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Chemical and mechanical activation of hybrid fly ash cement

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Hybrid fly ash cement is a binder with a composition between that of pozzolanic fly ash cement and alkali-activated fly ash cement. Its production requires less cement clinker than ordinary Portland cement, facilitating a much-needed reduction in the carbon dioxide footprint related to the production of high-clinker-containing cement. Research on activation methods is required to overcome the low early age strength and slow strength development in hybrid fly ash cements. In this study the activation of a South African siliceous fly ash (70%) for use along with Portland cement (30%) in a hybrid alkaline binder was investigated. Both chemical (the addition of sodium sulfate) and mechanical (milling) activation of fly ash was studied. The aim of this work was to develop a better understanding of the characteristics of compressive strength development of hybrid fly ash cement mortars over an extended curing period of up to a year. The results indicated that the combination of mechanical and chemical activation (sodium sulfate) can be considered a viable solution to improving early strength and slow strength development, so that hybrid cements are able to comply with the strength requirements of the BS EN 197 cement specification.

Introduction

Hybrid fly ash cement is a binder with a composition between that of pozzolanic fly ash cement and alkali-activated fly ash cement (Donatello *et al.*, 2013, 2014a; Garcia-Lodeiro *et al.*, 2015). The production of hybrid cement requires less clinker than that for ordinary Portland cement, and therefore produces less carbon dioxide. Portland cement accounts for approximately 7–8% of the total carbon dioxide emitted globally (approximately 0.8 t of carbon dioxide is released per tonne of clinker manufactured) (Duchesne *et al.*, 2010; Garcia-Lodeiro *et al.*, 2017; Olivier *et al.*, 2015; Palomo *et al.*, 2007). The inherent advantage of hybrid alkaline cements, over their alkali-activated counterparts, is that they do not require the addition of highly alkaline (and usually expensive) chemicals, but rely on a safe source of alkali formed in situ (sodium hydroxide) to facilitate both the dissolution of any amorphous (glassy) phases present in the source materials, and hydration at ambient temperature (see Equation II) (Donatello *et al.*, 2013, 2014b; Kovtun *et al.*, 2015; Shekhovtsova *et al.*, 2016).

During the production of blended cement, the maximum fly ash content is constrained due to insufficient early strength and slow strength development ascribed to the rate of the pozzolanic reaction between cement and fly ash (Blanco *et al.*, 2006; Heinz *et al.*, 2010). It is also well known that the degree of hydration and early-age compressive strength tends to decrease with an increase in level of fly ash (Al-Zahrani *et al.*, 2006). As a result a maximum of 55% fly ash is specified for

a CEM IV/B pozzolanic cement in the European standard on composition, specifications and conformity criteria for common cements (BS EN 197-1:2011, edition 2) (BSI, 2011). The lowest strength class of cementitious binder specified by EN 197 viz 32.5N, requires a minimum compressive strength of 16 MPa after 7 d, and 32.5 MPa after 28 d. Typically hybrid cements contain at least 70% fly ash by mass (Garcia-Lodeiro *et al.*, 2016; Palomo *et al.*, 2014), and cannot therefore be subject to current standards. If commercially viable fly ash-based hybrid cements are to be developed, it would be necessary to enhance the reactivity of fly ash so that strength develops at an acceptable rate and adequate strength values are ultimately achieved.

Fly ash reactivity can be improved by either chemical or mechanical activation or a combination of these two techniques (Donatello *et al.*, 2013, 2014b; Fernández-Jiménez *et al.*, 2011; Garcia-Lodeiro *et al.*, 2017; Kumar and Kumar, 2011; Kumar *et al.*, 2007; Qian *et al.*, 2001; Qiao *et al.*, 2006; Temuujin *et al.*, 2009; Velandia *et al.*, 2016). The pozzolanic reactivity of fly ash can be considered as the rate of reaction occurring between its amorphous phase and calcium hydroxide prevalent in moisture-laden cementitious materials (Kaur *et al.*, 2017; Velandia *et al.*, 2016). In light of this, the formation of precipitates and etching on the surface of fly ash particles placed in a saturated solution of calcium hydroxide can be regarded as indicative of fly ash reactivity (Chindaprasirt *et al.*, 2007; Donatello *et al.*, 2013).

When exploring the acceleration of the reactivity of fly ash in a fly ash–lime system by means of sodium sulfate, chemical activation significantly improved the rate at which strength increased, especially during the early stages (Shi and Day, 1995; Velandia *et al.*, 2016). Lee *et al.* (2003) investigated fly ash cement blends (40% fly ash and 60% cement clinker) using three different chemical activators, one of which was sodium sulfate at various levels of addition. The authors concluded that although all three activators accelerated the strength development at an early age, sodium sulfate was the most effective in accelerating the consumption of calcium hydroxide and also produced more ettringite than the other two activators. These results explain the improved early compressive strength of mortars when sodium sulfate was used (Lee *et al.*, 2003; Velandia *et al.*, 2016). The efficacy of using sodium sulfate as an activator was studied by measuring its influence on the early-age hydration of very high-volume fly ash cement (80% fly ash activated with 4% sodium sulfate) (Donatello *et al.*, 2013). The compressive strength at 2 d was predicted by extrapolation of data after 45 h of curing. The results showed a significant increase in the predicted 2 d strength when sodium sulfate was used as a chemical activator. Subsequently, efficiency of sodium sulfate as an activator for hybrid cement containing a high content of coal bottom ash was again investigated (Donatello *et al.*, 2014b). Although no strength results were reported, the team concluded that both the cement clinker phases and the ash glassy phases are highly reactive during the first 3 d of hydration.

The benefit of mechanical activation of fly ash has been reported by several authors as a viable method of achieving ambient temperature curing of both alkali-activated and blended cements (Fanghui *et al.*, 2015; Kumar and Kumar, 2011; Kumar *et al.*, 2007; Temuujin *et al.*, 2009; Zhao *et al.*, 2015). The research indicated that mechanical activation improves both bulk and surface reactivity. It also offers the possibility of changing the reactivity of solids without altering their overall chemical composition. It was shown that the reactivity of fly ash varies with the median particle size and increases rapidly when the size is reduced to less than 5–7 μm (Kumar and Kumar, 2011; Kumar *et al.*, 2007). Results indicate that mechanical activation of fly ash can be used to produce blended cements containing higher proportions of fly ash without degrading performance characteristics (Kumar *et al.*, 2007). The effect of mechanical activation of the fine fraction of fly ash was investigated by using milled fly ash. The results indicate that mechanical activation only had a slight effect on 28 d compressive strength, but was very effective in improving the strength at 90 d (Qiao *et al.*, 2006). As part of that study, a specimen of the mechanically activated fly ash was prepared with sodium sulfate added to the mix, thus effectively combining chemical and mechanical activation into the same fly ash–lime blend. It was concluded that the combination of sodium sulfate together with the milled ash produced results which significantly improved the strength characteristics

compared to the control sample (only mechanical activation) at both curing ages. Another fly ash–lime system was investigated by Qian *et al.* (2001) containing 80% fly ash (mechanically and chemically activated with sodium sulfate) and 20% lime (no cement clinker). After the mechanical activation of the fly ash, the lime–fly ash mortars hardly had any strength at 3 d, but achieved about 1 MPa at 7 d and 2.3 MPa at 28 d. When 3% sodium sulfate was added to the ground fly ash, the mortars achieved 2.5 MPa at 3 d, 5.5 MPa at 7 d and approximately 12.5 MPa at 28 d. The investigation focused on the compressive strength behaviour of mortar specimens, up to a maximum curing age of 28 d, and concluded that the combination of grinding along with the addition of sodium sulfate resulted in higher strengths than either grinding or sodium sulfate addition individually (Qian *et al.*, 2001).

It is evident that either sodium sulfate (chemical activation) or milling of fly ash (mechanical activation) are effective activation methods for high-fly-ash-containing cement–lime systems. However, the literature tends to discuss the compressive strength of fly ash–lime system (calcium hydroxide or calcium oxide) mortars rather than fly ash–cement systems. More emphasis is also placed on early-age strength development (2 d up to 28 d) as opposed to the evolution of strength of a protracted time of up to a year. Hence, it is not clear what effect the two activation techniques will have on compressive strength over an extended curing period. The aim of this study is to fill the gap by presenting and discussing the compressive strength results and strength characteristics of a hybrid fly ash–cement system at specific curing ages (1, 2, 7, 28, 90 and 180 d, and 1 year). The hybrid produced consists of 70% siliceous fly ash and 30% Portland cement to which a combination of chemical and mechanical activation methodologies are applied. The aim was to develop a better understanding of the activity/reactivity that takes place on the surface of activated fly ash particles after their exposure to a saturated calcium hydroxide system. In turn this may aid the development of a better understanding of the mortar compressive strength characteristics of a hybrid fly ash cement hydrated for up to a year.

Materials and methods

Materials

In this study three different, commercially available fly ashes were utilised along with Portland cement. The fly ashes, sourced from a South African ash merchant, included an ultra-fine air-classified ash (d_{50} about 5 μm , denoted FCFA), an unclassified ash (d_{50} about 60 μm , denoted UFA) and the mechanically activated (milled) residue (d_{50} about 7 μm , denoted MUFA) of the unclassified ash (Figure 1). The Portland cement was also sourced from a South African supplier; it was produced by milling clinker along with approximately 10% limestone and 5% gypsum in a vertical roller mill, until a mean particle size of approximately 13 μm was

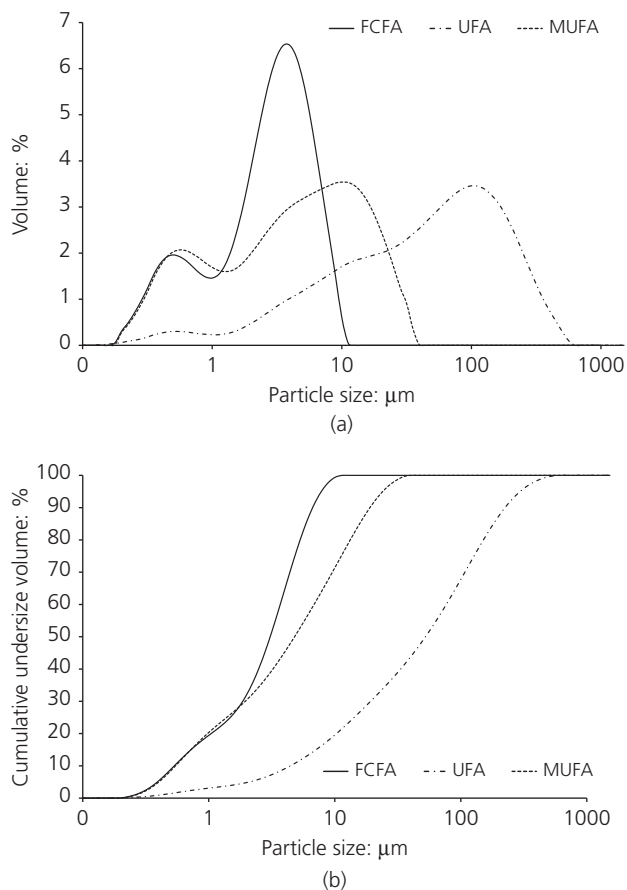


Figure 1. Particle size distribution of the three FA samples: (a) volume %; (b) cumulative undersize volume

achieved. Commercially available (99%, Merck) sodium sulfate (Na_2SO_4 , anhydrous) was used in all of the chemically activated mixes, and was directly added in powder form to each mix being prepared for the hybrid cements.

Characterisation methods

The chemical composition of these materials was determined by X-ray fluorescence (XRF) fused bead analysis (PANalytical Axios). The glass disc was prepared by mixing 1 g of the sample with 5 g of fluxing agent (analytical grade lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$)) and fusing the mixture at 1000°C . The fine powdered samples required no additional milling prior to the analysis. The loss on ignition (LOI) was determined by roasting the sample at 1050°C for 1 h until a constant weight was achieved.

The particle size distribution (PSD) was obtained by laser diffraction using a Malvern Mastersizer 2000 fitted with a Scirocco 2000 sample handling unit. Scattered light data were recorded for 25 s. A refractive index of 1.68 and absorption of 1 was chosen. Size data collection was performed within the recommended 10–20% obscuration range.

X-ray powder diffraction (XRD) measurements were carried out using a PANalytical X'Pert Pro powder diffractometer, an X'Celerator detector and variable divergence and fixed receiving slits, with Fe filtered $\text{Co-K}\alpha$ radiation ($\lambda = 0.1789$ nm). The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weight %) were estimated using the Rietveld method (Autoquan program). Twenty percent silicon (Aldrich 99% pure) was also added to each sample for the determination of amorphous content. The samples were then micronised in a McCrone micronising mill, and prepared for XRD analysis using a back-loading preparation method. XRD analysis of the fly ash specimens cured in calcium hydroxide did not include the addition of silicon, as only the crystalline phases were identified for the purpose of the study.

The morphology of the fly ash was studied in a Zeiss Ultra SS (Germany) field emission scanning electron microscope (FESEM), operated at an acceleration voltage of 1 kV under high-vacuum conditions. Specimens cured in calcium hydroxide were dried and then procured by dipping carbon stubs into the powders. Excess powder was removed by gentle blowing with compressed nitrogen. The samples were sputter-coated with carbon (Emitech K550X, Ashford, UK) and placed in the microscope for examination.

Experimental set-up

Characteristics of the fly ash surfaces exposed to a calcium hydroxide environment

In order to assess the effect of an alkaline environment on the reactivity of fly ash, it was exposed to a saturated calcium hydroxide solution. Five grammes of each of the three fly ash products, FCFA, UFA and MUFA, were placed in 1 litre glass containers to which 200 ml of the calcium hydroxide solution (2 g/l deionised water) was added to serve as the curing medium. In addition to this, chemical activation by addition of sodium sulfate was investigated (5%, calculated as a mass percentage of the total fly ash content). The glass containers were sealed and placed in a shaking water bath at 25°C and shaking speed of 150 min^{-1} . At specified curing ages (1, 7, 28 and 56 d), a small amount of the sample was removed, filtered and washed with deionised water followed by isopropanol, and dried at 40°C for 24 h, after which XRD and FESEM analyses were performed.

Mortar compressive strength of hybrid fly ash cement

Blends for all of the physical test work consisted of 70 wt % of the relevant fly ash product and 30% Portland cement. The blends were chemically activated by adding 1, 3 and 5% sodium sulfate, respectively, as a dry powder directly to each mix, calculated as a mass percentage of the total cementitious content. A constant water-to-binder (the binder only includes cement and fly ash) ratio of 0.5 was maintained for all blends. Preparation, mixing and compressive strength testing of all blends were done as per BS EN 196-1 (BSI, 2016).

At predetermined curing ages (1, 2, 7, 28, 90 and 180 d, and 1 year); samples were removed from the curing tanks and their compressive strength was determined. Compressive strengths reported are the arithmetic mean of six measurements ($n = 6$).

Results and discussion

Characterisation of the starting materials

Particle size distribution (volume % and cumulative undersize volume) of the three fly ashes are depicted in Figure 1. From this it is evident that, with all the particles being below 10 μm , FCFA is finer than MUFA, whereas UFA is significantly coarser than both of these. Although the particle size distribution of MUFA indicates a somewhat coarser material than FCFA, their mean particle size (d_{50}) of 8 and 5 μm , respectively, are almost identical. Owing to the greater abundance of smaller particles, FCFA will have the larger surface area and is therefore expected to be more reactive and achieve higher compressive strength than UFA and MUFA when used in cementitious binders. The larger number of smaller spherical particles in FCFA should also provide more nucleation sites for reaction, improve particle packing density and by implication the physical properties of blended cement (Tangpagasit *et al.*, 2005).

The chemical (XRF) and mineralogical (XRD) compositions are presented in Table 1. Although there are no major differences in chemical composition, the mineralogy of the fly ashes differ, particularly as far as amorphous and quartz content is concerned. The fly ash samples consist predominantly of an amorphous alumina silicate phase, which is higher in FCFA than in either UFA or MUFA. Mullite, the most abundant crystalline phase, occurs in comparable amounts. The haematite and quartz content of FCFA is, however, substantially lower than that of the other two ashes. The effect of milling UFA to produce MUFA decreased the mullite and quartz content slightly, accompanied by a concomitant increase of approximately 6% in the amorphous content, a result previously observed in the literature (Patil and Anandhan, 2012; Paul *et al.*, 2007). Based on mineralogical data composition,

FCFA should, by virtue of its higher amorphous content, be a more reactive and effective pozzolan (Kaur *et al.*, 2017). The composition of the Portland cement is typical of that produced in South Africa.

The morphology of the three fly ashes (Figure 2) indicates that spherical particles, which are known to improve particle packing density in mortar and concrete (Kearsley and Wainwright, 2003), are more predominant in FCFA than in either UFA or MUFA. Each of the specimens contained irregularly shaped particles, many of which are associated with mullite and quartz. The mechanically activated sample, MUFA, has a plethora of broken spheres as well as spherical particles seemingly unaffected by the milling process. Consequently, the remnants of the broken spheres may reduce the physical advantages associated with spherical morphology – namely, improved particle packing and lower water demand. This once again reiterates that, of the three, FCFA is expected to be the superior fly ash with regard to strength development. The validity of these statements relating to the contribution of these fly ashes towards compressive strength development is investigated in this study.

Characteristics of the fly ash surfaces exposed to a calcium hydroxide environment

It is important to bear in mind that within each fly ash sample examined there are countless individual particles, not one of which is identical in size, chemical composition and therefore ultimate reactivity to any of the others (van der Merwe *et al.*, 2014). Hence, the discussion and conclusions made in this aspect of the study only take into account the general trend observed during the FESEM imaging of a particular fly ash, and only relate to the overall predicted reactivity of the fly ash as manifested by changes in the topography.

It is postulated that the degree of alteration in the appearance and surface topography of fly ash spheres provides an indication of reactivity. Based on this assumption it is evident that, of the three fly ashes exposed to the saturated calcium

Table 1. Chemical composition (XRF, wt %) and mineralogical composition (XRD, wt % normalised) of the starting materials

	FCFA	UFA	MUFA	Cement		FCFA	UFA	MUFA	Cement
Silicon dioxide (SiO ₂)	50.09	54.83	54.87	20.36	Anhydrite	—	—	—	1.3
Aluminium oxide (Al ₂ O ₃)	34.35	30.86	31.11	4.73	Belite	—	—	—	7.7
Calcium oxide (CaO)	4.54	4.84	5.06	65.08	Alite	—	—	—	43.2
Iron (III) oxide (Fe ₂ O ₃)	3.09	3.62	3.83	2.80	Brownmillerite	—	—	—	12.9
Magnesium oxide (MgO)	1.28	1.17	1.19	1.78	Tricalcium aluminate	—	—	—	3.4
Potassium oxide (K ₂ O)	0.73	0.63	0.63	0.46	Calcite	—	—	—	9.9
Sodium oxide (Na ₂ O)	0.25	0.16	0.17	0.07	Gypsum	—	—	—	1.3
Titanium (II) oxide (TiO)	1.73	1.57	1.55	0.45	Haematite	0.3	1.0	0.8	—
Manganese oxide (Mn ₂ O ₃)	0.03	0.03	0.03	0.10	Mullite	28.9	31.5	27.5	—
Phosphorus pentoxide (P ₂ O ₅)	1.10	0.63	0.63	0.07	Quartz	3.7	12.2	10.3	0.8
Sulfur trioxide (SO ₃)	0.28	0.40	0.31	2.73	Amorphous	67.1	55.3	61.5	19.3
LOI	0.79	1.19	1.64	5.67		—	—	—	—

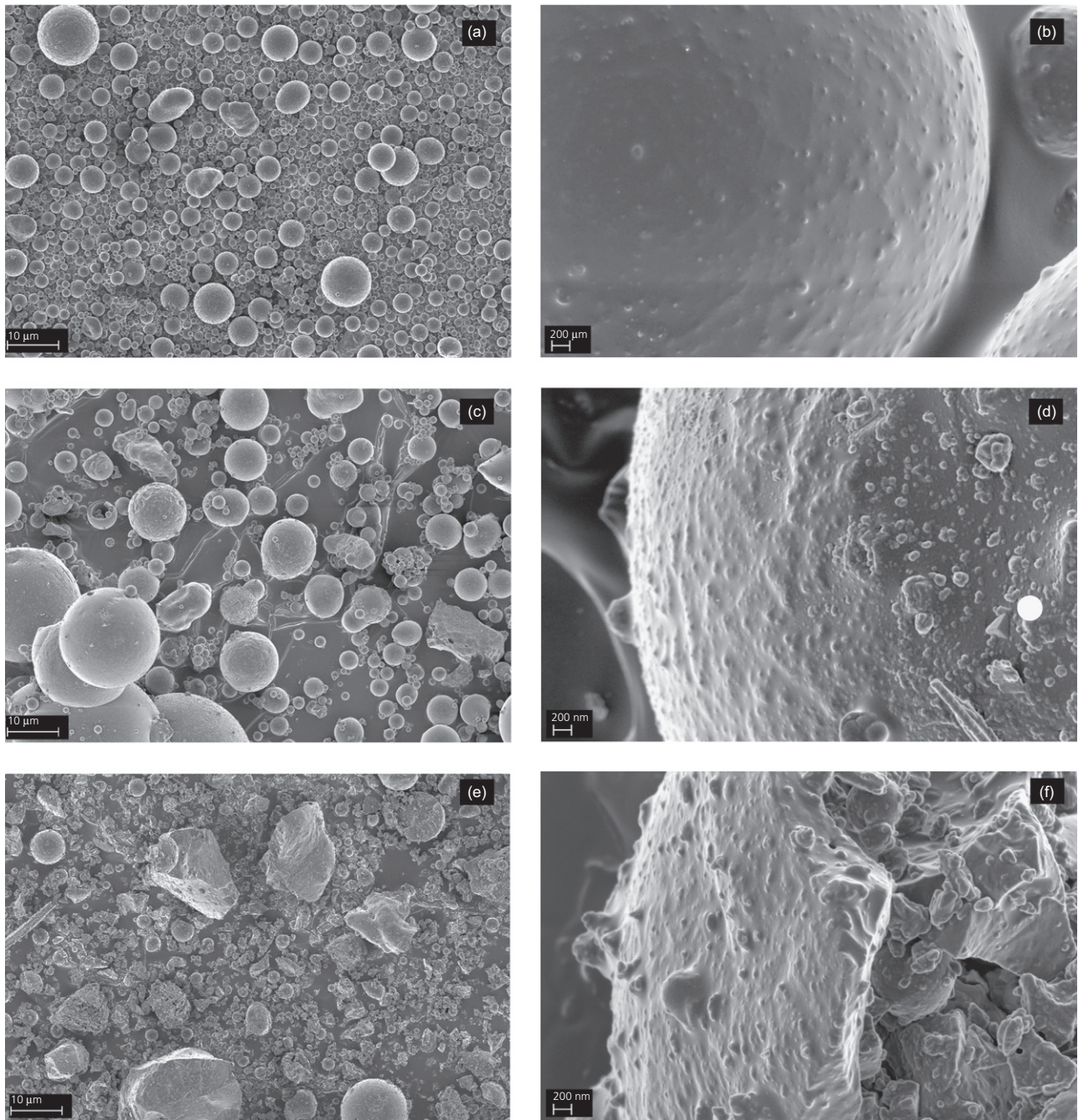


Figure 2. Scanning electron micrographs representing the morphology of untreated (a), (b) FCFA, (c), (d) UFA and (e), (f) MUFA

hydroxide solution, the surface of fly ash FCFA exhibited the least change (Figure 3). Even with the addition of chemical activation (Figures 3(b), 3(d), 3(f) and 3(h)), FCFA particles appear to be rather dormant. This suggests that it is relatively inert towards sulfate activation as well. Any compressive strength benefits that are realised from its utilisation in blended cement will most probably be ascribed to its contribution to improved physical properties, as discussed previously.

The appearance and surface topography of UFA (Figure 4), seems to suggest it is more susceptible to etching and therefore possibly more reactive. The etching to be seen on the surface after 7 d exposure to a saturated solution of calcium hydroxide containing 5% sodium sulfate could be an indication of its reactivity (Figure 4(d)). The reference sample, in which the specimen is exposed only to saturated calcium hydroxide, appears to be non-reactive, with very little, if any, surface

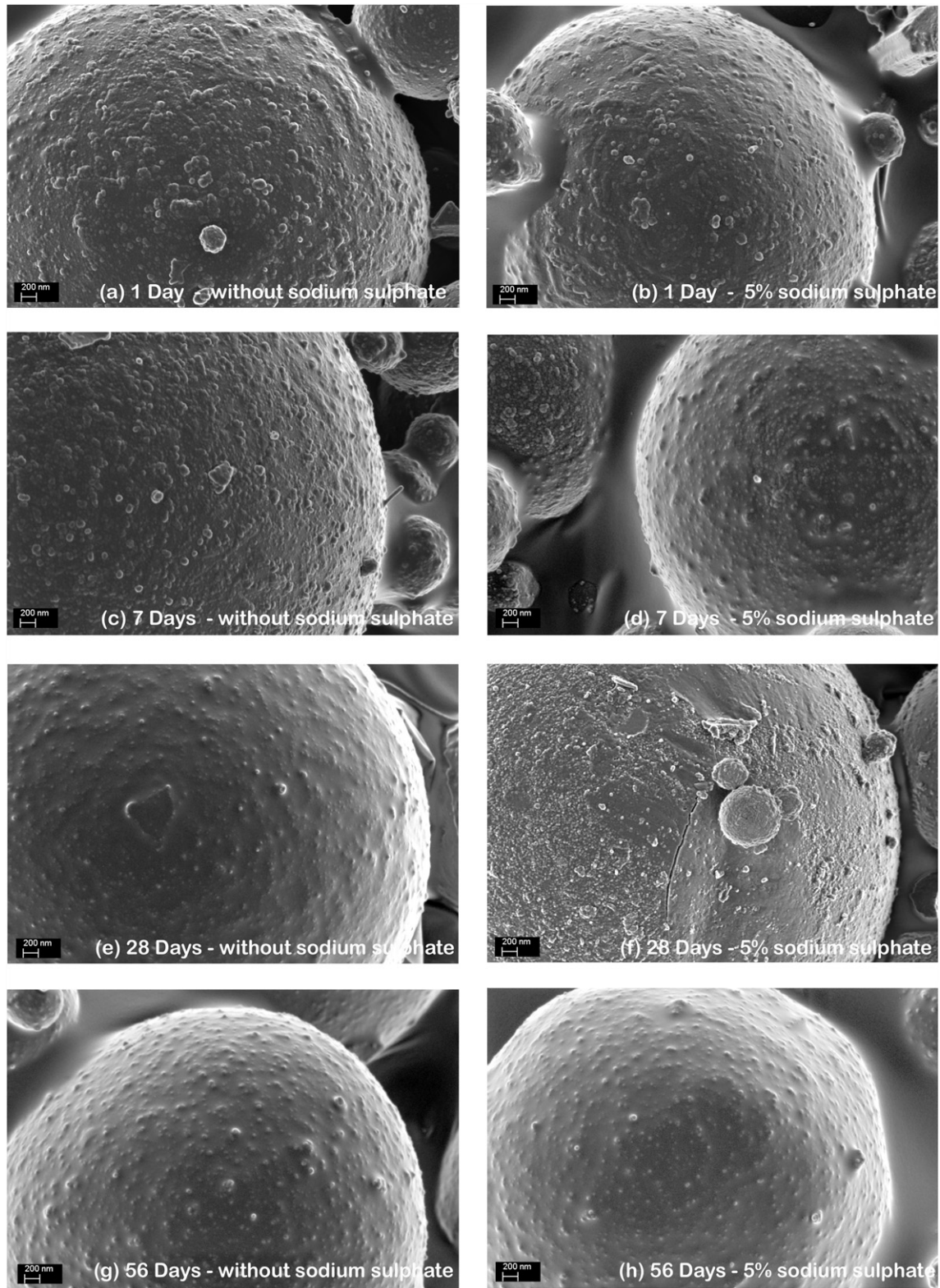


Figure 3. Morphology of FCFA after exposure (1 to 56 d) to a saturated solution of calcium hydroxide, with and without 5% sodium sulfate addition: (a) 1 d, without sodium sulfate; (b) 1 d, with 5% sodium sulfate; (c) 7 d, without sodium sulfate; (d) 7 d, with 5% sodium sulfate; (e) 28 d, without sodium sulfate; (f) 28 d, with 5% sodium sulfate; (g) 56 d, without sodium sulfate; (h) 56 d, with 5% sodium sulfate

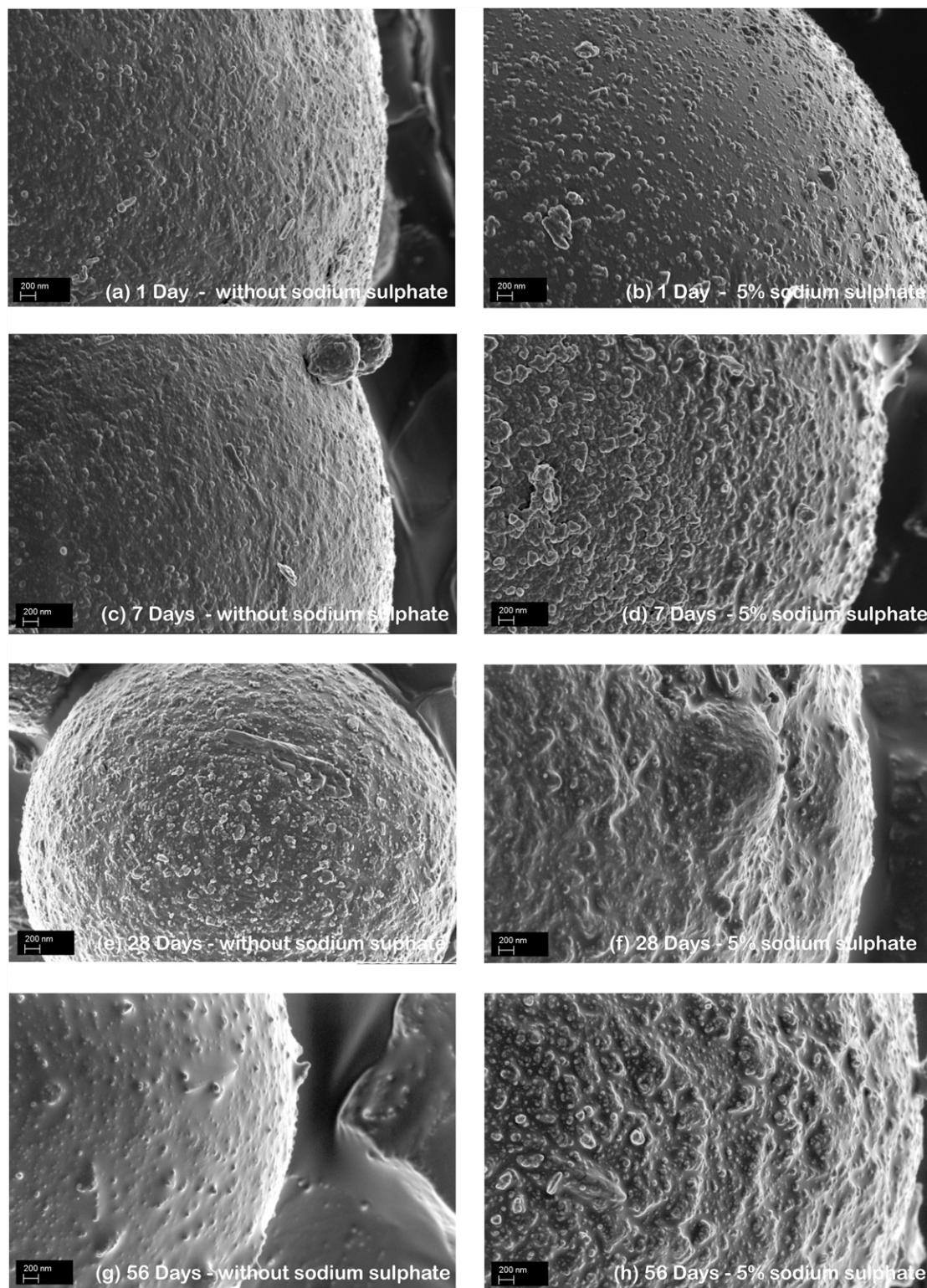
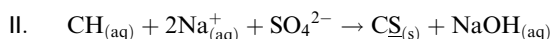
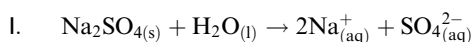


Figure 4. Morphology of UFA after exposure (1 to 56 d) to a saturated solution of calcium hydroxide, with and without 5% sodium sulfate addition: (a) 1 d, without sodium sulfate; (b) 1 d, with 5% sodium sulfate; (c) 7 d, without sodium sulfate; (d) 7 d, with 5% sodium sulfate; (e) 28 d, without sodium sulfate; (f) 28 d, with 5% sodium sulfate; (g) 56 d, without sodium sulfate; (h) 56 d, with 5% sodium sulfate

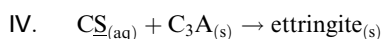
activity visible even after curing for 56 d (Figures 4(a), 4(c), 4(e) and 4(g)).

As can be seen in the micrographs (Figure 5), the situation changes quite significantly once the particles are mechanically activated (milled) (Figures 5(a), 5(c), 5(e) and 5(g)), and even more so when chemically activated with the addition of 5% sodium sulfate (Figures 5(b), 5(d), 5(f) and 5(h)). Some surface activity is already visible after 1 d on the mechanically activated reference sample (Figure 5(a)), and this continues throughout the curing process up to 56 d (Figure 5(g)). This activity appears in the form of a gel-like substance with some needle-shaped crystals on the surface of the particles.

Should the early-age hydration reactions of a fly ash-based hybrid cement, activated with sodium sulfate as hypothesised by Donatello *et al.* (2013), be applied, the following reactions may be possible within the fly ash–calcium hydroxide system. The reaction products will, however, be highly dependent on fly ash reactivity as well as calcium hydroxide and sodium sulfate concentration, in essence the availability of silica, aluminium, calcium and sodium in the system



Even though there is no cement present in this specific experimental environment, any dissolved aluminium and sulfate may react to form ettringite (Donatello *et al.*, 2013)



In this work the presence of ettringite was confirmed in some samples after being cured for 56 d (Figure 6). It was identified in FCFA specimens with and without the addition of sodium sulfate, as well as in UFA plus 5% sodium sulfate. However, the ettringite peaks are very small, indicating minor concentration. In the absence of any other source, it can be concluded that the required alumina was supplied by the fly ash. The XRD pattern of the 56 d specimens also indicated the presence of mullite and quartz as major crystalline phases, as well as a minor amount of calcite. Despite the presence of fractured needles in MUFA (Figures 5(d) and 5(f)), no ettringite needles were identified with XRD. It is possible that more ettringite may have existed at earlier curing ages; however, Equation II could have resulted in an increase in pH, which is known to

inhibit the formation of stable, well-crystallised ettringite. This may have resulted in ettringite not being detected by XRD (Donatello *et al.*, 2013). As was the case with UFA, the diffraction XRD patterns of the 56 d specimens also indicated the presence of mullite and quartz as the major crystalline phases, as well as a small amount of calcite as the minor crystalline phase.

Even though the mineralogical data of the fly ash products indicated that FCFA should be the most reactive, owing to it having the highest amount of amorphous alumina silica and the lowest amount of quartz, this is not evident from the etched surfaces observed in the FESEM images. In accordance with the results of the surface topography study, reactivity of the three fly ashes may be considered as follows: FCFA < UFA < MUFA. This result was unexpected and it was therefore necessary to carry out compressive strength tests on mortars at different curing ages to establish the validity of etching with calcium hydroxide as a means of predicting reactivity.

Mortar compressive strength of hybrid fly ash cement

During the production of hybrid cements, the fly ash content is constrained because of the low initial strength and subsequent slow strength development. This has been ascribed to the delay in pozzolanic activity (Hewlett, 2004). The strength development of the reference hybrid specimens produced without chemical activation is given in Figure 7. The graph shows the low early strength and slow rate of strength development for both the FCFA and UFA hybrids. The rate of strength development for MUFA is somewhat better, but by virtue of the manner in which it was procured (milling of UFA), it has in actual fact been mechanically activated. These results correlate with the observations made on the surface characteristics, which suggest that with FCFA having a larger surface area and being more amorphous, it should markedly improve the strength development characteristics of the hybrid cement. It is noteworthy that for all the hybrids the increase in strength between 1 and 365 d is around 94.5%. However, the graph also shows that the rates at which strength is gained differ significantly. The MUFA gains strength more rapidly and achieves a higher ultimate value. This behaviour is in agreement with the etching of fly ash surfaces exposed to calcium hydroxide. The strengths confirm that, without chemical activation, these 70% fly ash hybrid cements do not meet the minimum strength requirements of 16 MPa at 7 and 32.5 MPa at 28 d for a 32.5N cement (BSI, 2011).

Once chemical activation is applied, the strength of the FCFA (Figure 8(a)) hybrid increases along with increasing sodium sulfate content. This trend is only valid up to 90 d of curing with no significant strength gain for samples containing more than 1% sodium sulfate after 90 d. However, the strength continued to increase for 0% and 1% sodium sulfate addition between 180 d and 1 year of curing. Both the UFA

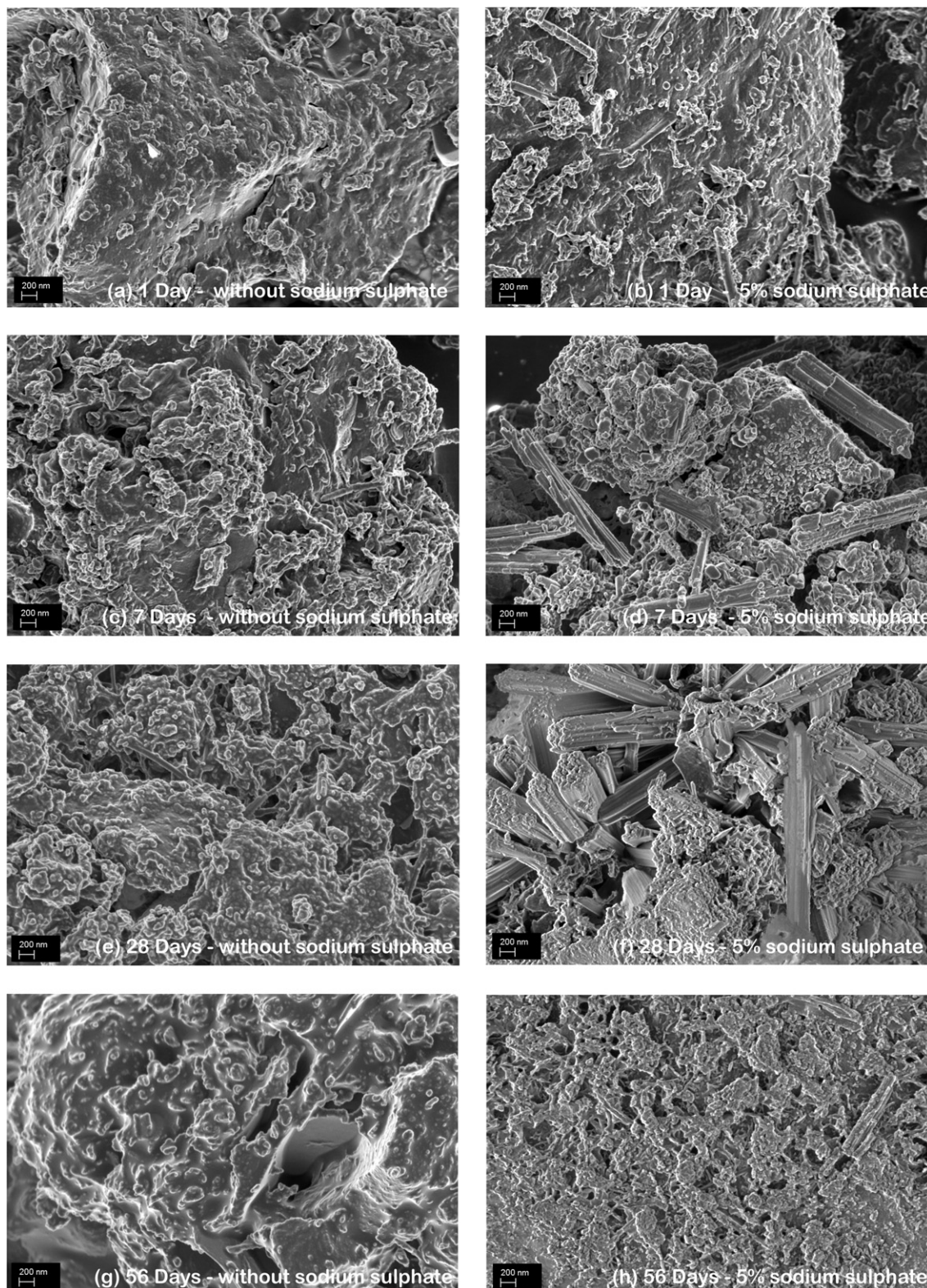


Figure 5. Morphology of MUFA after exposure (1 to 56 d) to a saturated solution of calcium hydroxide, with and without 5% sodium sulfate addition: (a) 1 d, without sodium sulfate; (b) 1 d, with 5% sodium sulfate; (c) 7 d, without sodium sulfate; (d) 7 d, with 5% sodium sulfate; (e) 28 d, without sodium sulfate; (f) 28 d, with 5% sodium sulfate; (g) 56 d, without sodium sulfate; (h) 56 d, with 5% sodium sulfate

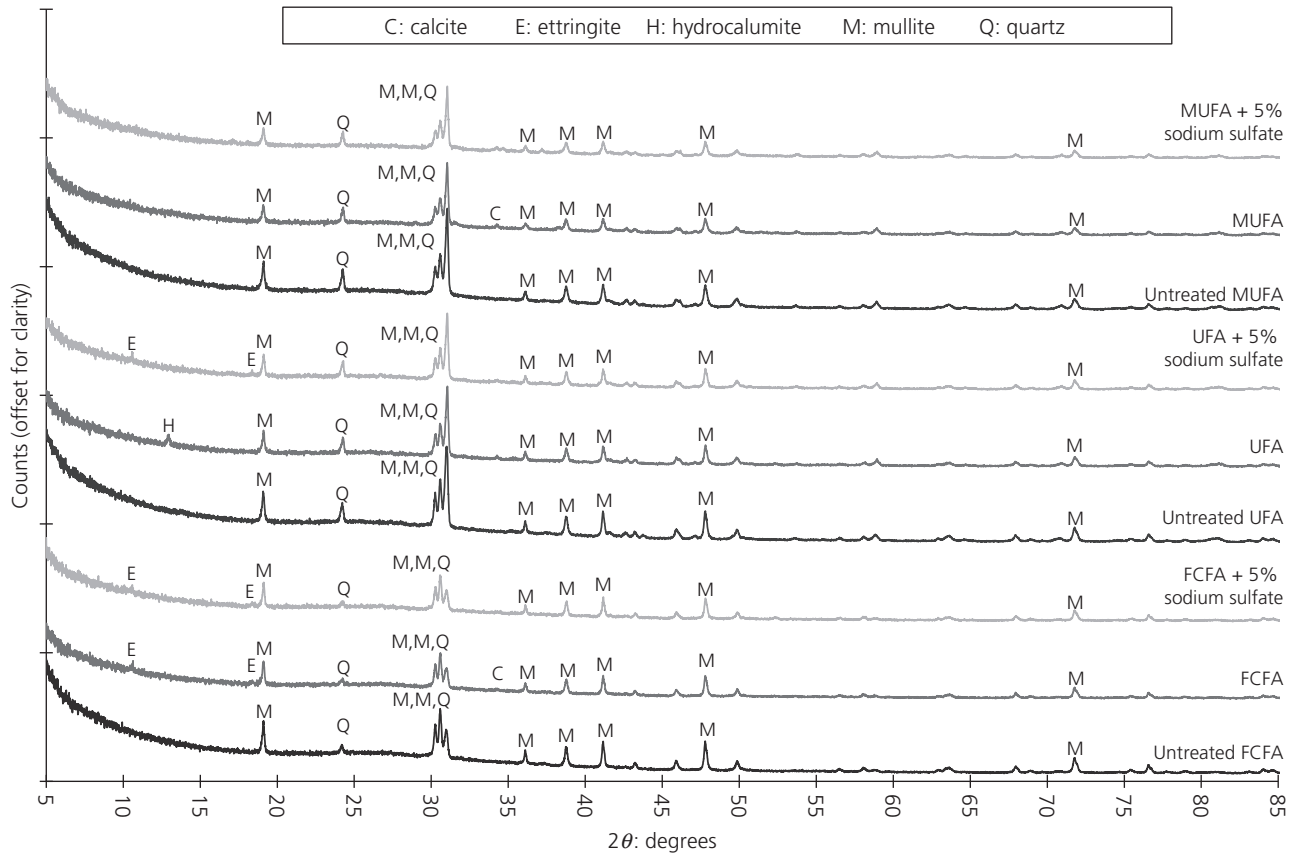


Figure 6. XRD phase identification of 56 d fly ash specimens exposed to a calcium hydroxide environment

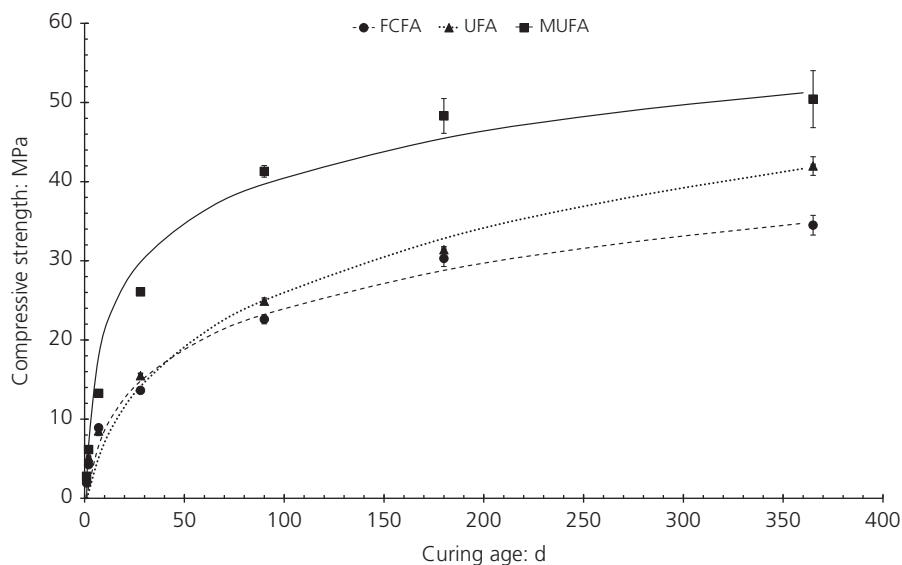


Figure 7. Mortar compressive strength of the reference fly ash cement hybrids (without sodium sulfate) produced from FCFA, UFA and MUFA ($n = 6$)

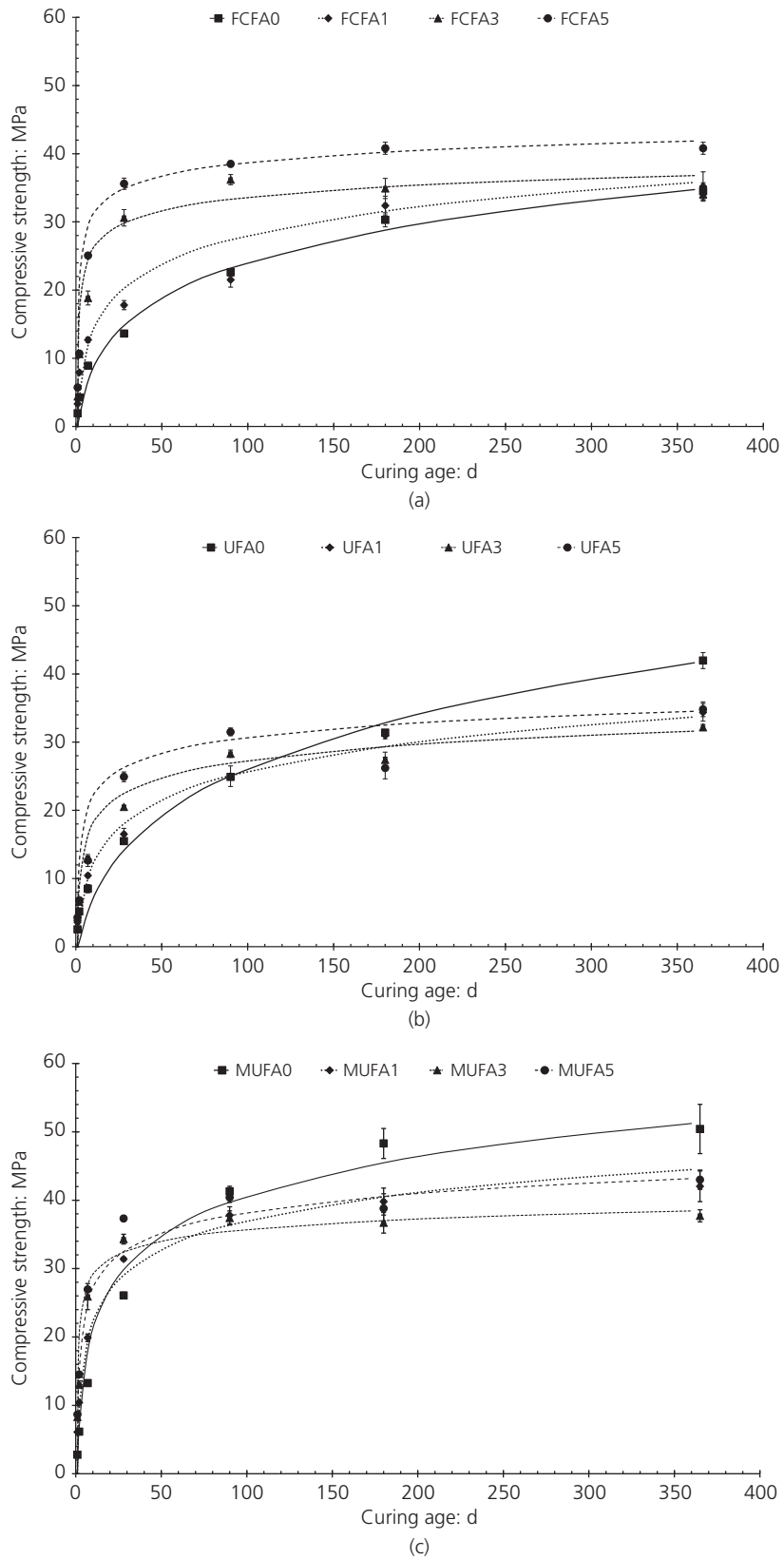


Figure 8. Mortar compressive strength of the fly ash cement hybrids produced from (a) FCFA, (b) UFA and (c) MUFA for up to 1 year of curing ($n=6$)

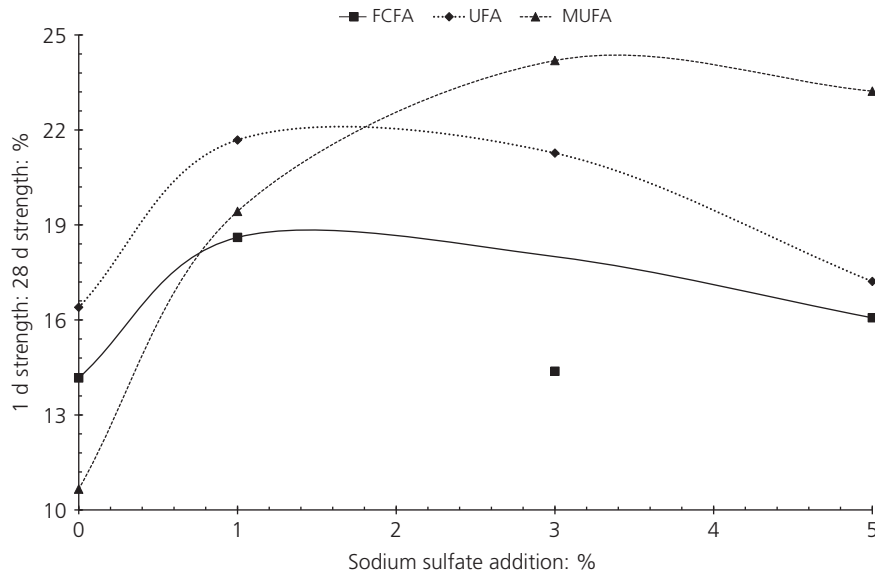


Figure 9. The 1 d strength expressed as a percentage of the 28 d strength of the fly ash cement hybrids produced from FCFA, UFA and MUFA

(Figure 8(b)) and the MUFA hybrids (Figure 8(c)) show similar, but less pronounced, initial trends in strength development to that of the FCFA hybrid with increasing sodium sulfate addition. For all curing ages the strength of the MUFA hybrid was higher than for both the FCFA and UFA hybrids. This trend also correlates with the work done by Qian *et al.* (2001) where the combination of grinding and addition of sulfate gave higher strength than any single activation method investigated. It should, however, be noted that for the MUFA hybrid (Figure 8(c)) the strength reached by the reference specimen (mechanically activated, 0% sodium sulfate) at 180 and 365 d exceeds that reached by the specimens where mechanical and chemical activation are combined. This was also true in the case of UFA at 365 d of curing. Hence, if high long-term strength (365 d) is required, mechanical activation of unclassified fly ash, without the addition of chemical activation, could be considered. The MUFA hybrid was the only blend that produced compressive strengths that complied with a 32.5R (rapid early strength gain) product criteria of BS EN 197 cement specification, at both 3% and 5% sodium sulfate addition. The strength development specified by the EN standard requires a minimum strength of 10 MPa at 2 d 32.5 MPa at 28 d. Even after activation, the unclassified fly ash hybrid did not produce any products complying with this cement specification, affirming once again the rationale behind the combination of chemical and mechanical activation.

Figure 9 provides a different depiction of the strength gained between 1 and 28 d. This graph expresses the 1-to-28 d strength ratio for each of the hybrids at the four levels of sulfate addition. These results indicate that the addition of sodium sulfate is a suitable activation method for increasing early-age

strength (after 1 d). For both the FCFA hybrid and the UFA hybrid, the highest early age strength is achieved when 1% sodium sulfate is added to the mix formulation of these hybrids. The most significant increase in strength was achieved when 3% of sodium sulfate activator was used in the preparation of the MUFA hybrid cement. This confirms once again that the combination of chemical and mechanical activation yields the best strength results.

Conclusions

- Curing fly ash in a saturated calcium hydroxide solution serves as a viable, easy and cost-effective method to evaluate surface properties of fly ash.
- Despite its favourable particle shape distribution and mineralogy, the FCFA proved not to be the most chemically reactive of the three fly ashes considered. Strength development in hybrid cement containing FCFA is likely to be attributable to physical and not chemical contributions.
- The MUFA hybrid achieved the highest compressive strength results at all curing ages considered.
- Considering the strength specifications of BS EN 197, FCFA only produced one product complying with a 32.5N cement after 5% sodium sulfate was added. The UFA hybrid, even after chemical activation, did not produce any strengths complying with the BS EN cement specification. The MUFA hybrid was the only blend that produced compressive strengths that comply with a 32.5R (rapid early strength gain) product according to BS EN 197, at both 3% and 5% sodium sulfate addition.

- The combination of mechanical and chemical activation (sodium sulfate) can be considered a valuable technique to address low early strengths and slow strength development, resulting in hybrid cements that comply with the EN 197 cement strength requirements.

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