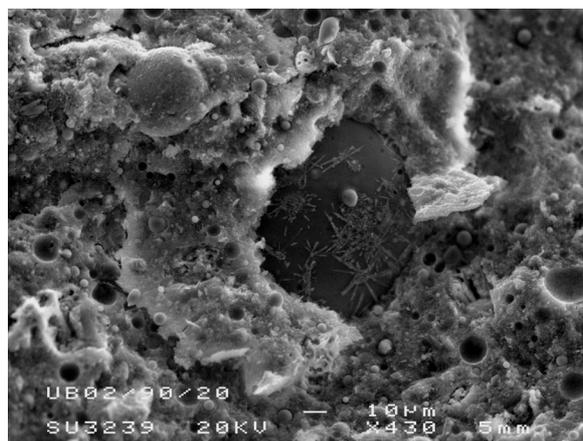


Fig 4. SEM SEI micrograph of a fracture surface of untreated Bulks02 cement hydrated for 90 days at 20°C

The main crystalline phase present in both the hardened untreated and pre-treated Bulks02 cement appears to be iron substituted siliated katoite, $C_3(AF)SH_4$. The low intensity of the XRD trace for this sample indicates that only a small amount of this phase is present, making it difficult to identify by SEM. This phase is normally formed hydrothermally [2], but in the Bulks 02 sample forms at 20 and 40°C. This is probably due to the floc particles being colloidal and therefore highly reactive. This katoite phase is chemically stable [2]. There are small crystalline particles forming on the surface of the PFA grains in the untreated and pre-treated Bulks 02 cements, but it is not possible to analyse this phase by EDS. The high w:s ratio of the floccs resulted in a porous hardened cement paste and is confirmed by visual inspection of an SEM BEI micrograph of the untreated Bulks 02 cement.

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