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# Micro- and nano-structural evolutions in white Portland cement/pulverized fuel ash cement pastes due to deionized-water leaching

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## ABSTRACT

Thin slices of white Portland cement-low calcium pulverized fuel ash (pfa) blended cement pastes containing 30 or 50% pfa were leached progressively in de-ionized water. The paste with 50% pfa was aged 13 years prior to leaching and those with 30% pfa were aged 1 and 13 years. Pastes were leached for up to 75 days and were characterized using thermal analysis, X-ray diffraction, analytical scanning and transmission electron microscopy, and solid-state nuclear magnetic resonance spectroscopy. Leaching affected the pastes in the following sequence: (i) crystals of $Ca(OH)_2$ large enough to be resolved by backscattered electron imaging were removed completely prior to any effect on C-A-S-H; (ii) the Ca/Si ratio of C-A-S-H reduced from ≈ 1.4 to ≈ 1.0 whilst the aluminosilicate structure was unaffected; (iii) further reduction in the Ca/Si ratio of C-A-S-H was accompanied by lengthening of the aluminosilicate chains; (iv) the Ca/Si ratio of C-A-S-H reduced ultimately to ≈ 0.6.

## 1. Introduction

Cementitious materials will be used in a wide range of applications in the geological disposal facility (GDF) for radioactive waste in the UK. These include: waste encapsulation grouts, concrete waste containers, vault/tunnel backfills, lining and plugs; fracture grouts; and floors and roads [1–4]. Hardened cements are porous materials that contain a pore solution that is highly alkaline, with an initial pH that may be as high as ≈ 13 [5].

There are great advantages of utilising cementitious materials as waste encapsulation grouts for the packaging of intermediate-level wastes (ILW), e.g.; an alkaline chemistry ensuring low solubility for many radionuclides; immobilization of radionuclides because the structure can accommodate foreign ions; cost –effectiveness; and ready availability [6]. The long-term ability of a cementitious backfill to maintain an alkaline environment and take up radionuclides from solution are important contributors to the containment of radionuclides in ILW after the closure of a GDF [7].

Formulations of blends of ordinary Portland cement (oPc) with ground granulated blast-furnace slag (ggbs) or pulverized fuel ash (pfa) are commonly used in the UK for the packaging of ILW [8]. In this work, white Portland cement (wPc) was blended with pfa. wPc was used instead of oPc, because the lower quantities of paramagnetic ions (e.g. $Fe^{3+}$) result in narrower peaks in the solid-state nuclear magnetic resonance (NMR) spectra [9]. Richardson et al. compared the data from [10–12] and concluded that the morphology of the outer product (Op) calcium aluminosilicate hydrate (C-A-S-H) in the hydrated cement is associated with a change of pH of the pore solution that occurs as the pfa reacts, the degree of saturation with respect to CH, and the Si concentration [13].

The cementitious materials will be leached by, and react with solutes in, groundwater moving through the vaults after closure of a GDF [14]. When these are leached by a groundwater with a low mineral content and approximately neutral pH, the main cement hydrate phases (e.g. first calcium hydroxide (CH) and later also C-A-S-H, AFt and AFm phases) will be dissolved or diffused out due to the concentration gradient between the pore solution of the cement and the surrounding groundwater, leading to a decrease of the pH of the pore solution and in the long-term the degradation of the cement [15,16]. The decrease of the pH in the long term may influence the performance of the GDF by increasing the solubility of radionuclides which are immobilized by the cementitious materials [6]. As the CH plays an important role in buffering the pH of the pore solution, the determination of its dissolution kinetics is important. In an oPc paste blended with pfa, wherein the CH is largely consumed by the pozzolanic reaction, the pH of the pore solution is mainly buffered by the C-A-S-H. Therefore, the dissolution kinetics and leaching behaviour of C-A-S-H and C-S-H have been the focus of significant efforts [17–19]. The purpose of this paper is to improve understanding of how the CH and C-A-S-H in wPc/pfa are affected by leaching, and thus to contribute to the knowledge underpinning the long-term evolution of the GDF.

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**Table 1**
Bulk oxide compositions of raw materials. ND, not determined.

| | 13-years-old sample | | 1-year-old sample | |
|---|---|---|---|---|
| | WPC | PFA (demagnetised) | WPC | PFA |
| $SiO_2$ | 25.00 | 51.80 | 24.81 | 50.41 |
| $TiO_2$ | 0.08 | 1.00 | ND | ND |
| $Al_2O_3$ | 2.14 | 26.14 | 2.35 | 24.10 |
| $Fe_2O_3$ | 0.36 | 5.93 | 0.49 | 10.63 |
| $Mn_3O_4$ | 0.02 | 0.06 | ND | ND |
| MgO | 0.78 | 1.59 | 0.80 | 1.60 |
| CaO | 71.02 | 1.67 | 70.64 | 3.40 |
| $Na_2O$ | < 0.30 | 1.48 | 0.15 | 0.89 |
| $K_2O$ | 0.09 | 3.79 | 0.06 | 2.97 |
| $P_2O_5$ | 0.08 | 0.24 | ND | ND |
| $Cr_2O$ | < 0.01 | 0.02 | ND | ND |
| $SO_3$ | ND | ND | 2.03 | 0.48 |
| Total | 99.57 | 93.69 | 101.3 | 94.48 |
| LOI at 1025 °C | 1.06 | 3.40 | < 0.01 | ND |

## 2. Experimental materials and techniques

Three sets of white Portland cement/pulverized fly ash (wPc/pfa) blended cement paste were used in the leaching experiments, i.e. one-year-old paste of 70 wt% wPc-30% pfa (1Y-WP30), 13-years-old paste of 70% wPc-30% pfa (13Y-WP30) and 13-years-old paste of 50% wPc-50% pfa (13Y-WP50). The 13-years-old cement paste was made by blending wPc (Aalborg, Denmark) with either 30% or 50% Class F pfa (National Powder, West Burton, U.K.) at a water/solid ratio of 0.50(mL/g). The resolution of the NMR spectra was improved by the removal of magnetic particles using the method described in [13]. The paste was cast in 5 mL polypropylene vials, sealed and cured at 25 ± 1 °C in a water bath for four years, then collected and stored in a desiccator. The 1-year-old wPc/pfa blended cement paste with 70% of wPc (Ribble wPc 8108, Castle Cement Limited, U.K.) and 30% of Class F pfa (Drax Power station, Selby, U.K.) was cast with the water/solid ratio of 0.50 (mL/g), and the paste was then cured in a water bath at 25 ± 1 °C. The bulk oxide compositions of wPc and pfa used in the study are shown in Table 1.

The paste was cut into 600 μm thick slices with a slow-speed diamond saw, placed on a stainless steel supporting frame, and then submerged into a sealed and continuously stirred water bath containing deionized water (liquid/paste mass ratio = 200), kept at room temperature (25 ± 1 °C). A photograph of the samples and supporting frame is shown in Fig. 1. Every five days, slices were collected and stored in a vacuum desiccator for later characterization. The leachate was replaced by fresh deionized water each time. The leaching experiments of the 1Y-WP30 13Y-WP30 and 13Y-WP50 cement paste took 75 days, 45 days and 55 days, respectively. Due to the limited amount of the 13-years-old pastes, the leaching experiment performed on those two samples was not continued for as long as for the one-year-old paste. This study involved multi-technique microstructural characterization, including use of simultaneous thermal analysis (STA), powder X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX), transmission electron microscopy (TEM) with EDX, and solid-state $^{29}$Si and $^{27}$Al magic-angle spinning (MAS) NMR. Whilst such an approach has obvious benefits, in that the results from the different techniques provide complementary information, it is nevertheless important to recognize that there are limitations to the complementarity for inhomogeneous samples. The limitations stem from the fact that whilst the XRD, NMR and STA are bulk techniques that provide average information for a sample, the electron microscopy techniques provide microstructural and microchemical data that are specific to a particular location; this is discussed further below and in Section 3.

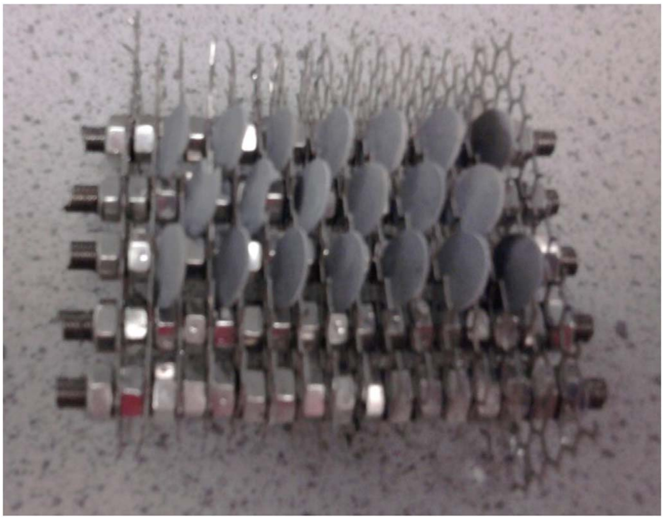

**Fig. 1.** The apparatus for leaching experiments.

Thermal analysis was performed using a Stanton Redcroft STA 1000 (U.K.) equipped with simultaneous thermogravimetric (TG) and differential thermal analysis (DTA). Before loading, the sample was crushed and ground to fine powder in an agate mortar. The sample was loaded in a platinum crucible and was heated up to 1000 °C from 25 °C at a rate of 20 °C/min, under a constant flow of nitrogen gas (BOC, U.K.) at 58 mL/min. The amount of CH present in the sample was calculated from the TG curve using the 'tangent' analysis method to exclude mass loss due the concurrent dehydration of other phases [20].

The XRD measurements were performed using a Panalytical X'PERT-PRO diffractometer system (with X'Celerator real time multiple strip detector), operated with Cu kα radiation at 40 mA and 45 kV. Before loading the sample, the paste was crushed and ground into fine powder in an agate mortar. The powder sample was mounted on a holder that was spun at 2 revolutions per second and the XRD pattern acquired in continuous scan mode over the range of 5 to 80° 2θ with a step size of 0.0334° 2θ (i.e. 2244 steps), leading the total acquisition time of about 1 h.

Samples for examination by SEM were prepared as follows: The slice of cement paste that had been dried in the vacuum desiccator was impregnated with epoxy-resin (Epofix Kit, Struers, UK) under vacuum and allowed to set for 1 day; it was demoulded and polished to a flat surface using a polishing/grinding machine (PdM-Force20 mounted on Struers Rotopol-35) using silicon carbide paper of two different grades (500 μm and 1200 μm grit) and subsequently with diamond paste cloth of 6, 3, 1, and ¼ μm (Struers, U.K.); the polished surface was then carbon coated in an EMSCOPE TB500 (U.K.) vacuum coating machine with a thickness of 15 nm to avoid charging during SEM examination. The SEM examinations were performed on a Carl Zeiss EVO MA15 variable pressure W SEM with Oxford Instruments INCA EDX system with a 80 mm X-Max SDD detector. The modes used in the study were backscattered electron imaging, EDX elemental mapping and EDX point analysis. The microscope was operated at an accelerating voltage of 20 kV, with a working distance of 8 mm and a spot size of 5. The magnification used in the study was 500 ×. The sample preparation procedure generally removed about 60 to 100 μm from the surface of each section – although sometimes less – and so most EDX analyses correspond to this approximate depth (an example is given in Section 3.2). However, four specimens of 1Y-WP30 were sectioned perpendicular to the leached surface, thus enabling measurement of a Ca/Si ratio depth profile for different leaching times (0, 15, 45 and 75 days); this was not possible for the 13-year-old samples because of the limited quantity available. Samples for examination by TEM were prepared as follows: (i) The slice of cement paste was thinned by hand using 1200 grit silicon carbide paper to get a flat surface, which removed approximately 35 μm of the section; (ii) the flat surface was glued to a