Cement and Concrete Research 38 (2008) 737–744

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

The influence of water removal techniques on the composition and microstructure of hardened cement pastes

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ARTICLE INFO

Article history:
Received 17 September 2007
Accepted 25 February 2008

Keywords:
Cement (D)
Drying (A)
Hydration (A)
Microstructure (B)
Arresting

ABSTRACT

The removal of water from hardened cement paste for analysis or to arrest ongoing hydration has been reported to affect the composition of hydrated phases and microstructure. The effect that arresting the hydration of hardened cement paste by replacing the pore water with acetone before drying, and by removing the water by freeze, vacuum and oven drying has on the hardened cement paste has been investigated. Two pastes were studied, a cemented iron hydroxide floc where a high proportion of ordinary Portland cement (OPC) had been replaced by pulverised fuel ash, and a pure hydrated OPC. The results showed that none of the water removal techniques caused any major deterioration in the composition and microstructure of the hardened cement pastes studied, but the pores appeared better preserved after arresting hydration using acetone quenching. Freeze drying appeared to cause more cracking of the microstructure than the other water removal techniques.

1. Introduction

Before the composition and microstructure of any hardened cement paste can be studied at a defined period of time, the ongoing hydration must be arrested. This is needed for several reasons, principally because 1) the preparation of samples for analysis may take several days, during which time the samples continue to hydrate and the phase composition could change, and 2) many analytical techniques, for example scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP), cannot be performed on wet samples.

Various methods are available to the cement chemist to facilitate the removal of water from hardened cement paste prior to sample analysis, but most, if not all, are reported to be detrimental to composition or microstructural arrangement. Some of the methods involve the physical removal of water by drying using an oven or a vacuum, while others replace the water with a liquid that has a lower surface tension, such as a hydrophilic organic liquid, before drying to reduce capillary forces. Sometimes a combination of these methods is used.

Generally, there are three classifications of water present in hydrating cement paste. Pore water, otherwise known as capillary water, is the water held in the pores of the cement paste, which is largely free from physical interactions and as such is available for reaction during hydration. The pores in which it is held generally have a diameter of the order of hundreds of nanometres. It is this water that requires removal when arresting hydration. Interlayer water, also known as gel water, is water that is held by capillary tension and strong hydrogen bonding on to the surface of the main cement hydration product, calcium silicate hydrate (C–S–H) gel. These pores have diameters of the order of nanometres and removal of this water by drying can cause considerable microstructural shrinkage. Chemically bound water is an integral part of the chemical structure of hydrated silicate phases present in the hydrating cement paste, and can only be extracted through hydrate decomposition. The removal of the latter two types of water is undesirable because the composition and microstructure of many of the cement hydrates may be altered and give incorrect information about the phases present in the hardened cement paste.

Most studies on water phases and drying have been carried out on pure Portland cement systems. Composite cements, where high levels of blast furnace slag or pulverised fuel ash (PFA) replace OPC, are used for immobilisation of intermediate and low level nuclear wastes. The composite cements used for immobilisation of wastes have a different microstructure to OPC pastes. The replacement materials react with Ca$(OH)_2$ (CH) to form additional C–S–H but the ultimate porosity is higher than encountered with normal hardened OPC pastes. To develop an understanding of the long term durability of such systems, a systematic study of the microstructure of the hardened matrix is needed.

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0008-8846/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2008.02.012

In this study, a number of cement hydration arresting techniques were examined to find the method that least affected the composition and microstructure of the hardened cement paste. Most of the investigation was performed on samples where an iron hydroxide floc had been encapsulated in a composite cement where a high level of PFA replaced OPC, but a sample of pure OPC paste was also investigated.

2. Review of relevant literature

Most researchers use one of four techniques to arrest the hydration of cement by removing pore water that is available for hydration reactions. These are the solvent replacement of water by a hydrophilic organic liquid, more generally referred to as solvent replacement, and oven, vacuum or freeze drying. However, each method of water removal has been reported to affect the fragile microstructure of the hardened cement paste and may result in the structural and physical collapse of some of the cement hydrates, especially ettringite (AFt), monosulphate (AFm) and C–S–H, as much water is associated with these phases. In hardened cement pastes containing large amounts of AFt, as in calcium sulphoaluminate cements, the dehydration of ettringite has been reported to cause shrinkage cracks large enough to be observed by SEM [1].

2.1. Solvent replacement

Replacing the bound/pore water in samples of hardened cement paste with organic liquids, such as propanone (acetone), methanol, and isopropanol, has been reported to affect the composition and microstructure of the hydrating samples. Taylor and Turner [2] suggested that organic liquids could sorb onto the surface of hydrating C_3S and not be completely removed without affecting the microstructure or phases present. They also suggested that reaction with CH could lead to aldol condensation, and subsequently affect thermogravimetric analysis (TGA) results. Similar observations were reported by Mitchell and Margeson [3] who reported that using acetone to arrest cement hydration affected the derivative thermogravimetric (DTG) peaks for calcium carbonate at approximately 630 °C. They speculated that these results could be due to an aldol reaction catalysed by the presence of CH.

In other work, Taylor [4] suggested that presence of organic matter such as acetone, may not matter when carrying out X-ray diffraction (XRD) studies. Konecny and Naqvi [5] concluded that compared to oven drying and freeze drying, solvent replacement with isopropanol produced samples where the fine pores were least damaged and that this technique best preserved the finest pores. Feldman and Beaudoin [6] studying solvent replacement showed that methanol and isopropanol applied least stress to the microstructure of the hardened cement pastes. By considering length and weight changes of particles in cement pastes immersed in isopropanol and methanol, Feldman [7] concluded that methanol interacts with hydrated cement by penetrating the C–S–H, but found that there was no interaction between isopropanol and hydrated cement. Beaudoin et al. [8] similarly concluded that methanol interacts with hardened cement paste and that the length of CH crystals increased when immersed in methanol, isopropanol, and acetone.

2.2. Freeze drying

Konecny and Naqvi [5] found that the pores of hardened cement pastes were damaged by freeze drying, and Gallé [9] suggested that, while freeze drying was an adequate drying technique for use with MIP, it probably generates significant damage in the C–S–H related to thermomechanical stress. Diamond [10] commented that freeze drying left a significant amount of water in the microstructure of the hardened cement paste, while Taylor [4] felt that for thermogravimetric analysis and scanning electron microscopy, freeze drying was satisfactory.

2.3. Oven drying

Konecny and Naqvi [5] also found that in oven dying, pores in hardened cement pastes were damaged, and Taylor [11] stated that oven drying at 105 °C partially dehydrated the C–S–H. Feldman and Beaudoin [6], and Kanna et al. [12], both found that after oven drying, cracks were formed in the microstructure of the hardened cement paste with the crack density increasing as the drying conditions became more severe. Gallé [9] also concluded that in oven drying at 105 °C, ettringite and C–S–H probably lost a significant amount of non-evaporable water, so that oven drying at 105 °C and even 60 °C was unsuitable for preserving the fragile microstructure of hardened cement paste.

2.4. Vacuum drying

Zhang and Glasser [1], in their study of CSA cement, showed that high vacuum drying degraded ettringite and monosulphate, and seriously damaged the pore structure, increasing the pore volume of hardened cement paste. Gallé [9] found that vacuum drying samples of hardened cement paste produced stresses and microcracks similar to those found for samples dried in an oven at 60 °C and 105 °C, while Diamond [10] commented that vacuum drying removed significantly less water than oven drying at 105 °C.

Based on this survey of the published literature, the advantages and disadvantages of each technique are summarised in Table 1.

3. Experimental

3.1. Sample mixing and curing

This study was carried out on a sample of iron hydroxide floc encapsulated in a PFA/OPC composite cement and on samples of hydrated OPC. The floc was an aqueous colloidal suspension of iron hydroxide (approximately 15 wt.% solids) [13] and as such no extra water was added to the mix when preparing the samples of cement paste. The cemented floc samples were prepared using a composite PFA:OPC cement with a PFA:OPC weight ratio of 5:4 and a floc: composite cement ratio of 1:1 resulting in a water:composite cement ratio of ~0.85. The samples of OPC cement paste were prepared with distilled water at a water:cement ratio of 0.31. All samples were hydrated in sealed polypots at ambient temperature for 7 days.

Table 1
Advantages and disadvantages of cement hydration arresting techniques

	Advantages	Disadvantages
Solvent replacement	Least damage to pore structure. Gives finest pore size distribution. Preserves region of finest pore size. Applies least stress. Isopropanol does not react with cement. Adequate for use with XRD.	Reaction with CH — could affect TGA results. Could sorb into cement phases and not be removed without affecting microstructure. Methanol interacts with cement.
Freeze drying	Adequate for use with MIP. Suitable for use with TGA and SEM.	Damages pores of cement. Generates stresses in C–S–H. Leaves water in cement.
Oven drying	Reaches steady state rapidly.	Damages pores in cement. Dehydrates C–S–H at 105 °C. Causes cracks in cement. Crack damage increases as drying temperature increases. Removes bound water from ettringite. Does not preserve microstructure.
Vacuum drying		Degrades ettringite and monosulphate. Seriously damages pore structure and increases pore volume. Produces stresses and microcracks. Removes less water than oven drying at 105 °C.

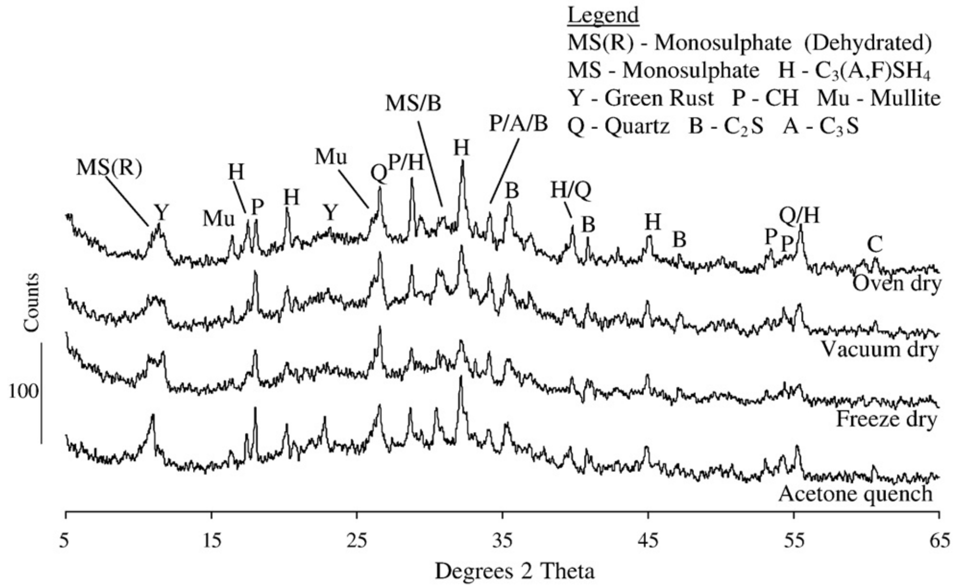

Fig. 1. XRD traces of hardened cemented floc hydrated for 7 days where hydration had been arrested by acetone quenching, freeze drying, vacuum drying and oven drying.

To mix the samples of cement paste, the required masses of cement powders were blended in a figure of eight mixer for 5 min. The required mass of floc or water was placed into a polypot and the cement powder was gradually added over a 5 min period while continually mixing by hand. The fresh cement paste was then placed in 50 ml polypots and, after vibrating for 1 min to remove air voids, the pots were sealed and left to hydrate at ambient temperature and relative humidity.

3.2. Sample preparation

Before hydration of the samples was arrested they were removed from their polypots and lightly crushed by hand, if necessary using a percussion mortar, to a particle size of approximately 8×8×8 mm. Hydration was then arrested using either acetone quenching, or freeze, oven or vacuum drying described below. Hydration of the hardened OPC samples was arrested using either acetone quenching or freeze drying.

3.2.1. Acetone quenching (solvent replacement)

The samples of hardened cement paste were immersed in acetone for 7 days, and then placed in a vacuum desiccator held at a vacuum of 1×10^{-2} mBar for 3 days to remove the acetone.

3.2.2. Freeze drying

The samples were frozen in liquid nitrogen for 2 h and then freeze dried in an Edwards Modulyo — 4K Freeze Dryer operating at a temperature of −48 °C and a vacuum of 5×10^{-2} mBar for 4 days.

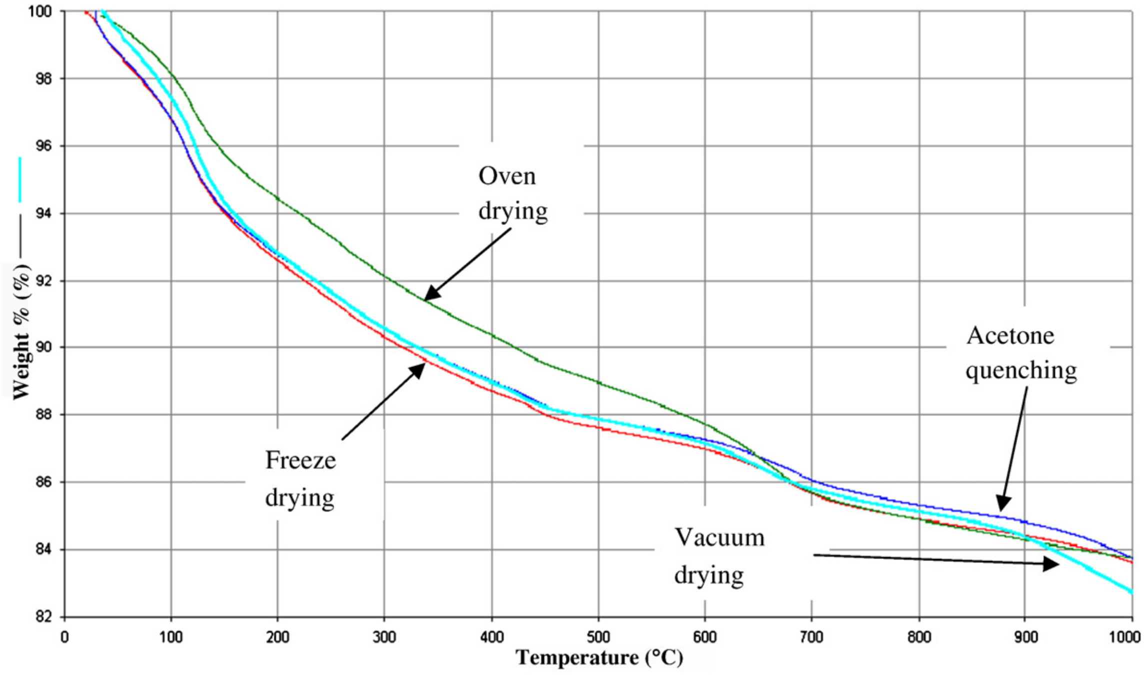

Fig. 2. TGA curves of hardened cemented floc hydrated for 7 days where hydration had been arrested by acetone quenching, freeze drying, oven drying and vacuum drying.

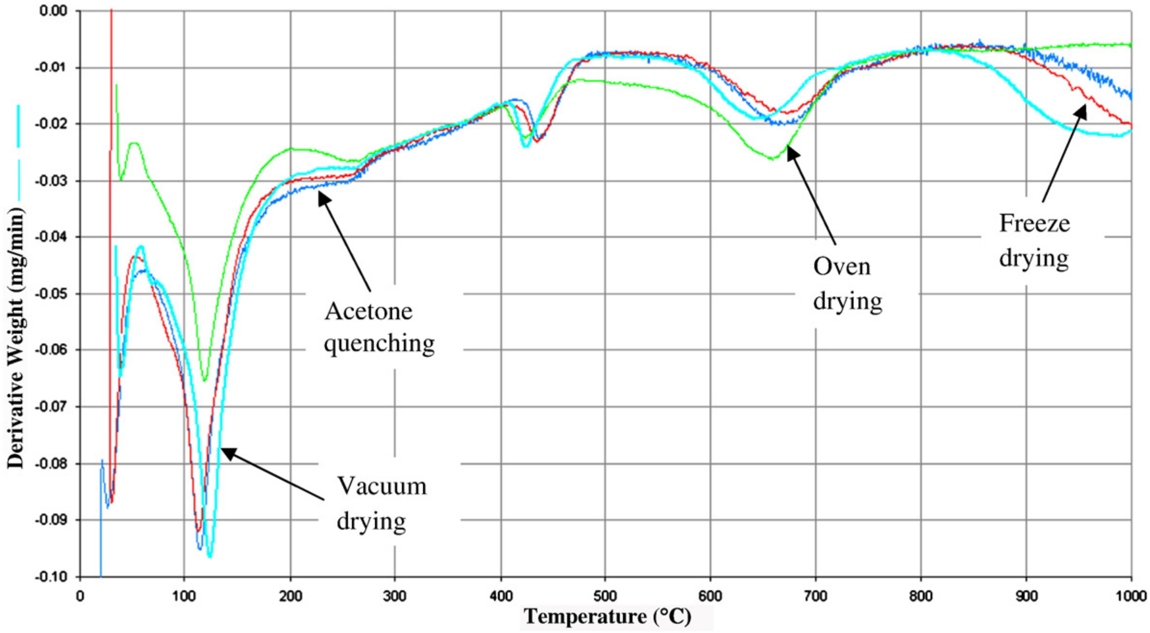

Fig. 3. DTG curves of hardened cemented floc hydrated for 7 days where hydration had been arrested by acetone quenching, freeze drying, vacuum drying and oven drying.

3.2.3. Oven drying

The samples were dried in an oven at 60 °C for 7 days.

3.2.4. Vacuum drying

The samples were dried in a vacuum desiccator at 1×10^{-2} mBar for 7 days.

3.3. Analysis of samples

The dried samples were analysed using XRD, TGA, SEM and MIP. For analysis by XRD, the hardened cement paste was crushed and ground in an agate mortar to pass a 63 μm sieve. XRD spectra were run on a Siemens D500 diffractometer operating at 2°/min and step size of 0.02° between 5 and 65° 2θ. The powder sample prepared for XRD was also used for TGA. A Perkin Elmer Pyris 1 Thermogravimetric Analyzer programmed with a heating profile of 30–1000 °C at 10 °C/min in a flowing atmosphere of nitrogen was used. SEM was used to analyse fracture surfaces and polished surfaces of samples of hardened cement paste approximately 6×6×6 mm in size. For fracture surface analysis, a freshly fractured particle of hardened cement paste was adhered to an aluminium microscope stub using silver dag paint, and, after drying, was carbon coated. For analysis of polished surfaces of hardened cement paste, samples were mounted in epoxy resin and after setting were hand ground and polished. All SEM analysis was performed using a Jeol JSM 6400 electron microscope. For analysis by MIP, samples approximately 3×3×3 mm with a combined weight of approximately 0.6 g were analysed using a Micromeritics Poresizer 9320 MIP machine.

4. Results

All analysis techniques were used to investigate the effect that the hydration stopping technique had on the composition and microstructure of the hardened cemented floc, whereas the samples of hardened OPC were analysed only using SEM.

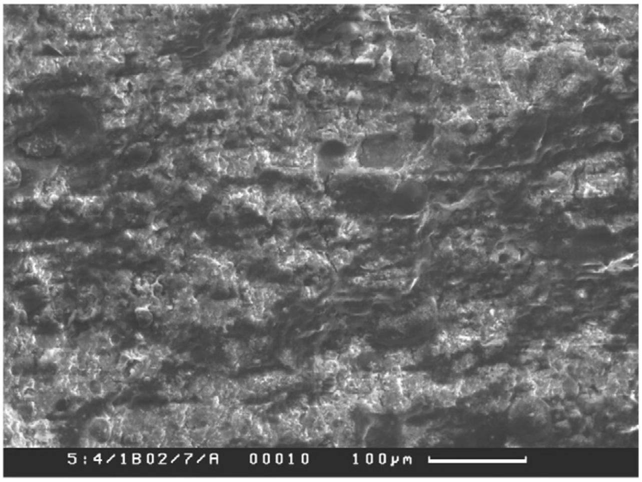

Fig. 4. SEM SEI micrograph of fracture surface of hardened cemented floc hydrated for 7 days where hydration had been arrested by acetone quenching.

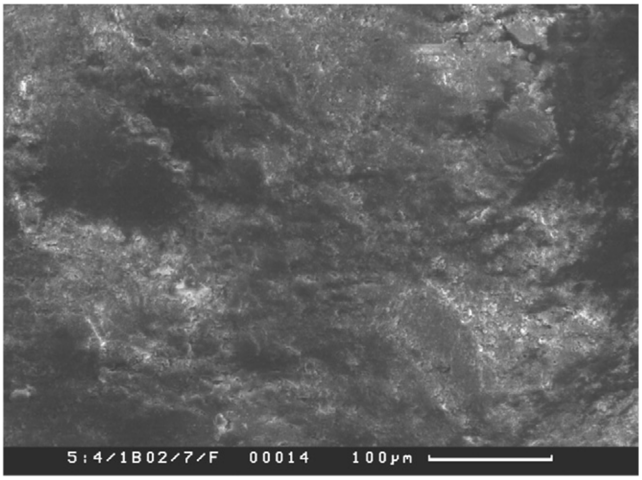

Fig. 5. SEM SEI micrograph of fracture surface of hardened cemented floc hydrated for 7 days where hydration had been arrested by freeze drying.

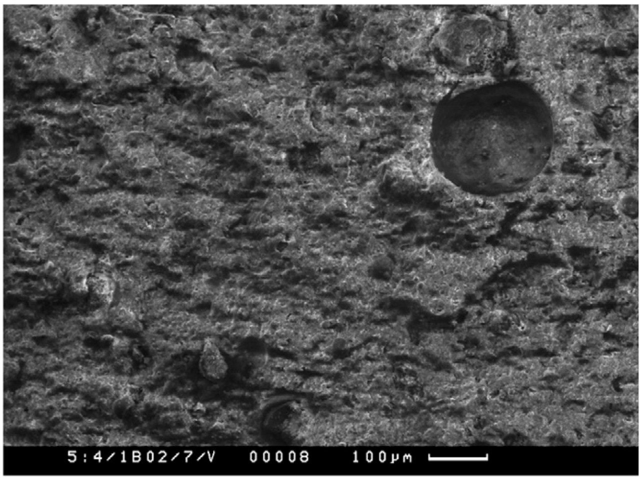

Fig. 6. SEM SEI micrograph of fracture surface of hardened cemented floc hydrated for 7 days where hydration had been arrested by vacuum drying.

4.1. XRD analysis

Fig. 1 shows the XRD traces of the cemented floc after 7 days where the hydration was stopped using the four arresting techniques. The counts were low and there was a distinct amorphous hump centred at approximately 33° 2θ indicating that the samples were generally amorphous. The magnitude and position of the main peaks was very similar for all samples. The main crystalline phase detected in all samples was a hydrogarnet (C_3AH_6) type phase, in which some of the aluminium had been replaced by iron and OH^- groups had been replaced by SiO_4^{4-}, to form a solid solution with katoite, $Ca_3AlFe(SiO_4)(OH)_8$, referred to as $C_3(A,F)SH_4$ in this paper. Other crystalline phases detected in all samples were monosulphate, Green Rust (an iron hydroxy carbonate phase ($Fe_6(OH)_{12}(CO_3)$)), CH, quartz and mullite ($Al_6Si_2O_{13}$) from the PFA, and the anhydrous cement phases C_3S and β-C_2S. A dehydrated form of monosulphate, $C_3A.CaSO_4.H_{10,}$ labelled as MS(R) was detected in the freeze, vacuum and oven dried samples but not in the sample quenched in acetone. Small quantities of the more common form of monosulphate ($3CaO.Al_2O_3.CaSO_4.12H_2O$) were detected in all samples although the main peak at 9.9° 2θ was overlapped by the main 11.74° 2θ peak for Green Rust. Apart from the detection of different forms of monosulphate, the same crystalline phases were found in all samples.

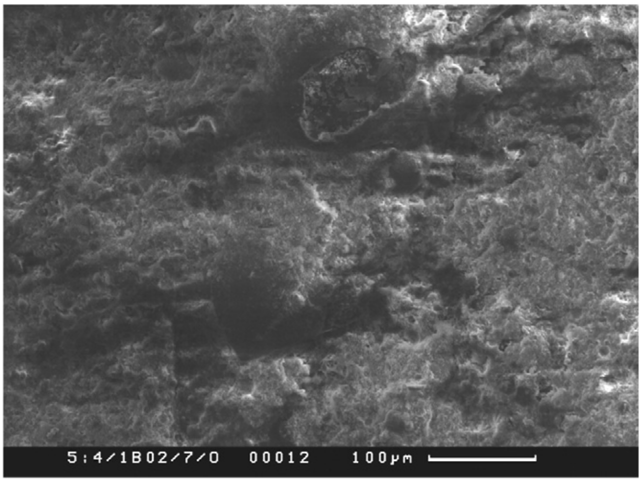

Fig. 7. SEM SEI micrograph of fracture surface of hardened cemented floc hydrated for 7 days where hydration had been arrested by oven drying.

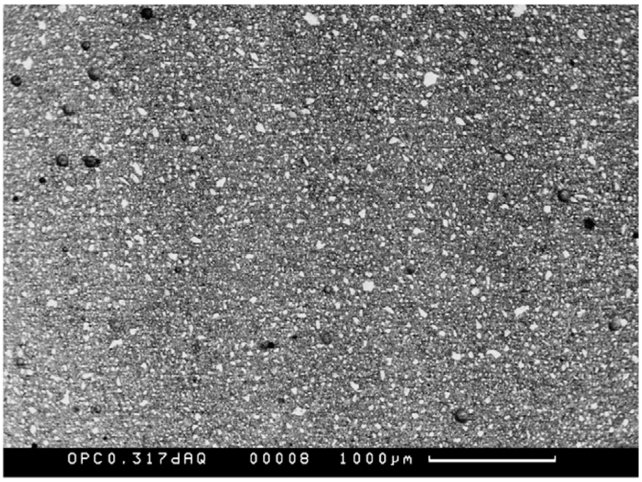

Fig. 8. SEM BEI micrograph of hardened OPC paste hydrated for 7 days where hydration had been arrested by acetone quenching.

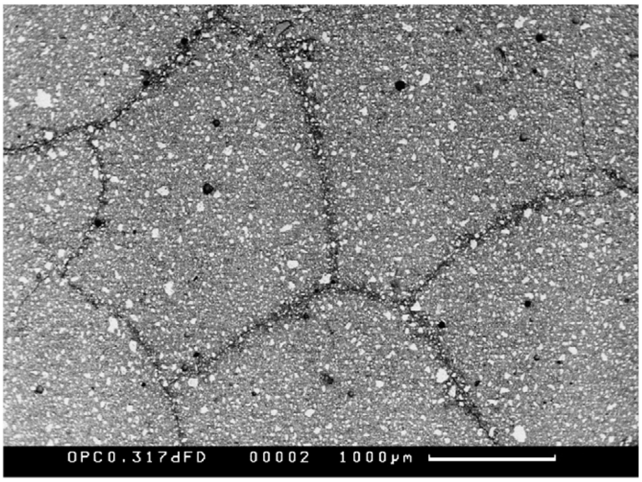

Fig. 9. SEM BEI micrograph of hardened OPC paste hydrated for 7 days where hydration had been arrested by freeze drying.

4.2. Thermal analysis

TGA curves of all four samples are shown in Fig. 2. The weight loss curves were very similar for all samples which lost approximately 15%

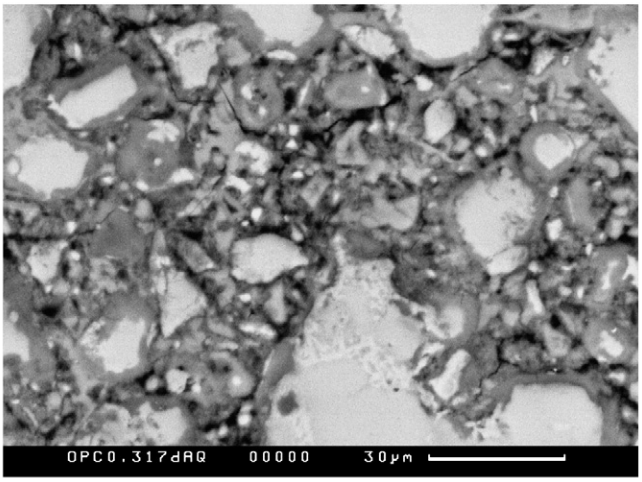

Fig. 10. SEM BEI micrograph of hardened OPC paste hydrated for 7 days where hydration had been arrested by acetone quenching.

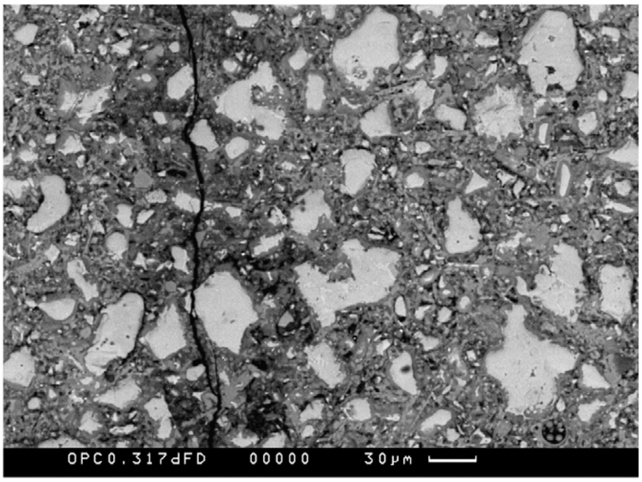

Fig. 11. SEM BEI micrograph of hardened OPC paste hydrated for 7 days where hydration had been arrested by freeze drying.

of their original mass during decomposition. Approximately 70% of the total mass was lost between 50 and 500 °C. This was due to the release of water from cement binding phases, the principal phase being C–S–H. The oven dried sample was most dissimilar from the other samples and showed a higher weight loss associated with the release of CO_2 from calcite in the range 580–710 °C.

The DTG curves of all samples (Fig. 3) were very similar and showed a broad C–S–H loss between approximately 50 and 500 °C on which were superimposed sharper peaks at approximately 120 and 430 °C, followed by another at ca. 650 °C. These correspond to the highest rate of release of water from C–S–H, the dehydroxylation of CH and the decarbonation of calcite, respectively. In all traces, excluding that for the oven dried sample, there was a small weight loss at 900–1000 °C. This could be due to release of oxygen from hematite in the PFA during its reduction from Fe^{3+} to Fe^{2+}. The DTG traces for the acetone and freeze dried samples were the most similar with the same peaks occurring at almost the same temperatures. The trace for the vacuum dried sample differed from that of the acetone and freeze dried samples in that there was an additional small peak at approximately 75 °C which could be liquid water, and the C–S–H peak was approximately 10 °C higher and the CH and calcite peaks occurred approximately 20 °C lower. The most noticeably different trace was that for the oven dried sample where the size of the C–S–H peak was much less than in the other samples. The C–S–H and CH peaks for the oven dried sample were approximately 10 °C higher and 20 °C lower respectively than for the acetone and freeze dried samples and there was no peak at approximately 1000 °C.

4.3. Electron microscopy

SEM micrographs of the fractured surfaces of the cemented floc where the hydration had been stopped using the four arresting techniques are shown in Figs. 4–7. It was not possible to obtain clear micrographs of polished surfaces of these samples using backscattered electron imaging (BEI), probably because the samples had very low strength due to the very high water:solids ratio (approximately 0.85:1) and also due to the short hydration period of only 7 days. Therefore, when polishing, rather than the top layer of particles being cut through, it was likely that they were knocked off as there was insufficient strength to hold them in the hardened cement matrix. This produced an uneven surface which was very difficult to resolve at any useful magnification on the SEM. To produce a clear BEI image, a very flat sample surface is required in order to scatter enough of the electron beam back to the detector, but this is not necessary for a secondary electron image.

The microstructure of each sample at low magnification was very similar and appeared disordered and irregular. For each sample, no obvious crystalline particles were present and the amount and size of pores appeared to be similar.

Clear BEI images of the polished surfaces of hydrated neat OPC samples where the hydration had been stopped by acetone quenching and freeze drying are shown in Figs. 8 and 9 at low magnification and in

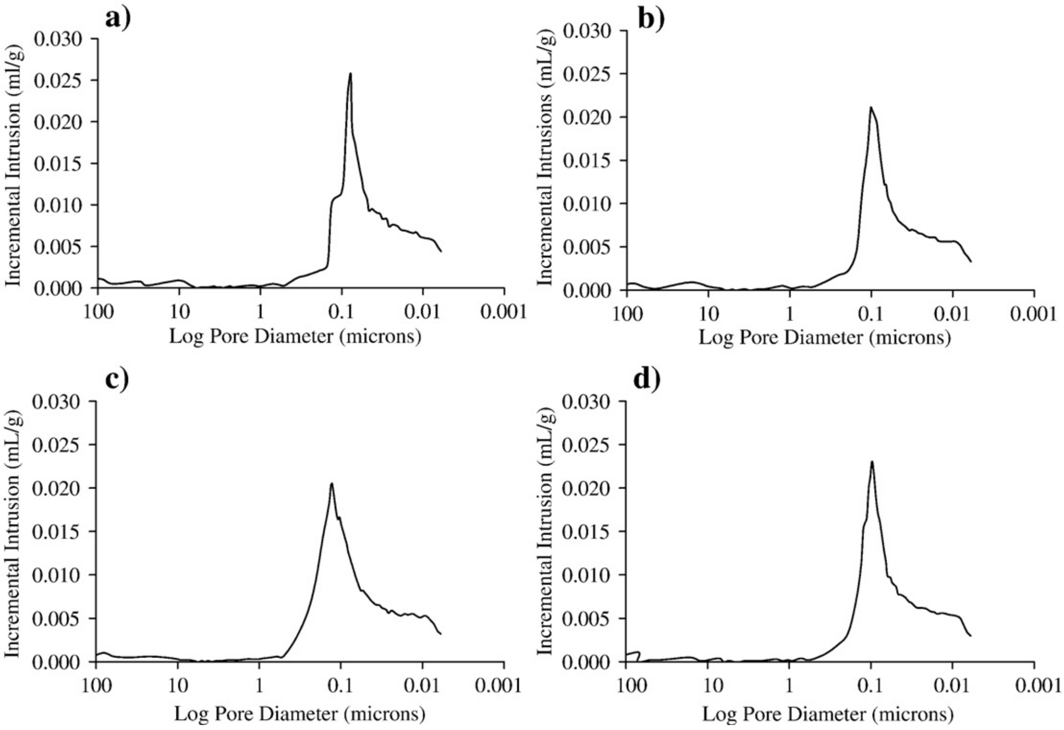

Fig. 12. MIP curves for the hardened cemented floc samples where the hydration had been arrested by a) acetone quenching, b) freeze drying, c) oven drying and d) vacuum drying.

Table 2
MIP results for hardened cemented floc hydrated for 7 days where hydration had been arrested by acetone quenching, freeze drying, vacuum drying and oven drying

Method Of hydration arresting	Total porosity (%)	Majority pore size (μm)	Total pore area (m^2/g)
Acetone quench	52	0.09	59
Freeze dry	53	0.10	50
Oven dry	53	0.10	45
Vacuum dry	53	0.09	49

Figs. 10 and 11 at higher magnification. Many microcracks (approximately 0.1 μm in width) were present in both samples, but there appeared to be more in the freeze dried sample (Fig. 9) than in the acetone quenched sample (Fig. 8). Additionally, cracks through the anhydrous cement grains were evident at higher magnification in the freeze dried sample (Fig. 11). These cracks may have been caused by sample preparation but the fracture of anhydrous cement grains is unusual and is more likely to be the result of drying. Large cracks (approximately 5 μm in width), with much porosity in close proximity, were observed in the freeze dried sample (Fig. 11). These large cracks could have been caused by some of the ice in the frozen sample melting before the vacuum was applied. Thus, evaporation of liquid rather than solid water would have applied a higher surface tension to the microstructure of the hardened cement paste which could have cracked the soft C–S–H. Additionally, the increase in volume due to the freezing of water during the freeze drying process may have cracked the hardened cement paste [14]. The micrograph shown in Fig. 10 is, however, a better representation of the microstructure of the hydrated cement, clearly showing hydration rims around the anhydrous cement grains.

4.4. Porosity

The MIP curves for the hardened cemented floc samples where the hydration had been arrested using the four techniques are shown in Fig. 12 and a summary of the results is shown in Table 2.

The results for all samples were very similar with the total porosity of each sample approximately 53%, while the diameter of the majority of all pores in each sample was approximately 0.1 μm.

The main difference is that the total pore area of the acetone quenched sample was significantly greater than that of the other samples. This indicates that either the fine pores in this sample were retained by the drying method, or that the capillary forces caused by the other drying methods had acted to reduce the size of pores. The latter was more likely because the higher surface tension of water compared to acetone would result in higher capillary forces being applied to the pores giving partial collapse. This suggests that for the acetone quenched sample the pores were least affected by the drying method and were closest to their original size.

5. Discussion

Reports in the literature suggest that any drying method can alter the composition and microstructure of hardened cement paste, with perhaps the least harm being done by replacing pore water with organic liquids before drying [2,5,9,6]. However, in this study where the matrix has high porosity, the method of arresting cement hydration does not appear to have had a major influence on the crystalline phase composition and microstructure from the various characterisation methods used.

5.1. Hardened floc cement

The main phase present in all samples of cemented floc was C–S–H. Very small amounts of CH, which had mostly been consumed in the pozzolanic reaction, were detected. The weight losses on heating for the various samples were almost identical, especially those where acetone quenching, freeze and vacuum drying were used. These results appear to be contrary to the suggestions made by Taylor and Turner [2] and Mitchell and Margeson [3] who stated that organic liquids such as acetone affect thermogravimetry results by reacting with CH. The quantity of CH detected in these samples was so low, that any changes caused by the different drying methods were difficult to detect.

The XRD traces for all samples were very similar with essentially the same small amounts of crystalline hydrates $C_3(A,F)SH_4$, monosulphate, Green Rust and CH. The one exception is the dehydration of AFm in vacuum drying. This agrees well with the conclusion by Taylor [4] that acetone quenching is probably safe when analysing hardened cement pastes using XRD.

The microstructure of all fracture surfaces of hardened cement paste showed similar generally disordered matrices and the total porosity and majority pore size of each sample was very similar. The pores of the acetone quenched sample appeared to be least affected by the drying technique suggesting that acetone quenching preserves the pores better than the other hydration arresting techniques, which is in agreement with results reported by Konecny and Naqvi [5] and Feldman and Beaudoin [6]. This may be due to the fact that there is a large inherent porosity in these samples as there is insufficient CH produced by the hydration of the cement to react with all the PFA, leaving a porous matrix dominated by coarse pores.

5.2. Hardened OPC

When compared to the acetone quenched sample of hardened OPC, the cracks observed in the freeze dried sample were more prevalent, were larger in size and were seen to cut through anhydrous cement grains.

The size of cracks and porosity appeared to be less in the samples where cement hydration had been arrested by acetone quenching than when the samples had been freeze dried. This compares well with the conclusions reported by Konecny and Naqvi [5] and Gallé [9] where both groups of researchers reported that freeze drying damaged the pores and microstructure of hardened cement paste more than acetone quenching.

6. Conclusions

- None of the methods of arresting cement hydration studied appeared to cause any major difference to the composition and microstructure of the hardened composite cement pastes studied.
- The pores of the hardened cement pastes appear to be better preserved after arresting hydration using acetone quenching.
- Using freeze drying to stop hydration appeared to cause more microstructural cracking than acetone quenching.
- Solvent replacement, using acetone, is probably the least damaging method, but there is some concern that the quantitative determination of the CH content of the hardened cement paste could be erroneous.
- Due to the similarity of results, the decision of which method to use when analysing hardened cement paste comes down to one of logistics, or ease of use. For composite cements, the removal of pore water by immersion in acetone, and subsequent drying in a vacuum desiccator has the advantage of ease of operation and handling.

Acknowledgements

The authors would like to thank the Engineering and Physical Sciences Research Council (EPSRC) and the Nuclear Decommissioning Authority (NDA) for funding this study.

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