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Effect of grinding on early age performance of High Volume Fly Ash ternary blended pastes with CKD & OPC

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Abstract

This study investigated setting times and early age compressive strength of the high volume fly ash (HVFA) blended pastes prepared with ground materials. The pastes consisted of 60% Fly Ash + 30% Portland cement (CEM I) + 10% cement kiln dust (CKD) and tests were carried out for four different fly ashes. In phase 1, all the constituent binder materials (class F-fly ash, CEMI and CKD) were initially mixed in the relevant proportions and were ground for varying time periods (1, 2 and 4 hours). In phase 2, the CEM I and CKD were mixed and ground for different time periods (1 and 2 hours) and then added to the unground fly ash. Both wrapped and submerged curing were used for compressive strength test samples. Overall, grinding of constituents appeared to be largely ineffective at increasing 2 day compressive strength although strength enhancements at 28 days were generally observed. Paste samples that were made from interground constituents generally achieved higher 28 day strengths than corresponding pastes where only the activators were ground, although this was not consistent throughout so further investigation is suggested in this area. Submerged curing is generally less effective in increasing compressive strength than wrapped curing as leaching of CKD is suspected to have occurred.

Keywords: CKD, intergrinding, separate grinding, particle size distribution (PSD), HVFA ternary pastes

Introduction

Use of high volume fly ash (HVFA) concrete has numerous performance benefits as well as the obvious economic and environmental benefits. Incorporating high volumes of fly ash within a mix improves mix cohesion, reduces heat of hydration, reduces permeability and increases resistance to alkali silica reaction. However, the pozzolanic reaction occurs relatively slowly and therefore increases setting times and reduces the initial rate of strength gain. Increased setting times means that more time has to be allowed before removal of formwork and propping, which would lead to delays and increased formwork costs. The overall aim of this project is to reduce setting times and increase the early age strength of concrete containing high volumes of fly ash. Previous work [1] investigated use of cement kiln dust (CKD) as an activator for fly ash and examined proportioning of binder constituents. The optimum binder proportioning established is investigated within the current study with mechanical grinding of binder constituents to instigate further early age strength enhancements.

Review of previous work

Effect of particle size

Erdogdu and Turker [2] tried to interpret the strength of Portland cement – fly ash mortars in terms of the chemical, mineralogical, morphological, and physical properties of different fly ash size fractions. They found that finer fraction groups resulted in higher compressive strength and that using < 45µm ashes gave higher strength than the original ashes containing all size fractions, at all ages tested. For the low lime fly ash tested, the difference in chemical composition between the various size fractions was negligible so the strength enhancement was primarily attributed to particle size (although the same could not be confirmed for the high lime fly ash tested). They calculated equivalent strength from a weighted average (based on the particle size distribution of the original ashes) of the strengths from the various size fractions and found that calculated strengths were lower than measured strengths for both of the original ashes at all ages. This is attributed to the uniform grading distribution in the various size fractions leading to increased porosity in the mortars. The importance of grading of ash particle size for compressive strength gain was highlighted.

Chindaprasirt et al [3] investigated fineness of fly ash through sieving and separation using an air classifier. Sieving produced two graded fly ash portions, finer than 75 µm and finer than 45 µm. Separation produced “single size” portions with 65% of the original ash in the “coarse” portion, the next finest 25% in the “medium” portion and the finest 10% in the “fine” portion. Mortars produced with 40% of fly ash samples generally required less water for a given flow than for an equivalent Portland cement mortar. The water demand of mortar made using < 45 µm ash was greater than for < 75 µm ash due to the increase in the surface area of the finer particles. 3 day compressive strength of mortars made with < 75 µm ash and < 45 µm ash increased relative to the original ash by 35% and 74% respectively. Mortars made with separated ash portions with varied water content based on the consistencies observed 3 day strengths 26% lower for coarse, 43% higher for medium and 117% higher for fine portions relative to the mortar with the original ash. Blaine fineness was measured for all ash portions and the fineness of the graded < 45 µm ash was similar to the medium separated portion. However, the compressive strength of the graded < 45 µm ash was appreciably higher as it included fine particles (unlike the medium separated portion), which again emphasizes the importance of ash particle size grading.

In a separate investigation, Chindaprasirt et al [4] examined compressive strength and pore structure of two Class F fly ash portions of median size, 19.1 µm and 6.4 µm. A Mercury intrusion porosimeter was used to measure porosity and average pore diameter within the pastes. The total porosity was consistently lower for the finer ash at all ages and the average pore diameter was smaller as a result of better dispersing and packing of the finer particles. These observations were in agreement with observed higher compressive strengths of the finer ash.

Kiattikomol et al [5] investigated the effect of ash fineness through both separation using an air classifier and grinding. They established that there was no significant difference in compressive strength of mortars made with classified or ground fly ashes of similar median particle size. They found that the strength activity index of mortars for a given test age increased with increasing ash fineness. For example, mortars made with ash of median size of 30 µm achieved an activity index of 80% after 14 days but mortars from ash with a median size of 15 µm achieved the same strength after only 3 days. Between 7 and 14 days, ≈ 3% increase of strength activity index was observed when using fly ash with d_{50} = 30 µm, while < 10% increase of strength was observed during the same period for an ash of d_{50} = 2 µm. They also found that when the fineness of each fly ash was increased, mortar setting times reduced.

Aydin et al [6] studied strength of mortars with cement replacement levels up to 60% with unground and ground fly ash. They reported a 3 day strength of 18.1 MPa when the ash was ground to 907 m^2/kg, which was substantially higher than the 6.0 MPa strength recorded for the unground ash (290 m^2/kg). They also examined the effect of various curing regimes and found that higher replacement levels were more sensitive to choice of curing method. Air curing was found to cause a 43% reduction in 28 day compressive strength (relative to standard water curing) for the mortar including 60% of the ground ash, which highlights the importance of appropriate curing.

Effect of grinding time

Grinding of cementitious materials is very expensive and energy intensive so investigation of various grinding times is merited with a view to establishing a minimum grinding time beyond which, no significant improvement in paste performance will be observed. Paya et al [7] investigated grinding times for fly ash and reported a 62% reduction in median diameter after 20 minutes but just a further 15% reduction up to 60 minutes. They reported that fly ash particles with diameter greater than 30 µm were easily crushed using a laboratory mill and the percentage of particles > 30 µm after 30 minutes of grinding was negligible. The specific gravity of the ground particles increased, primarily due to the crushing of cenospheres and porous carbon particles. They found that the grinding process caused fly ash particles to become less spherical, thereby lessening their potential for reducing water demand of a concrete mix.

Felekoglu et al [8] studied the effect of grinding on strength activity and on water demand of ground high-calcium fly ash. They observed a 6% reduction in 2 day compressive strength due to grinding for 43 minutes but this was attributed to the 6% increase in water content to achieve a constant mortar workability. They noted that the change in water demand due to grinding is heavily dependent on initial ash particle shape, surface morphology and porosity. They suggested an optimum fineness of 480 m^2/kg for the high calcium ash that they tested where the reactivity of the ash was increased but without significantly increasing the specific area and therefore the water demand.

Paya et al [9] tested compressive strength of mortars containing 60% fly ash and 40% cement within the binder at a curing temperature of 20°C for a range of grinding periods for the ash. They found an increase in 3 day compressive strength of 8.8% for 10 minutes of grinding and 27.5% for 60 minutes of grinding (relative to the 3 day strength of the mortar containing unground ash). Corresponding strength developments at 28 days were 16.8% and 48.1% for 10 minutes and 60 minutes of grinding respectively.

Bouzoubaa et al [10] investigated the effect of grinding fly ashes over a 10 hour period. They observed that the main increase in specific gravity occurred up to two hours due to the crushing of plerospheres and cenospheres. Blaine fineness continually increased over time with the main increase occurring within the first two hours (126%, 53%, and 67% increases in fineness after two hours for the three ashes tested and 272%, 146% and 116% after ten hours). Water demand initially decreases due to crushing of plerospheres but increases after four hours due to an increase in irregular shaped particles. Peak strength activity index was recorded after four hours of grinding and this corresponds with the observed trough in water demand.

Wang et al [11] investigated various activation methods including intergrinding on blends of 50% Class F fly ash and 50% CKD. For the unground blend, 14.9% was retained on a 45 µm sieve but this reduced to 0.11%, 0.04%, and 0% after two hours, four hours and six hours of grinding respectively. Although particle size reduction essentially ceased beyond two hours of grinding, further grinding was thought to increase the amorphous phase content of the material. 3 day strength of pastes increased by 28% and 164% relative to the unground blend after six hours and twelve hours of grinding respectively. The marked increase in strength up to twelve hours of grinding is largely attributed to mechanochemical activation whereby particle surface modification increases surface free energy, making the particles more reactive.

Bouzoubaa et al. [12] carried out an initial series of tests on fly ash – cement binders and used Blaine fineness as a control measure for grinding duration used. However, when comparing the particle size distribution curves of blended cements with laboratory produced Portland cement for a given Blaine fineness, it was found that in the low particle size range (< 5 µm) the blended cements were coarser, whereas for the high particle size range the reverse is true. They found that although the grinding time for the blended cements to achieve a particular Blaine fineness was shorter, their compressive strength was lower and they attributed this to coarser clinker particles.

Intergrinding or separate grinding of constituents

Bouzoubaa et al [12] carried out a second series of tests on fly ash – cement binders where the effect of both grinding fly ash and cement separately and intergrinding for a period of four hours was investigated. They reported that adding ground fly ash to cement gave consistently higher compressive strengths of mortars than for unground fly ash with 1 day strength increases of 27% - 46%. Observed increases in Blaine fineness of the ash due to grinding correlated well with observed strength increases with greater strength increases observed for originally coarser ashes. Compressive strength of mortars when fly ash and cement were interground were noticeably higher (than for equivalent mixes where the ash and cement were ground separately) for two of the three ashes tested with minimal change in strength for the third ash. The general increase in strength due to intergrinding is largely attributed to the improved homogeneity of the binder although it is acknowledged that further investigation in this area would be beneficial.

Ghiasvand et al [13] suggested that intergrinding binder constituents can influence the relative content of each constituent in different size fractions. For example, a component that is hard to grind becomes concentrated in coarse fractions and vice versa. They investigated inter-grinding and separate grinding on the properties of mortars and concretes made from a Portland cement – Trass blend and observed that intergrinding produced finer particle size distributions in all cases. Cement paste consistency and setting times were found to be unaffected by grinding approach (intergrinding or separate grinding). However, compressive strengths were consistently higher for interground samples (e.g. for 35% cement replacement, 7 day strengths were 7.5% - 9.5% higher for interground constituents).

Erdogdu et al [14] investigated intergrinding and separate grinding of 75% cement with 25% natural pozzolan and found that separate grinding consistently produced an equal or larger amount of material above a given sieve size. This effect was more pronounced for greater mill energy consumption (i.e. longer grinding periods). 2 day strengths of separately ground pastes were 94% of interground pastes of equivalent Blaine fineness but the difference in strength decreases with age. This was attributed to the overall coarser particle size distribution and lower homogeneity of the separately ground blend.

Ryou [15] blended 65% cement kiln dust (CKD) with 35% fly ash and examined the effect of grinding separately or intergrinding over various periods of time. When comparing blends ground separately or together for the same time period (of 4 hours), he observed that the mean particle size was smaller and a greater proportion was passing a 0.45 µm sieve when the constituents were ground separately. Initial paste setting times were also 27% shorter for the ground separately blend.

Bentz et al [16] suggested that one limitation of the cement manufacture industry is that Portland cement is optimized for use as a pure cement as opposed to within a blended cement. Their approach was to optimize the particle sizes of cement and fly ash to maximize strength of the blended product and found that using a finer cement (with a similar ash size) generally gave a higher early age strength but the magnitude of the increase reduced as the replacement level increased. They found that blending a finer cement with a relatively course ash boosted early ash strength without significantly affecting the overall particle size distribution and therefore water demand for a particular workability. Therefore, although the majority of literature available suggests that intergrinding the constituent materials enhances early age strength, Bentz's study highlights the beneficial effects of grinding the cement only.

Significance of the current study

From the review of previous work in this area, most studies of cement and fly ash binders focus on fly ash levels only up to 50%. Only one study, Wang et al. 2007, has investigated intergrinding of CKD and fly ash (without cement clinker). In this study, no setting time measurements were recorded so any effect that grinding has on setting time cannot be evaluated. They also did not examine the effect of separate grinding of the activator on compressive strength or grinding efficiency in relation to median particle size or compressive strength. The significance of this work is to study if grinding can be effective in reducing setting times and increasing early age strength of pastes containing high volumes of fly ash with CEM I and CKD and to evaluate parameters such as intergrinding vs. activator only grinding, grinding duration and curing condition.

Experimental work

In this study, four different class F fly ash samples, Portland cement (CEM I) and cement kiln dust (CKD) were ground for varying time periods. The powder proportions were taken from the optimum proportions (60% fly ash, 30% CEM I and 10% CKD) established in previous work [1]. The chemical composition of the raw materials was determined using X-ray fluorescence (XRF) carried out using a PAN analytical Axios Advanced XRF spectrometer and the resulting oxide proportions are given in Table 1. The density, Blaine fineness and percentage retained on a 45 µm sieve for the raw materials were determined in accordance with BS EN 196-6 and these physical properties are presented in Table 2. Particle size distribution of the raw materials (Figure 1) was carried out using a Malvern Mastersizer 2000 with a Hydro MU sampler and the median particle size established is also included in Table 2.

In phase 1 of the experimental work, all the constituent binder materials (class F-fly ash, CEMI and CKD) were initially mixed in the relevant proportions and were ground for varying time periods (1, 2 and 4 hours), based on the observations from references [12 – 14]. In phase 2, the CEM I and CKD were mixed and ground for varying time periods (1 and 2 hours) and then added to the unground fly ash, in line with observations from Bentz [16] where only the activator material was ground. Grinding took place in a laboratory scale ball mill and 3 kg of each of 12 mm, 18 mm and 24 mm diameter grinding media was used to grind 3 kg of powder. Where intergrinding of all constituents took place, grinding continued for one hour, two hour and four hour durations and where only the activators (CEM I and CKD) were ground, grinding durations of one hour and two hours were used. Measurement of particle size distribution of the blends was also carried out once grinding was complete. Also, the morphology of the ground powders was assessed from scanning electron microscopy (SEM) images taken by a JOEL 6060LV Scanning Electron Microscope.

Paste mixes were prepared for blends of both the unground and ground constituents using a Hobart style mixer. All powder materials were initially dry mixed to ensure homogeneity (if not already premixed through the grinding process). Water was subsequently added with a water to binder ratio of 0.3 used throughout the experimental programme. A portion of the paste mixture was used to measure initial and final setting time in accordance with BS EN 196-3. From each paste mix, eighteen 50 mm cubes were cast to measure compressive strength. The specimens were compacted in three layers using a vibrating table, covered in plastic sheeting and left to set for 24 hours. Samples were then demoulded and nine of the samples were submerged under water maintained at 20°C. The remaining nine samples were shrink-wrapped with plastic sheeting and kept in a moist curing container with water beneath the mesh that the samples were placed on. These samples were kept at approximately 20°C and 90% relative humidity until required for testing. This curing regime was selected to ensure that no leaching occurred due to the presence of CKD as an activator, which may be the case for submerged curing. 2 day, 7 day and 28 day compressive strength was determined, taken as the average of three samples for each test age and curing regime. Note that strengths for the pastes with unground particles were measured for wrapped curing only and these results are shown in the relevant graphs to provide a frame of reference. Subsequent to compressive strength testing, pieces of the crushed samples from selected mixes were retained for assessment of paste chemical composition by XRF analysis.

Results and discussion

When presenting and discussing results, the following coding system is used:

UG = unground (i.e. original raw materials)

IG = interground (i.e. blending fly ash, cement and CKD in the relevant proportions and then grinding)

AG = activator grinding (i.e. blending cement and CKD in the relevant proportions, grinding and then mixing with the unground fly ash)

0 / 1 / 2 / 4 = time of grinding in hours
FA1 / FA2 / FA3 / FA4 = fly ash sample based on information given in tables 1 and 2
W / S = wrapped / submerged curing regime

For example, IG-1-FA2 is referring to the powder blend or resulting paste mix where fly ash 2 was interground with cement and CKD in the relevant proportions for 1 hour.

<u>Fineness and particle shape</u>

Table 3 shows the specific gravity and median particle size for all interground samples of fly ash, cement and CKD and also for samples of cement and CKD that were ground in the relevant proportions before being blended with the unground fly ash. The variation in specific gravity between interground samples containing different fly ashes generally correlated with the specific gravity of the raw materials as expected (e.g. ash 2 had a significantly higher specific gravity than the other ashes and interground samples containing this ash had higher specific gravity values). For fly ash 1, 3 and 4, the specific gravity of interground blends tended to increase with prolonged grinding. This can be attributed to crushing of low-density cenospheres exposing higher density wall material and plerospheres liberating small dense particles. However, for fly ash 2, a slight reduction in the interground blend specific gravity was observed for increasing grinding time, which suggests fly ash 2 contains denser, solid particles that are resistant to fragmentation and contains few cenospheres and plerospheres.

When evaluating the effect of grinding duration on median particle size values from Table 3, particle size generally appeared to decrease after one hour of grinding. From the grinding efficiency diagrams (Figure 2), the minimum particle size was achieved after one hour for ash 1, 3 and 4 and after two hours for ash 2. Further grinding was not effective due to agglomeration of the particles or overgrinding of the softer material with the harder material. These two effects meant that particle size did not reduce further with increased grinding time. To investigate this further, sample particle size distribution plots for interground blends made with ash 1 and ash 2 were produced and plots for the corresponding unground blends were included (Figure 3). The unground blend was coarsest throughout the range and the largest reduction in particle size occurs near the coarse end of the range in both cases. As can be seen for interground blends made with ash 1 and ash 2, D90 changed from 62.5 µm to 45.5 µm and 37.7 µm respectively while D10 did not change significantly. This is largely attributed to crushing of hollow cenospheres within the fly ash. Felekoglu et al [8] emphasize that small particles within raw fly ash are naturally more reactive due to their rapid rate of cooling during processing and that reduction in coarse particle size should be prioritized. Looking specifically at the coarser end of the range, the fineness of the ground blend achieved was virtually identical for all three grinding durations, which suggests that grinding beyond one hour is largely ineffective.

Figure 4 shows particle size distribution plots when grinding the activators only (i.e. 75% CEM I + 25% CKD) and again includes the corresponding unground blend. Grinding caused a reduction in particle size throughout the range. D90 reduced from 48.9 µm to 41.7 µm and median particle size changed from 20.5 µm to 13.0 µm while D10 had a reduction from 4.7 µm to 2.0 µm. These are all large reductions considering the percentage size reductions. Therefore, reduction in activator particle size has contributed to the observed reduction in the interground blends. Again, there appeared to be little benefit to grinding beyond one hour for activator only grinding.

Figure 5 compares particle size distribution plots for unground blends with one hour interground blends and one hour activator ground blends (after being blended with unground fly ash). For both ash 1 and ash 2, only a slight reduction in particle size was observed for activator only grinding at the coarse end of the particle size range caused by a reduction in particle size for CEM I and more particularly, the coarse CKD particles. As expected, intergrinding caused a more significant reduction in particle size at the coarse end of the range as the fly ash (which constitutes 60% of the material by mass) was included in the grinding process. However, when considering the finer end of the particle range for blends with both ashes presented, grinding the activator only produced a slightly finer overall blend. This is largely attributed to grinding of CKD particles, which was more effective when the CKD constitutes 25% of the material being ground when only the activators were ground.

Figure 6 shows SEM images of the individual raw materials. Visual comparison of the different types of fly ash shows that ash 1 and ash 3 are more porous with more coarse particles than ash 2 and ash 4 (which correlates with observations from PSD curves). It is apparent that all fly ash samples contain spherical particles whereas CEM I has irregular shaped particles and CKD particles have a spongy appearance. Figure 7 shows SEM images for interground blends made with ash 1 and ash 2 for varying time periods. For both ashes shown, the porosity of the blend after two hours and four hours of grinding appears to be lower than for one hour of grinding. However, the most uniform and dense blend seems to result after two hours of grinding. Having said that, some relatively large spherical fly ash particles are still apparent from the images, even after four hours of grinding. Figure 8 shows activator only ground powders prior to addition of the unground fly ash. By comparing these images to those for the raw CEM I and CKD, it is apparent that the porosity of the activator reduces with increased grinding time. This generally correlates with observations from the relevant PSD curve, Figure 4.

Setting times

Figure 9a shows initial and final setting times for the pastes with unground constituents and corresponding pastes with interground constituents. For all four fly ashes, initial and final setting times were consistently longer for increasing grinding times. Similar trends were observed for pastes with ground activators and unground fly ash (Figure 9b) although shorter setting times than for equivalent interground pastes were generally observed. The shortest setting times were generally recorded for pastes with the finest particles after one hour of intergrinding or activator only grinding. These observations agree with the findings from Kiattikomol et al [5] and Ryou [15] where setting times reduced with increasing particle fineness. The current investigation used a water to binder ratio of 0.3 based on consistence of pastes with unground constituents from previous work [1]. However, Kiattikomol et al [5] used water binder ratios of 0.67 – 0.73 and Ryou [15] used a water binder ratio of 0.5. Felekoglu et al [8] found that increasing fineness of fly ash increases water demand caused by the increase in specific surface of ash particles. It is acknowledged that the shape of the particles also affects the water demand. Grinding produces fine angular and fragmented particles which tends to increase water demand but Chindaprasirt et al. [3] found that the use of fine fly ash reduces the water requirement of the mortar mix if the fine fly ash surface is smooth. In this study the water to binder ratio of 0.3 showed enough water for having a fluid mix based on the observation. However, where grinding is being used to increase reactivity of binder constituents, the increased fineness of the constituent particles should be taken into account when selecting an appropriate water to binder ratio.

Compressive strength of pastes

Figure 10 compares 2 day, 7 day and 28 day compressive strengths of the pastes with unground constituents to the corresponding strengths for interground blends ground for varying time periods. Figure 10a shows results for wrapped cured interground pastes and Figure 10b show results for submerged cured pastes. The submerged cured samples were taken out of the curing tank 24 hours before crushing so that the specimen condition was similar to the wrapped cured samples for strength measurement. The strengths for unground pastes were measured for wrapped curing as a frame of reference and the highest strength for the unground pastes at different ages was for ash 2, which was the ash with the smallest median particle size and highest density. When examining wrapped curing results, grinding appeared to have a negligible or a negative effect on 2 day strengths. Apart from ash 2, samples after one hour and two hours of intergrinding achieved similar strengths to the unground sample. Over time, the main increases in strength were typically observed between 7 and 28 days. Longer term strengths generally appear to increase up to two hours of intergrinding but a decrease in strength is observed for continued grinding up to four hours. This agrees with grinding efficiency diagrams (Figure 2) which show the minimum median particle size resulted for around two hours of grinding. Observed strengths generally correlated well with the fineness of interground blends. For submerged curing, increasing grinding time generally appeared to increase 2 day strength. However, as with wrapped cured samples, two hours of intergrinding appeared to be the optimum duration to maximize 7 day and 28 day strength.

Figure 11 compares 2 day, 7 day and 28 day compressive strengths of the pastes with unground constituents to the corresponding strengths of pastes with ground activators and unground fly ash. When examining 2 day strength results for wrapped cured pastes (Figure 11a), grinding of the activators appeared to have mixed effects. For two hours of activator grinding, increases in 2 day strength (relative to the corresponding control paste) were observed for ash 1, ash 3 and ash 4. The median size of the ground activators was lower than these ashes (Tables 2 and 3), which makes the activators more reactive to increases the rate of dissolution of fly ash at early age. However, as with the corresponding interground samples, a reduction in 2 day strength relative to the control was observed for the ash 2 paste due to grinding of constituents as the median size for ash 2 was lower than the ground activators. The effect of activator grinding on 7 day strengths was relatively low but increased activator grinding time generally tended to increase 28 day strengths. However, for a given grinding duration, interground samples (that were wrapped cured) generally achieved higher 28 day strengths than activator only ground samples. This is in line with observations from Bouzoubaa et al [12] and Ghiasvand et al [13]. For the corresponding submerged cured samples (Figure 11b), observations in relation to 2 day strengths were similar to those for the wrapped cured samples. However, longer term strengths are more sporadic and no clear trend is evident. For submerged curing, the beneficial effect of intergrinding (as opposed to activator only grinding) on 28 day strength was not as evident as it was for wrapped curing.

When comparing strength results from the different ash sources, the 2 day strength of the control paste made with ash 2 is appreciably higher than for the remaining ashes (16.36N/mm^2 compare to others which were 9.57 to 11.11N/mm^2) (Figure 10). This links to the observations made above that grinding of constituent materials appears to reduce the 2 day strength of samples made with ash 2. With the exception of the coarse end of the range for ash 4, ash 2 is notably finer than the other ashes throughout the particle range, Figure 1, which goes some way towards explaining those observations. As can be seen in Figure 12, there is little variation in 7 day strengths for the control pastes but the 28 day strength of the paste made with ash 4 is notably lower than for the other ashes.

As stated above, submerged curing led to higher 2 day strengths for interground samples but the curing regime had minimal effect on 2 day strengths for activator only ground samples. However, wrapped curing generally appeared to be more effective than submerged curing at increasing 28 day compressive strength for all pastes. This is apparent from Figure 13 which shows correlations between compressive strength and median particle size for wrapped cured and submerged cured samples. Compressive strength tended to decrease at all ages with increasing median particle size as would be expected. However, 28 day strengths of submerged cured samples did not follow this trend. Kunal et al [17] emphasise that many phases in CKD are unstable or highly soluble and may dissolve completely upon contact with water. Therefore, leaching of CKD may have occurred for submerged cured samples over the 28 day curing period and hindered compressive strength gain.

Chemical analysis of cementitious products

XRF analysis was carried out on crushed paste samples from 28 day testing for selected mixes and results are shown in Table 4. In this investigation, CKD was used as an activator and the water-soluble alkalis (Na_2O+K_2O) that are responsible for the activation of fly ash are shown in Table 4. Comparing this information with the initial proportion of alkalis content in the mixes (can be calculated by multiplying the oxide content of individual raw materials (Table 1) by the proportion of the raw materials in a given mix (i.e. 60% fly ash, 30% CEM I and 10% CKD) and then calculating the total. The result shows that 70% to 86% of alkalis in CKD contributed to the activation of fly ash. Overall, the variation in oxide composition between control pastes and the corresponding pastes that include ground constituents is relatively low. Therefore, any observed changes in paste behaviour due to grinding are primarily attributable to physical changes in particle size and shape. An indication of the level of reactivity can be established by comparing the proportion of calcium content observed in the paste samples (Table 4) to the total proportion of calcium content in the original mixes. The initial proportion of calcium content in the mixes can be calculated using the same process as for the alkalis content. The percentage of reacted calcium content was calculated for selected mixes and is presented at the bottom of Table 4. When comparing interground with activator only ground pastes for ash 1 and ash 2, activator only ground pastes showed higher proportions of reacted calcium content. It should be mentioned that the reacted fly ash in different formulation gives rise to the calcium silicate hydrate and alkali calcium silicate hydrate gels in different cases.

Conclusions

Within the current investigation, the following conclusions can be reached:

1. When examining PSD curves of ground constituents, grinding beyond one hour is not effective at reducing particle size.
2. The shortest setting time for interground blends pastes seems to occur for the finest blend but the setting time for equivalent activator only ground pastes are generally shorter.
3. When examining compressive strength values, two hours of grinding appears to be the optimum grinding duration which suggests that mechanical activation induces further strength enhancements beyond one hour of grinding.
4. Grinding of constituents appeared to be largely ineffective at increasing 2 day compressive strength but generally enhanced 28 day compressive strength.
5. 2 day strengths of activator only ground pastes were slightly better than for equivalent interground pastes, particularly when the median particle size of the ground activators was less than that for the unground fly ash.
6. Paste samples that were made from interground constituents generally achieved 18% to 40% higher 28 day strengths than corresponding pastes where only the activators were ground, and this trend was more apparent for the wrapped curing regime.
7. Submerged curing is generally less effective in increasing compressive strength than wrapped curing as leaching of CKD is suspected to have occurred.

Table 1: Relative oxide contents and loss on ignition (LOI) of raw materials

Oxides	Fly ash 1	Fly ash 2	Fly ash 3	Fly ash 4	CEM I	CKD
SiO_2	52.15	51.16	56.62	58.70	19.63	15.46
TiO_2	0.87	1.01	0.93	1.030	0.26	0.23
Al_2O_3	19.61	24.34	22.21	27.96	4.71	3.80
Fe_2O_3	7.10	10.17	5.96	4.28	3.25	2.55
MnO	0.07	0.05	0.05	0.04	0.09	0.08
MgO	2.00	1.46	1.79	1.23	1.17	0.97
CaO	4.40	2.79	5.69	2.24	64.09	54.18
Na_2O	1.06	1.28	0.83	0.71	0.27	0.56
K_2O	1.93	2.57	1.95	2.13	0.73	4.90
P_2O_5	0.45	0.35	0.38	0.33	0.20	0.15
SO_3	0.54	0.26	0.61	0.29	2.94	3.84
LOI	9.48	4.35	2.98	1.00	3.22	13.25
Total	99.66	99.79	100.00	99.94	100.56	99.97

Table 2: Physical properties of raw materials

Material	**Density (g/cm^3)**	**Fineness (cm^2/g)**	**Retained on 45 µm sieve (%)**	**Median particle size (µm)**
Fly ash 1	2.37	3987	15.6	20.1
Fly ash 2	2.72	3657	12.6	12.5
Fly ash 3	2.37	4110	15.3	19.4
Fly ash 4	2.33	3741	2.8	15.9
CEM I	3.21	3495	4.8	19.3
CKD	2.77	2454	20.5	26.7

Table 3: Specific gravity and median particle size of unground and ground blends

Sample type	**Specific gravity**	**Median particle size (µm)**
IG-0-FA1	2.66	20.5
IG-1-FA1	2.66	15.7
IG-2-FA1	2.63	17.7
IG-4-FA1	2.70	18.9
IG-0-FA2	2.88	15.9
IG-1-FA2	2.74	12.8
IG-2-FA2	2.73	12.3
IG-4-FA2	2.71	14.1
IG-0-FA3	2.67	20.1
IG-1-FA3	2.66	15.1
IG-2-FA3	2.63	17.0
IG-4-FA3	2.71	18.2
IG-0-FA4	2.64	18.0
IG-1-FA4	2.62	13.9
IG-2-FA4	2.60	14.7
IG-4-FA4	2.67	16.1
AG-1*	3.06	14.7
AG-2*	3.08	13.7

* prior to adding unground fly ash (i.e. 75% CEM I + 25% CKD only)

Table 4: Relative oxide content, loss on ignition (LOI) and percentage of reacted fly ash in cementitious products

Oxides	UG-0-FA1	IG-2-FA1	AG-2-FA1	UG-0-FA2	IG-2-FA2	AG-2-FA2	UG-0-FA3	AG-2-FA3	UG-0-FA4	AG-2-FA4
SiO_2	35.34	40.91	36.43	34.30	35.51	35.41	38.59	38.67	39.30	39.31
TiO_2	0.59	0.56	0.59	0.65	0.67	0.68	0.66	0.65	0.70	0.71
Al_2O_3	12.22	11.73	12.47	14.43	15.02	15.19	14.09	14.04	17.06	17.06
Fe_2O_3	4.62	4.41	4.61	6.09	6.62	6.31	4.29	4.30	3.33	3.32
MnO	0.04	0.04	0.04	0.04	0.06	0.04	0.04	0.04	0.03	0.03
MgO	1.49	1.39	1.46	1.19	1.24	1.19	1.40	1.39	1.09	1.07
CaO	26.36	22.55	24.48	26.55	23.97	24.56	25.37	25.46	24.18	23.84
Na_2O	0.61	0.63	0.61	0.74	0.75	0.78	0.56	0.54	0.48	0.47
K_2O	1.28	1.56	1.24	1.78	1.80	1.88	1.61	1.63	1.74	1.71
P_2O_5	0.28	0.27	0.28	0.22	0.25	0.23	0.25	0.25	0.22	0.22
SO_3	2.17	1.98	1.68	2.64	1.81	2.07	1.71	1.94	1.68	1.66
LOI	14.61	14.02	16.16	11.36	12.40	11.84	11.31	11.08	10.08	10.46
Total	99.61	100.05	100.05	99.99	100.10	100.18	99.88	99.99	99.89	99.86
Reacted	96.60	82.63	89.70	100.87	91.07	93.31	90.41	90.73	93.04	91.73

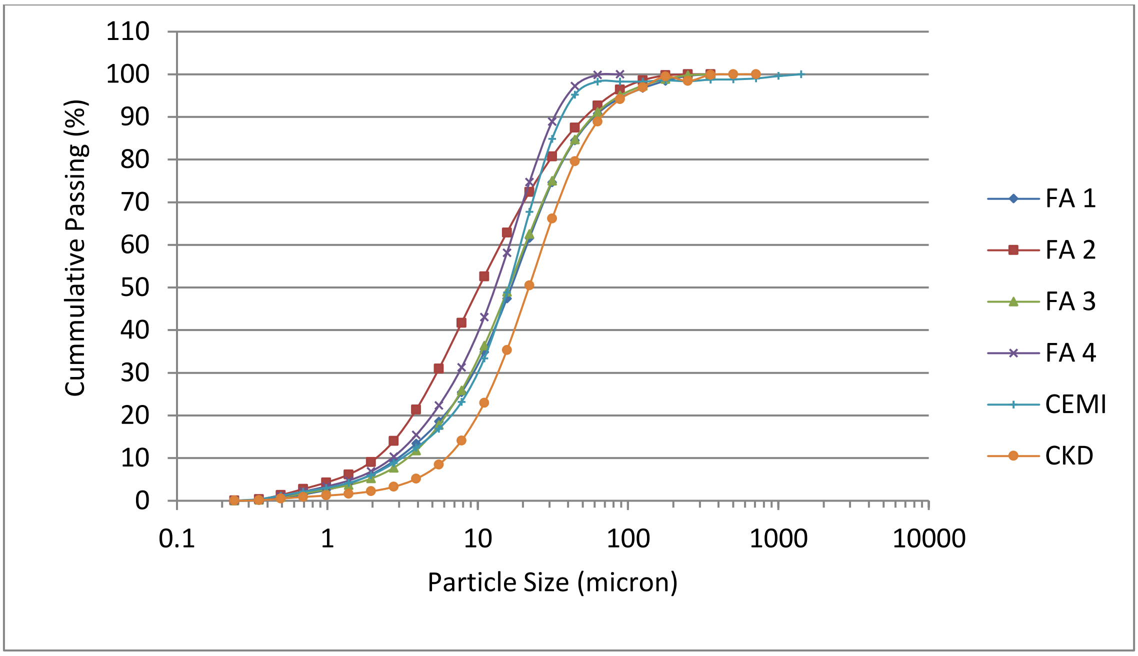


Figure 1: Particle size distribution plots for raw binder materials

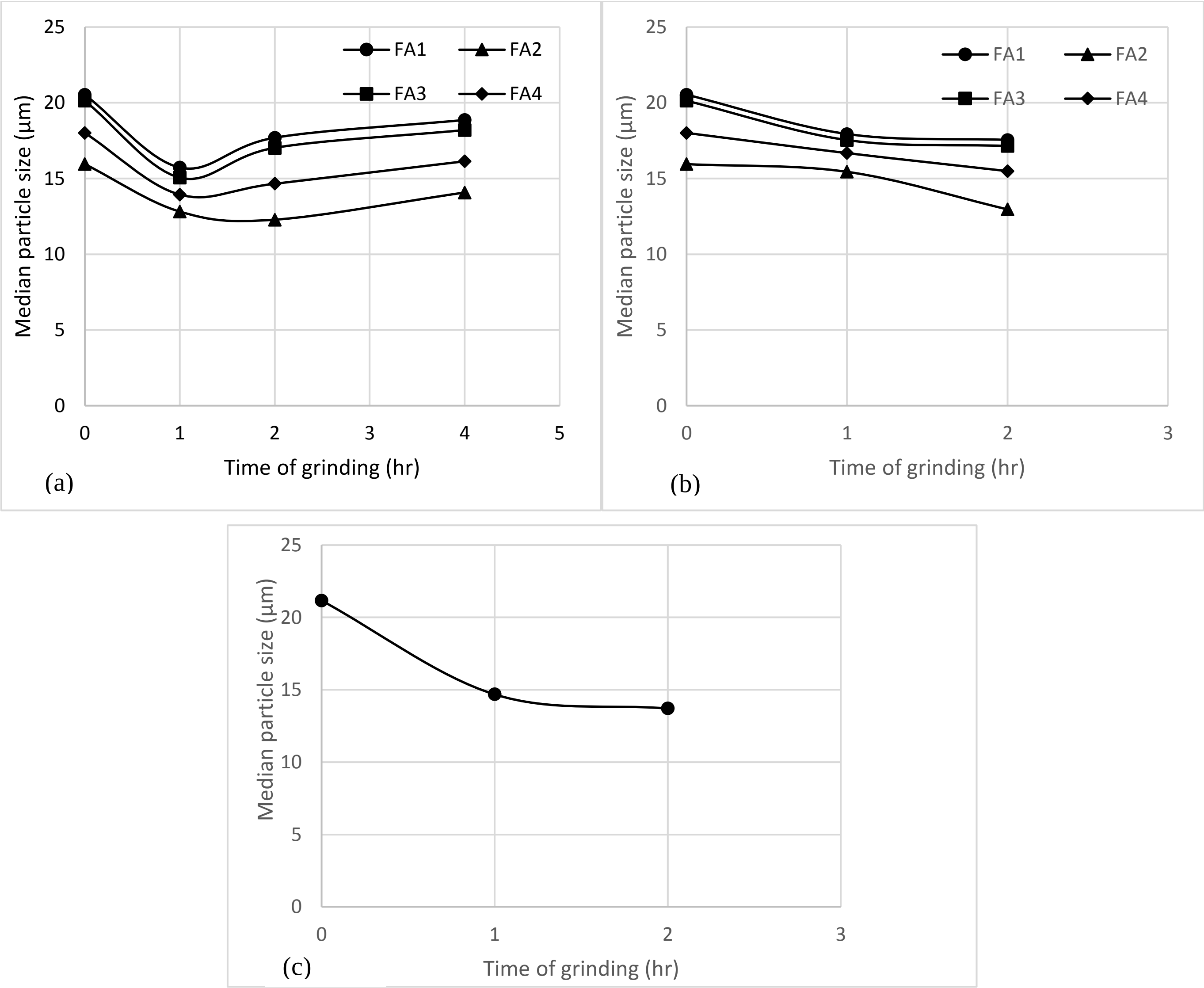


Figure 2: Grinding efficiency diagram (a) interground blends (b) activator ground blends (c) activator ground alone

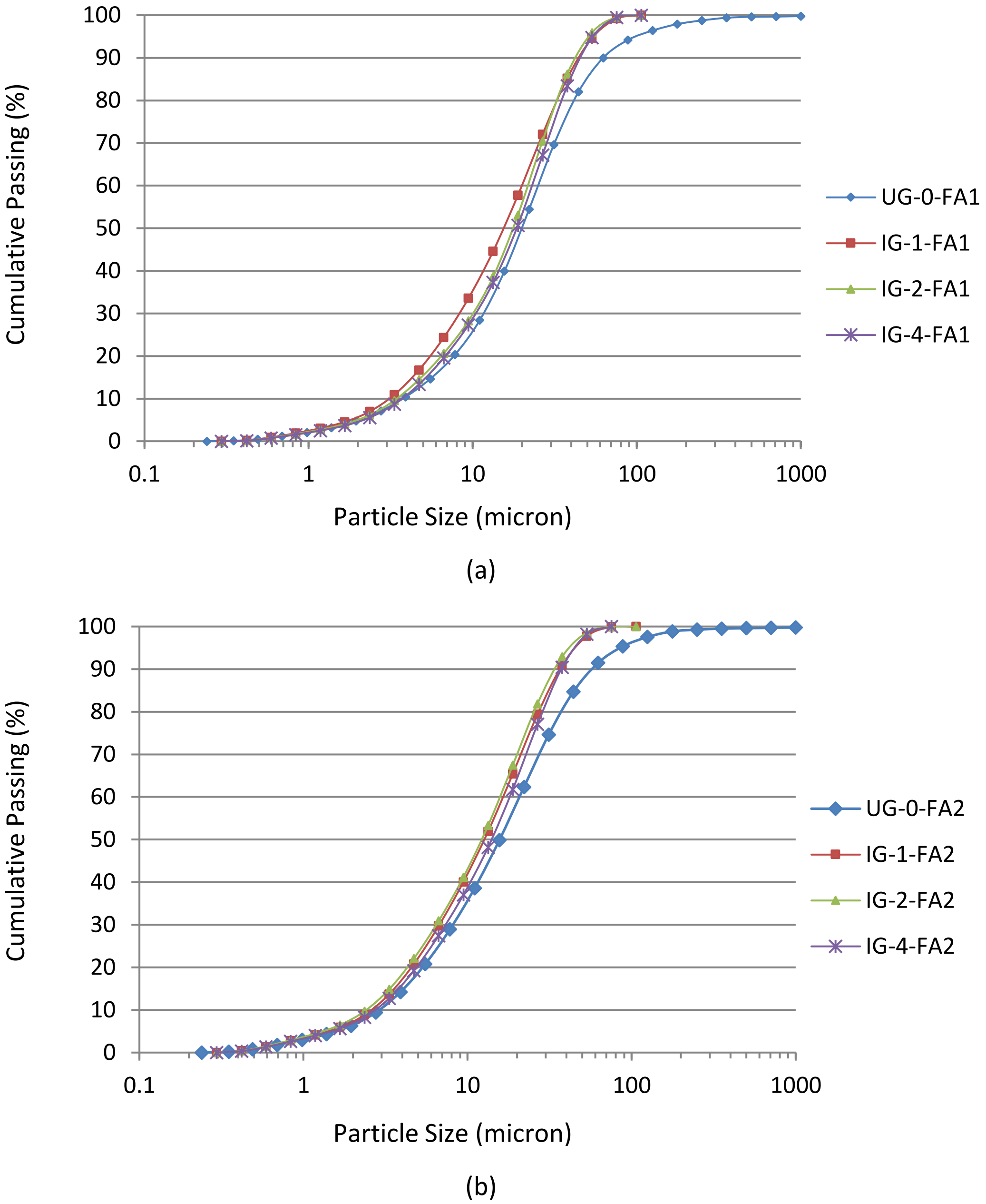


Figure 3: Particle size distribution plots for interground blends made with (a) fly ash 1 and (b) fly ash 2 ground for varying time periods

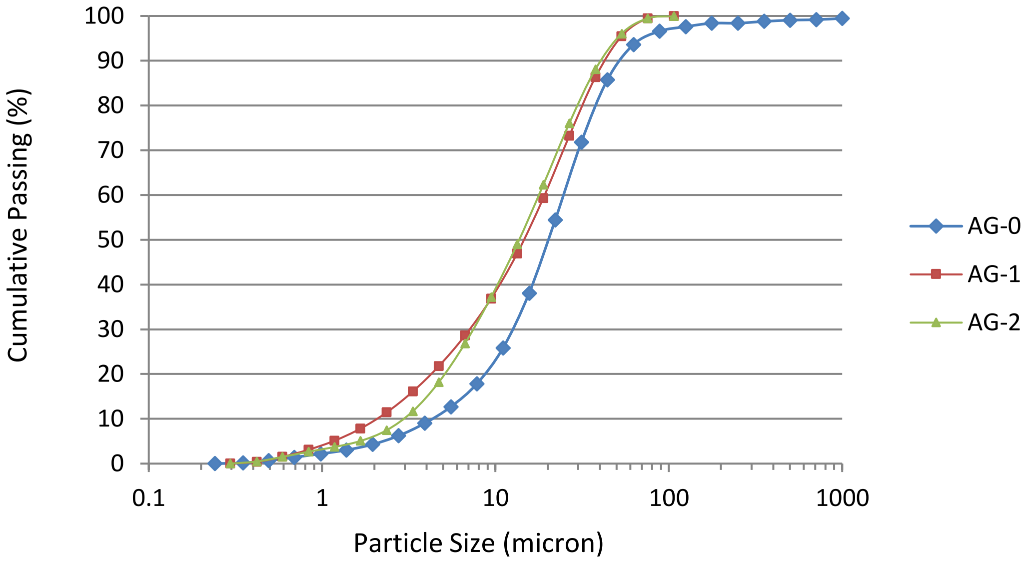
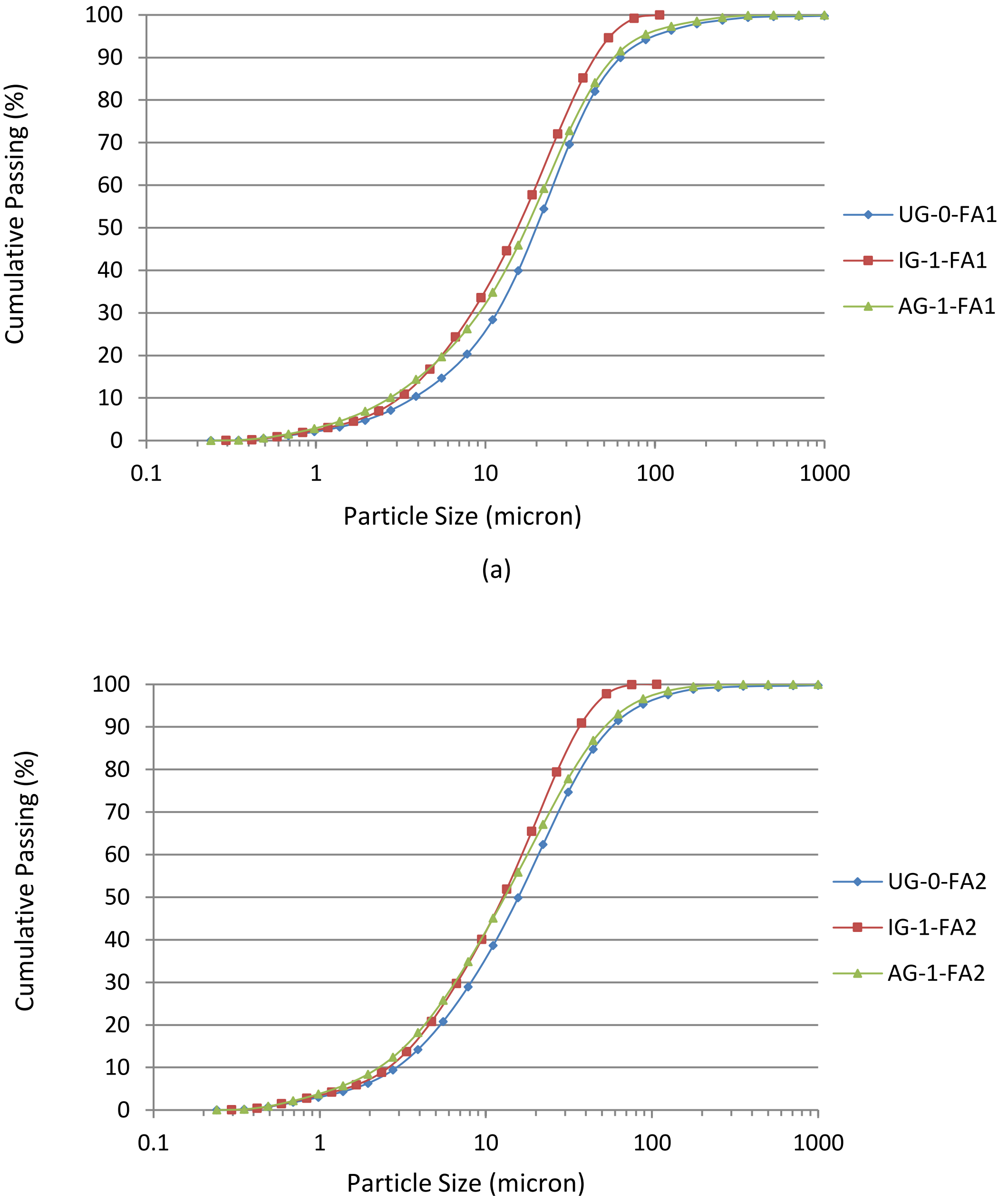


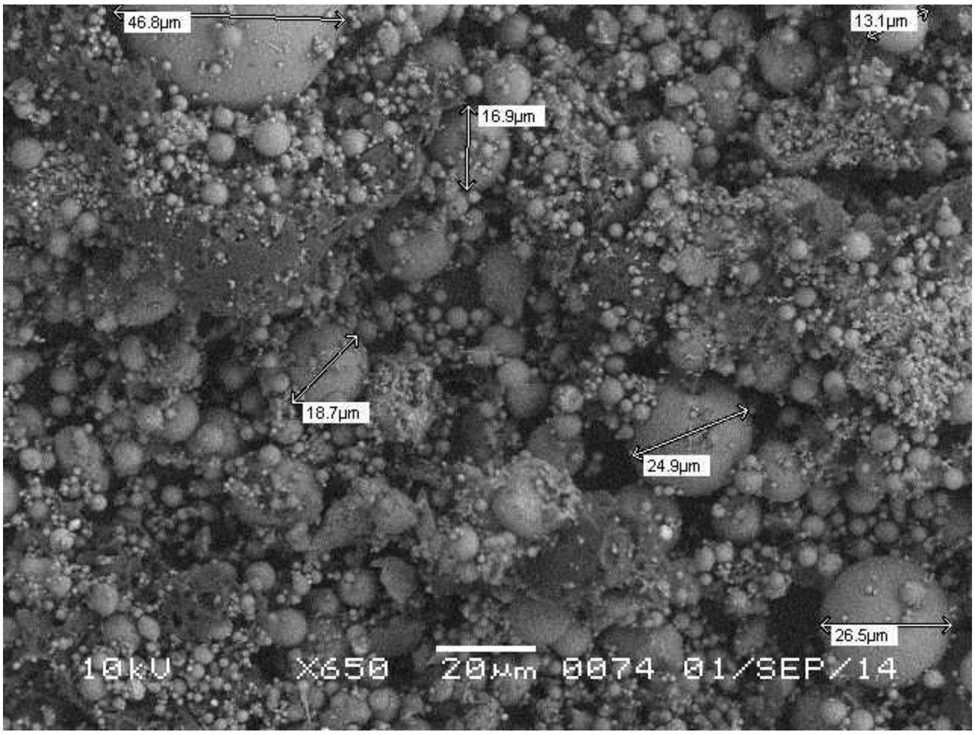
Figure 4: Particle size distribution plots for activator ground blend (i.e. 75% CEM I + 25% CKD) for varying time periods



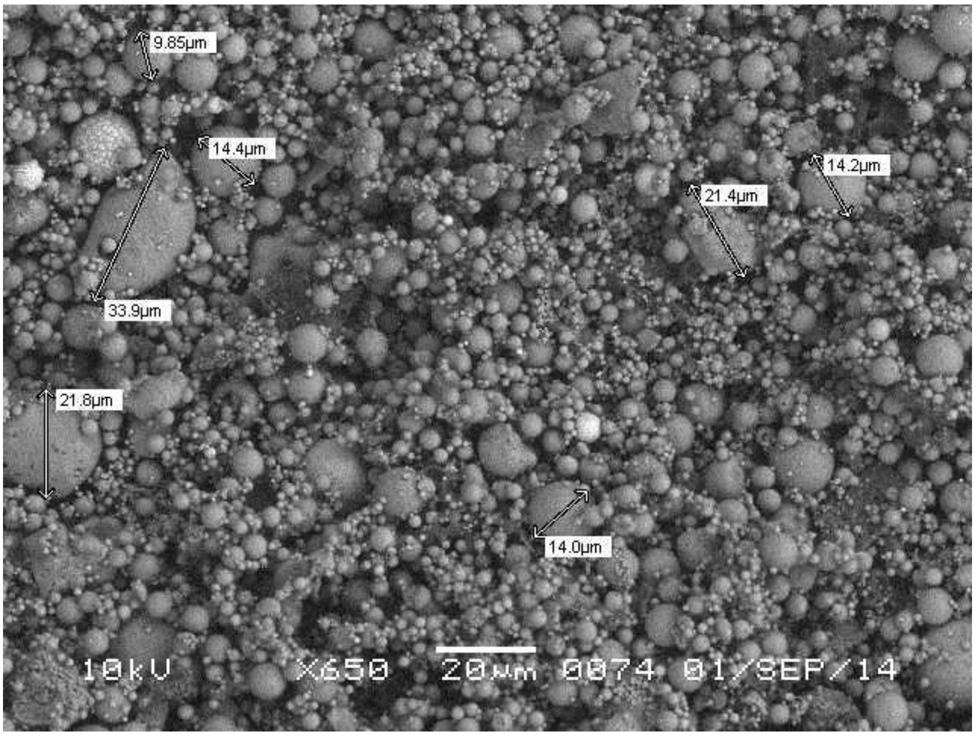
(a)

(b)

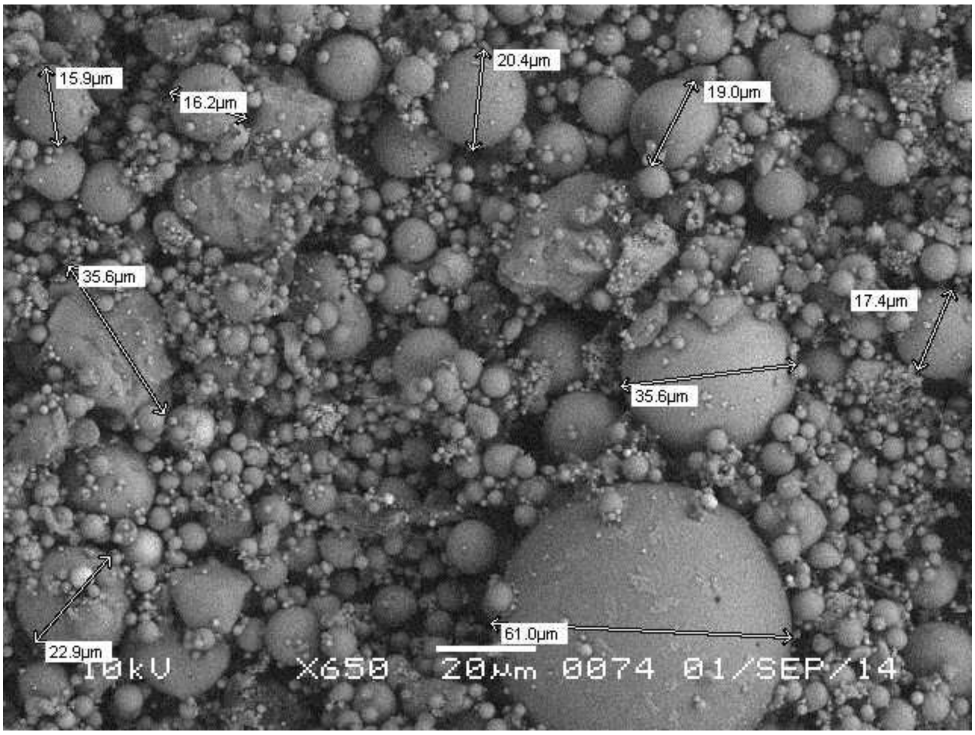
Figure 5: Particle size distribution plots comparing unground blends with one hour interground blends and activator ground blends (after unground fly ash has been added) made with (a) fly ash 1 and (b) fly ash 2


46.8μm
13.1μm
16.9μm
18.7μm
24.9μm
26.5μm
10kV X650 20μm 0074 01/SEP/14

(a) FA1

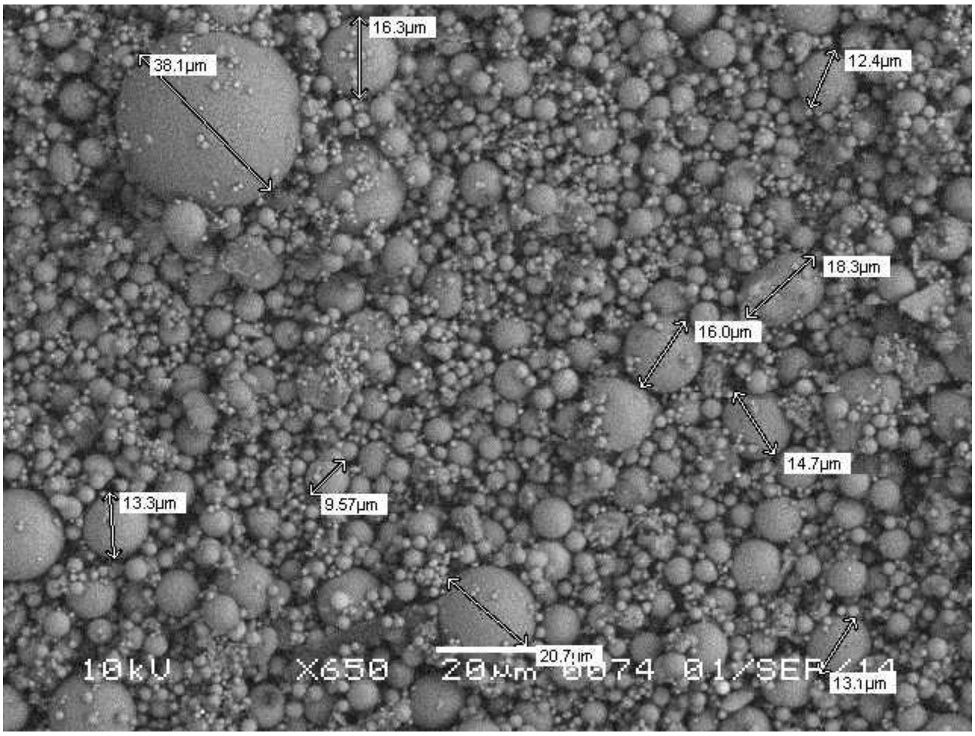

9.85μm
14.4μm
14.2μm
21.4μm
33.9μm
21.8μm
14.0μm
10kV X650 20μm 0074 01/SEP/14

(b) FA2



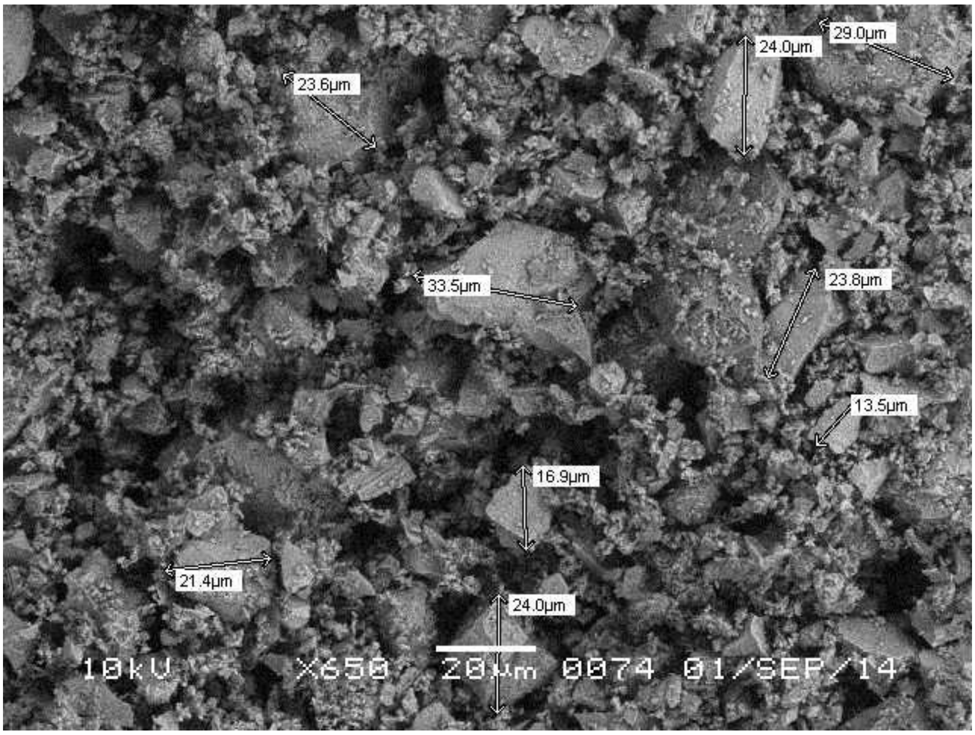
15.9µm
16.2µm
20.4µm
19.0µm
35.6µm
17.4µm
35.6µm
22.9µm
61.0µm
10kV X650 20µm 0074 01/SEP/14

(c) FA3

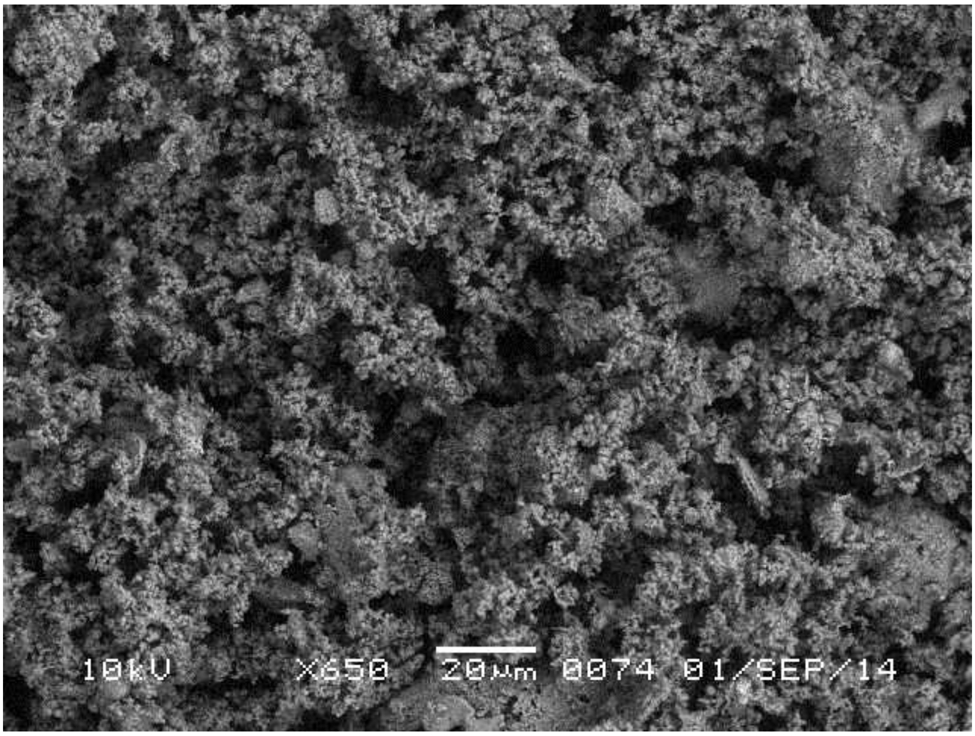


16.3µm
38.1µm
12.4µm
18.3µm
16.0µm
14.7µm
13.3µm
9.57µm
20.7µm
13.1µm
10kV X650 20µm 0074 01/SEP/14

(d) FA4

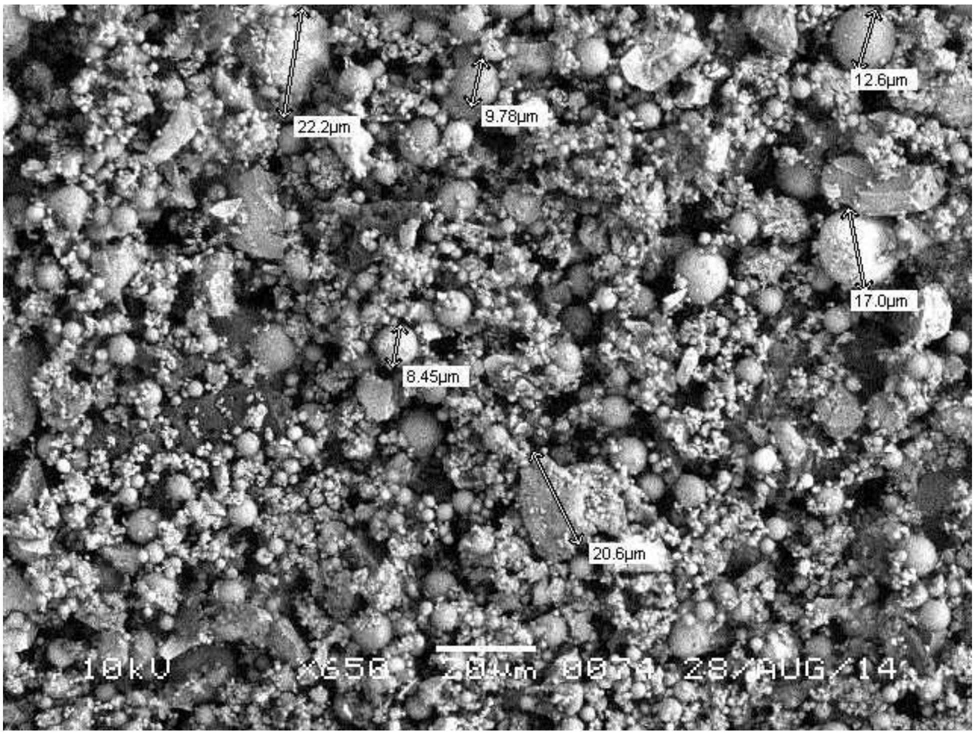


(e)CEM I

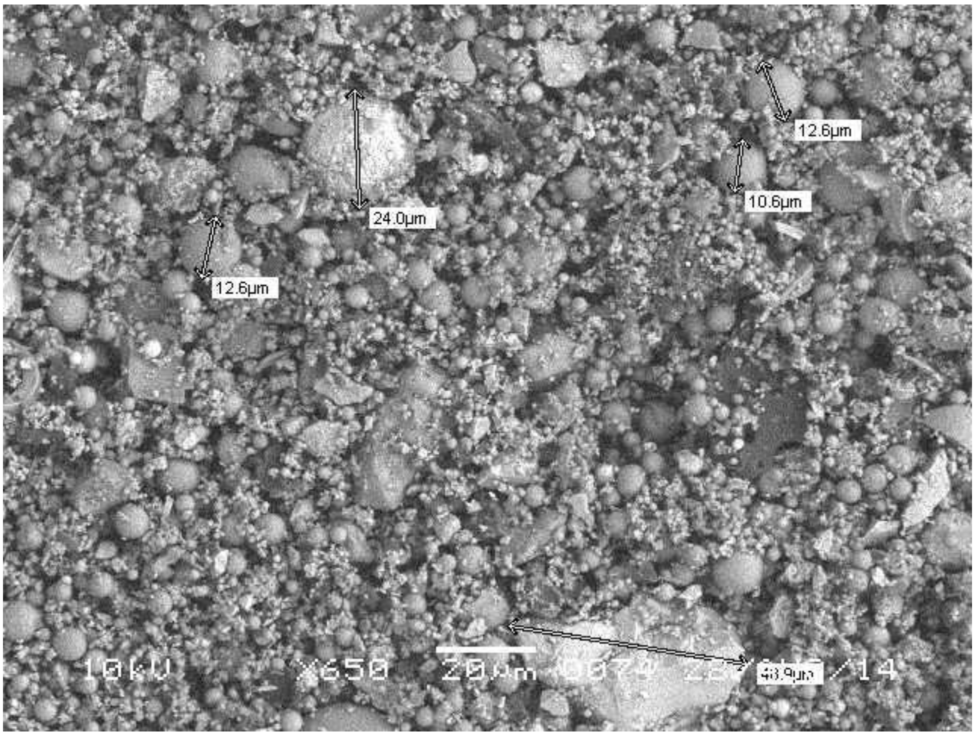


(f) CKD

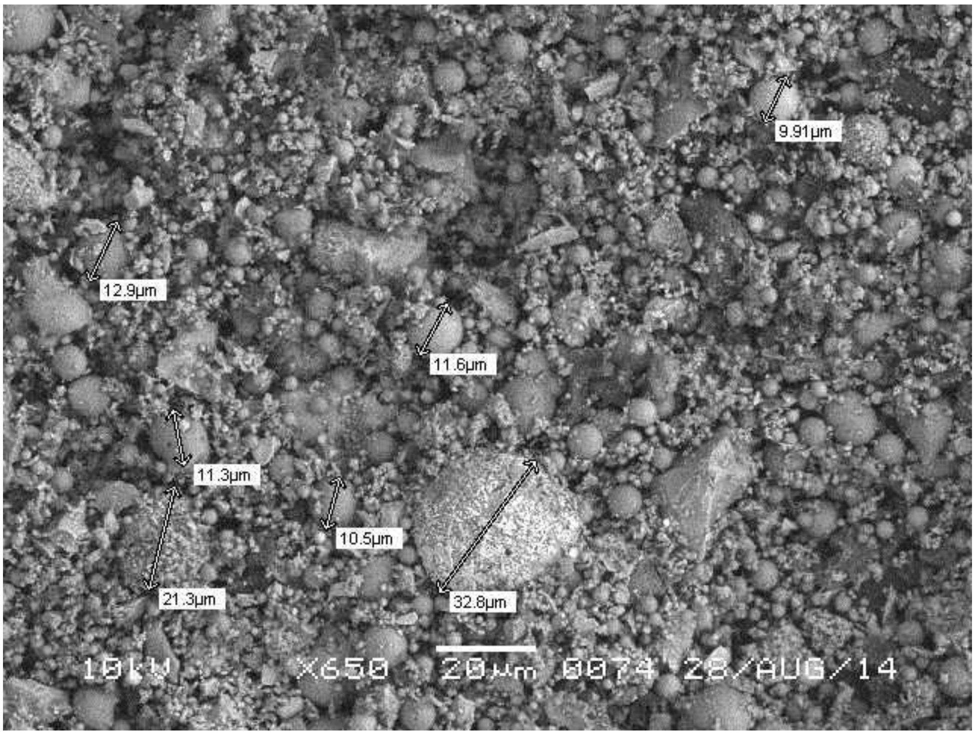
Figure 6: SEM images of raw materials



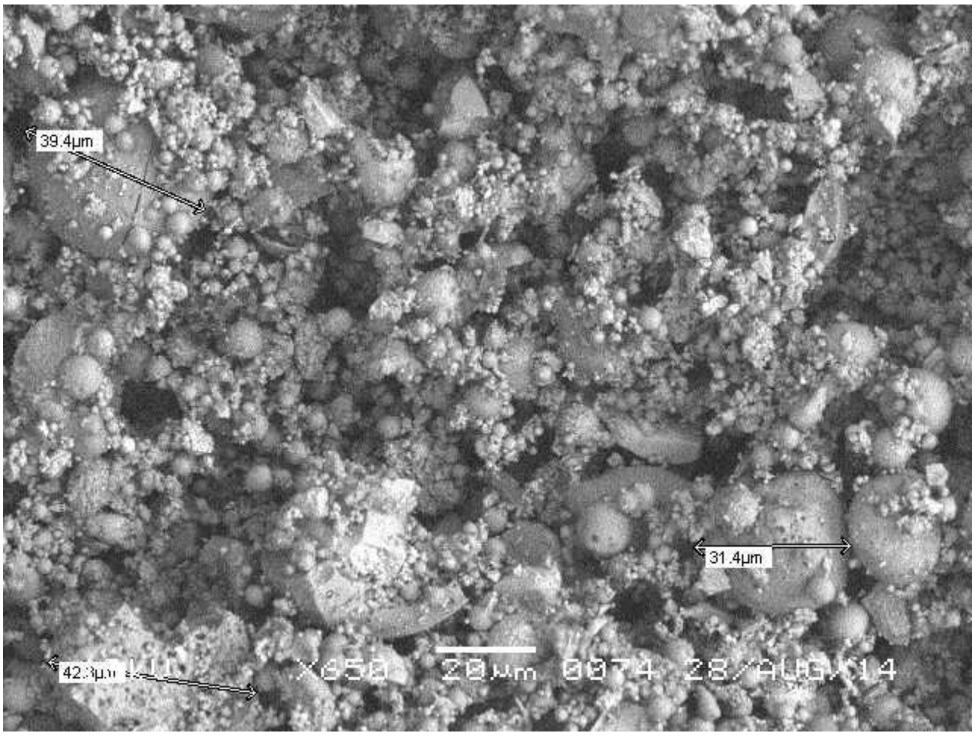
(a) IG-1-FA1



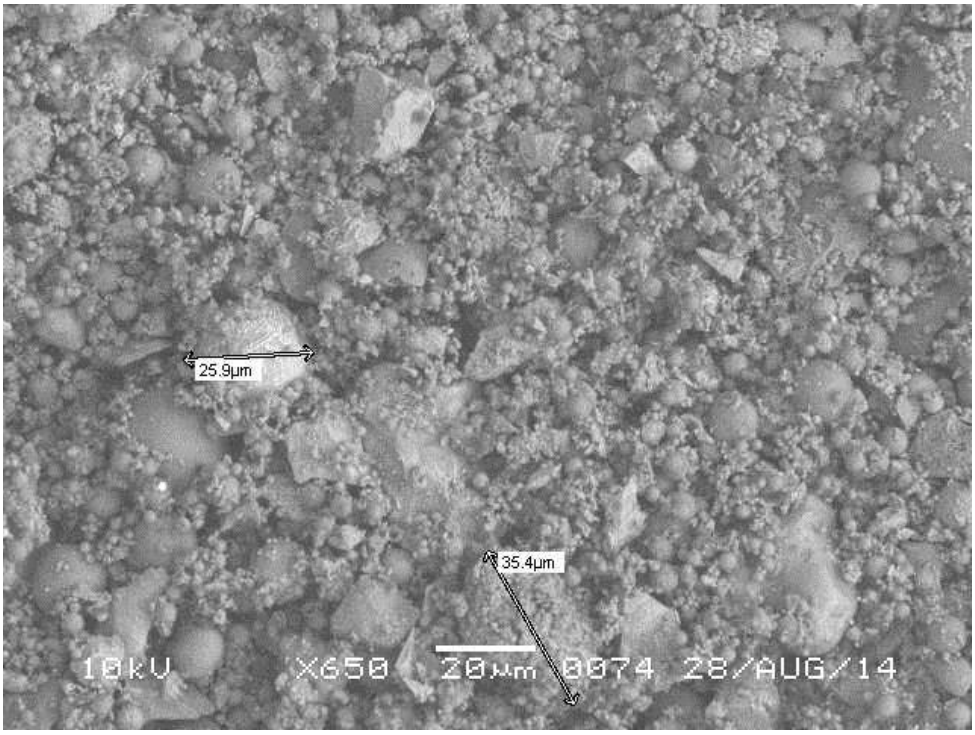
(b) IG-2-FA1



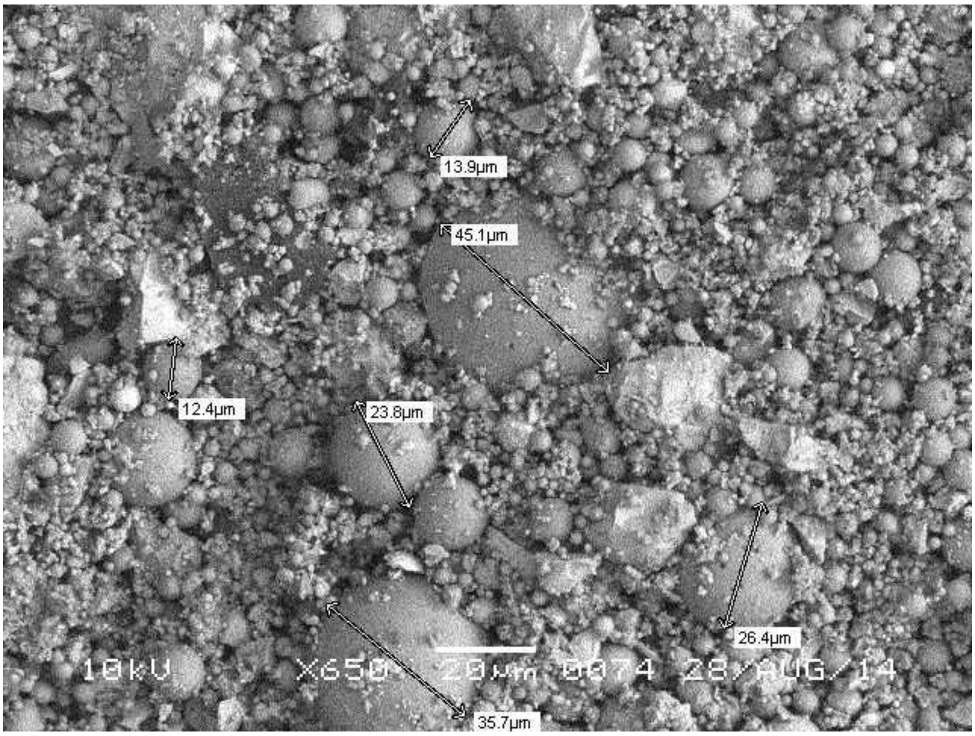
(c) IG-4-FA1



(d) IG-1-FA2

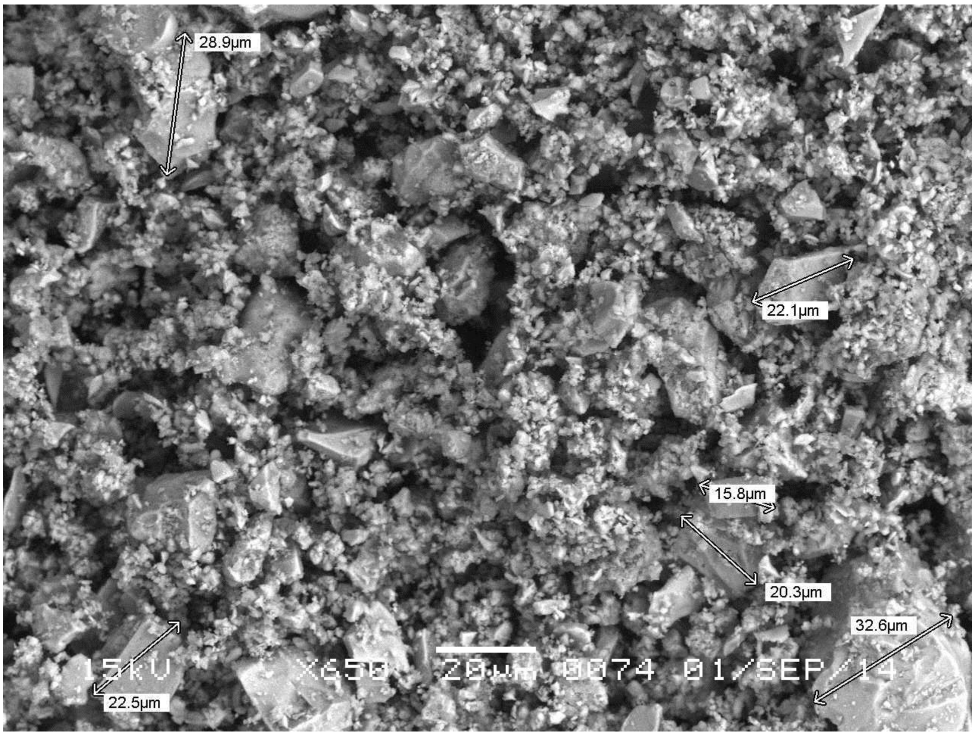


(e) IG-2-FA2

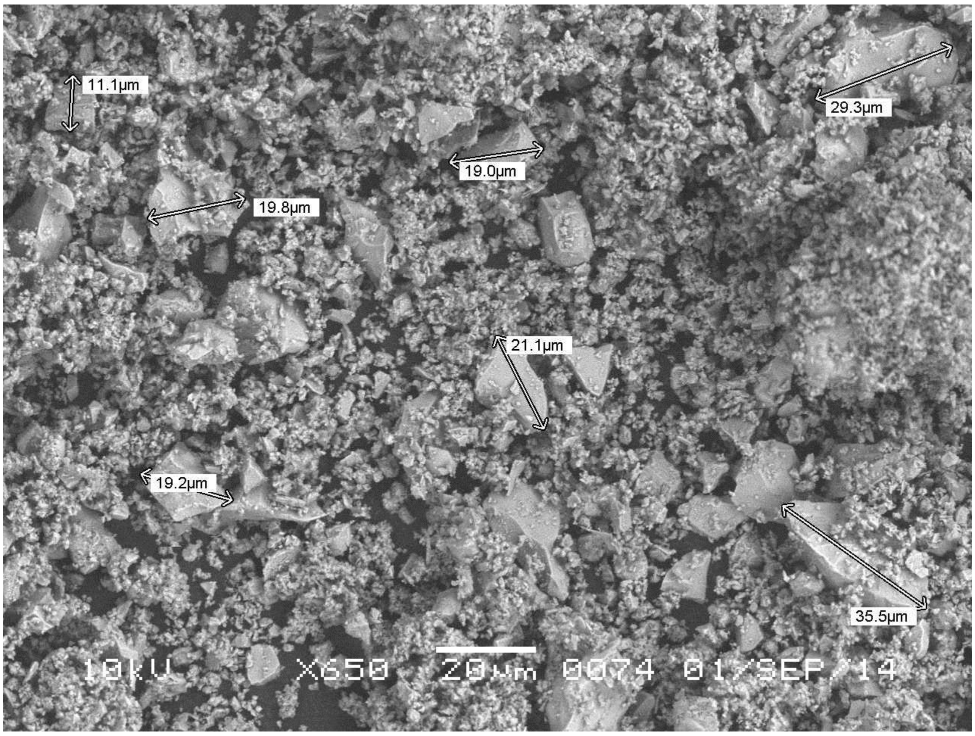


(f) IG-4-FA2

Figure 7: SEM images of selected blends - interground blends made with fly ash 1 and fly ash 2 ground for varying time periods

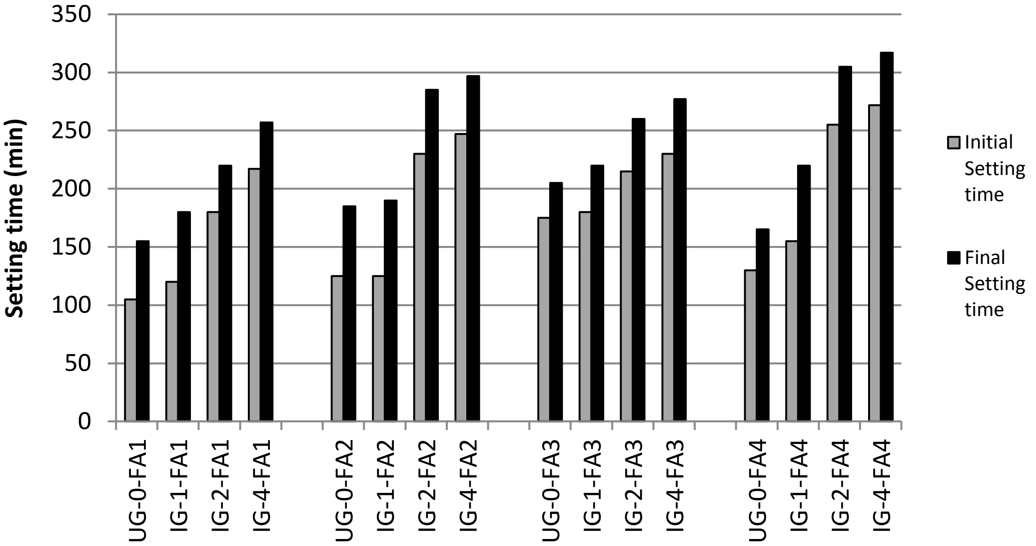


(a) AG-1

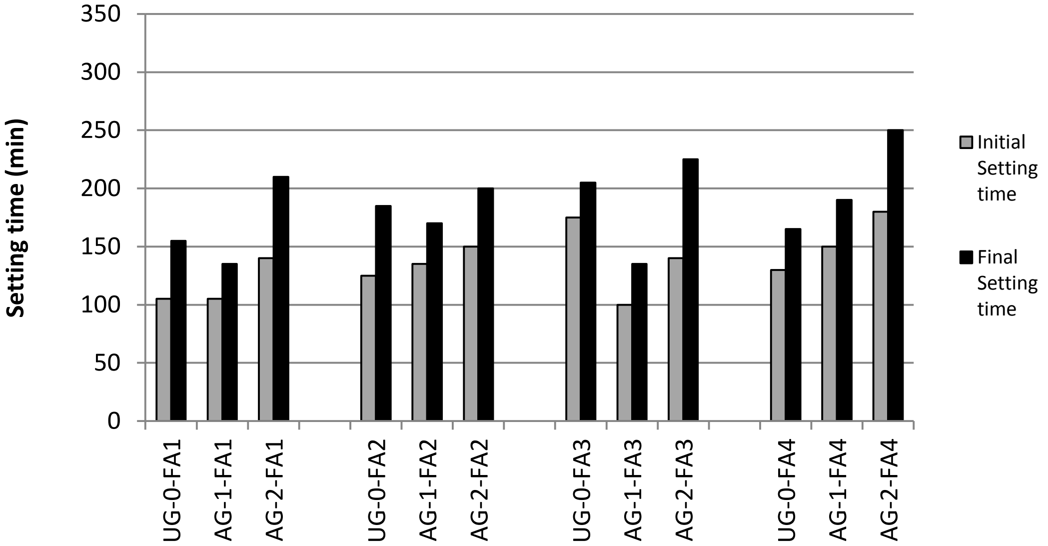


(b) AG-2

Figure 8: SEM images of activator ground blend (i.e. 75% CEM I + 25% CKD) for varying time periods

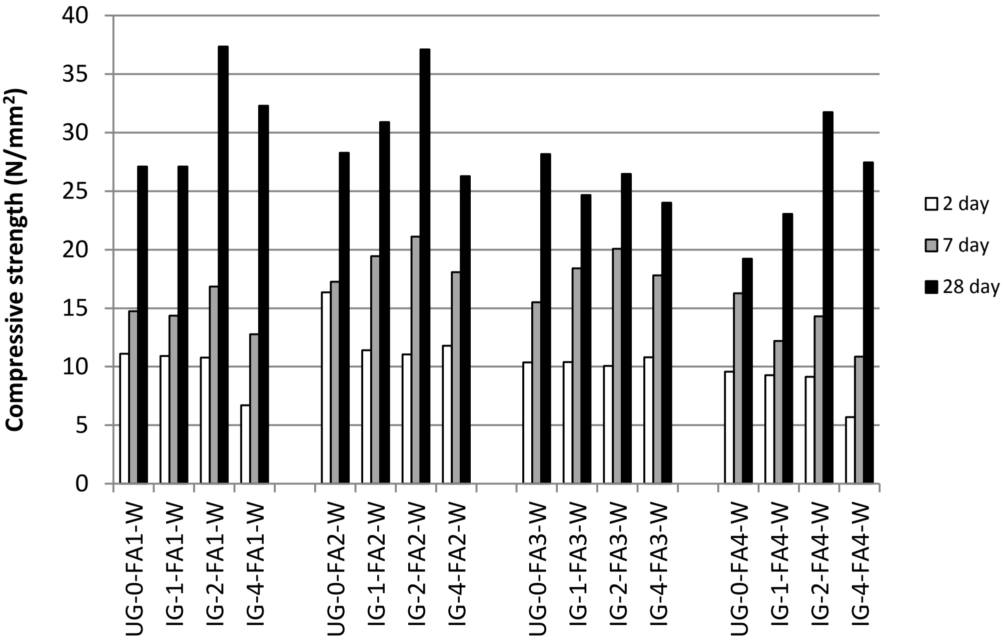


(a)

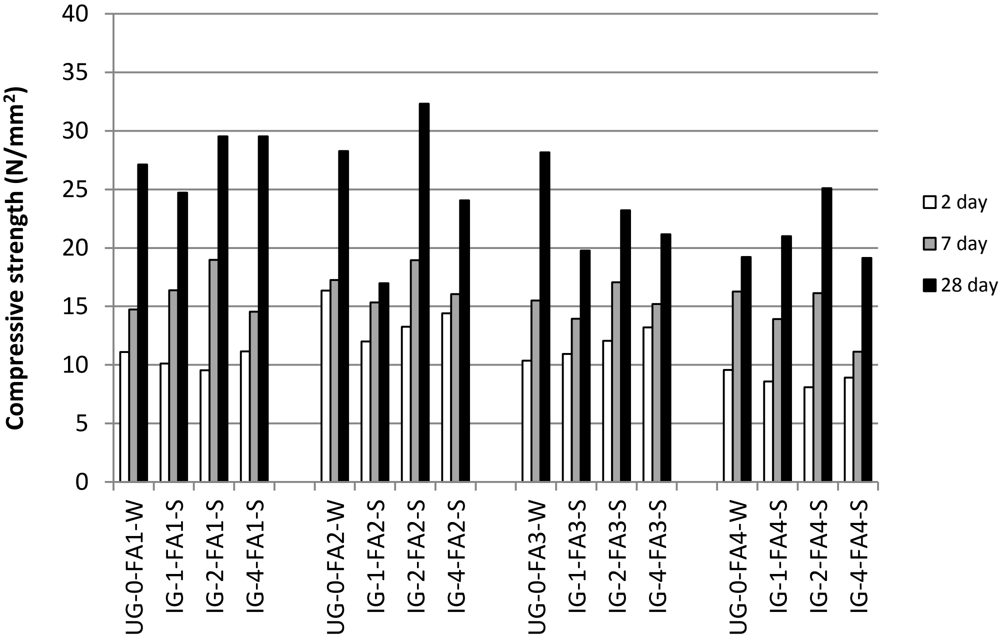


(b)

Figure 9: Initial and final setting times for control pastes and (a) pastes made with interground constituents and (b) pastes made with unground ash and ground activators

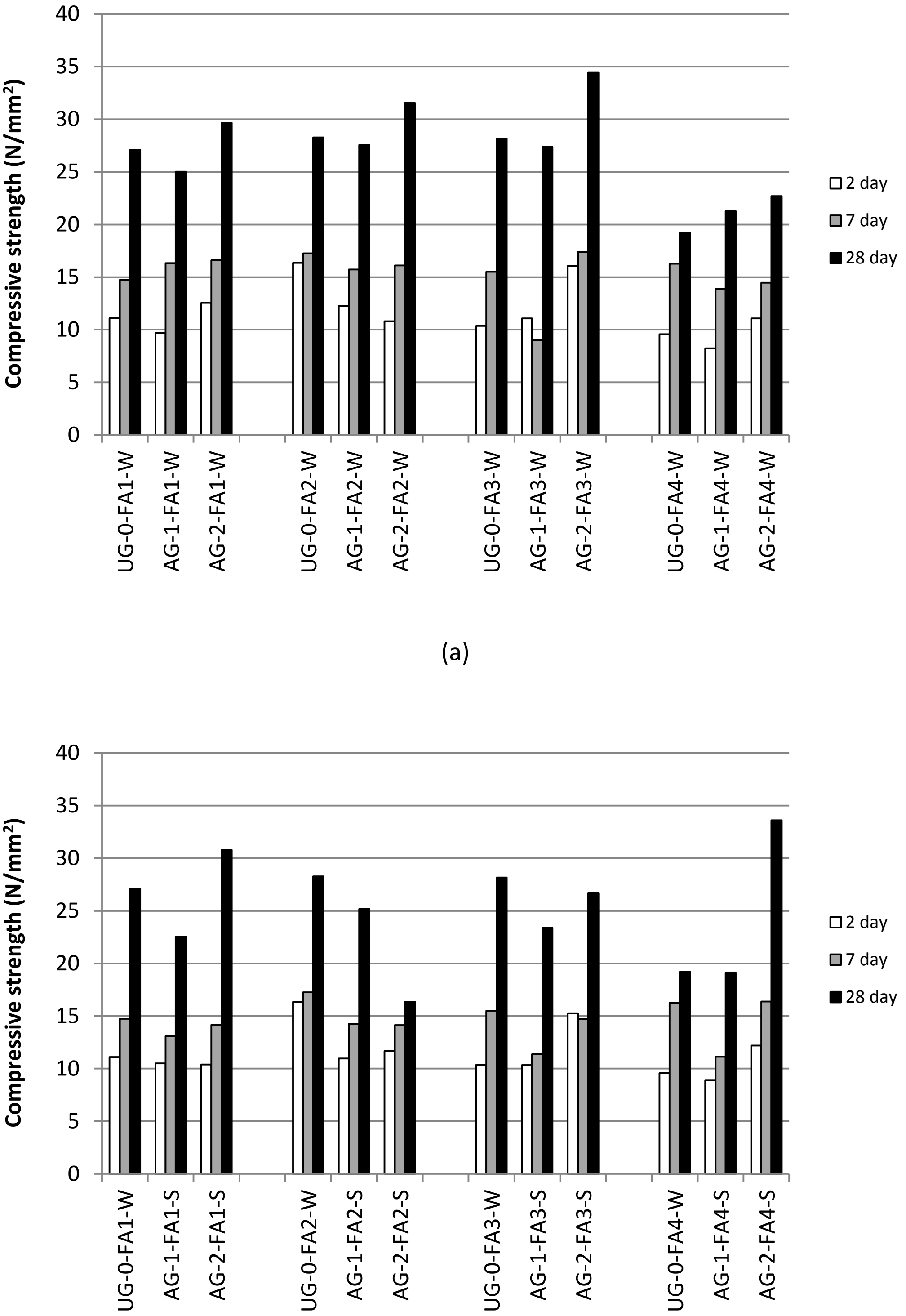


(a)



(b)

Figure 10: Compressive strength of paste samples interground for varying time periods for (a) wrapped curing and (b) submerged curing



(a)

(b)

Figure 11: Compressive strength of paste samples with activators only ground for varying time periods for (a) wrapped curing and (b) submerged curing

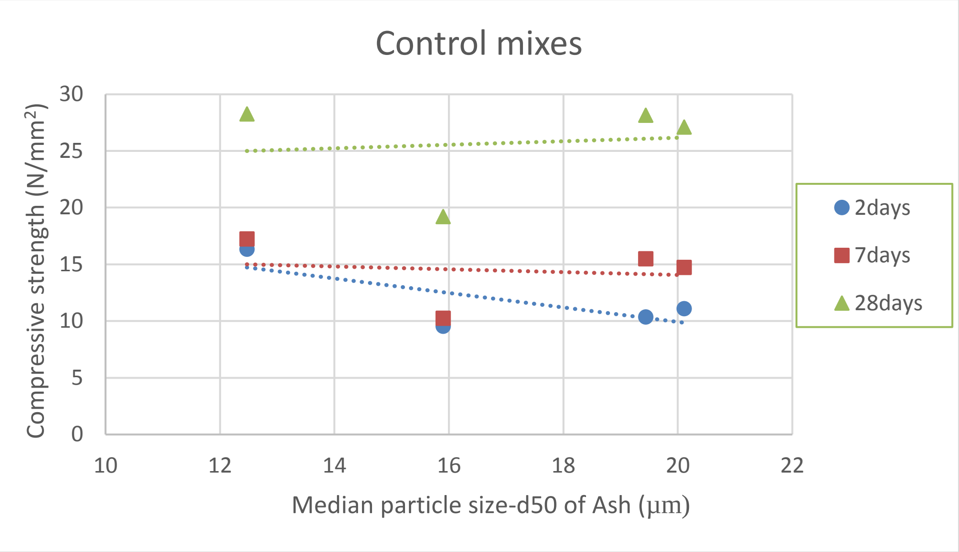


Figure 12: Compressive strength of control paste samples for varying median particle size of different ashes

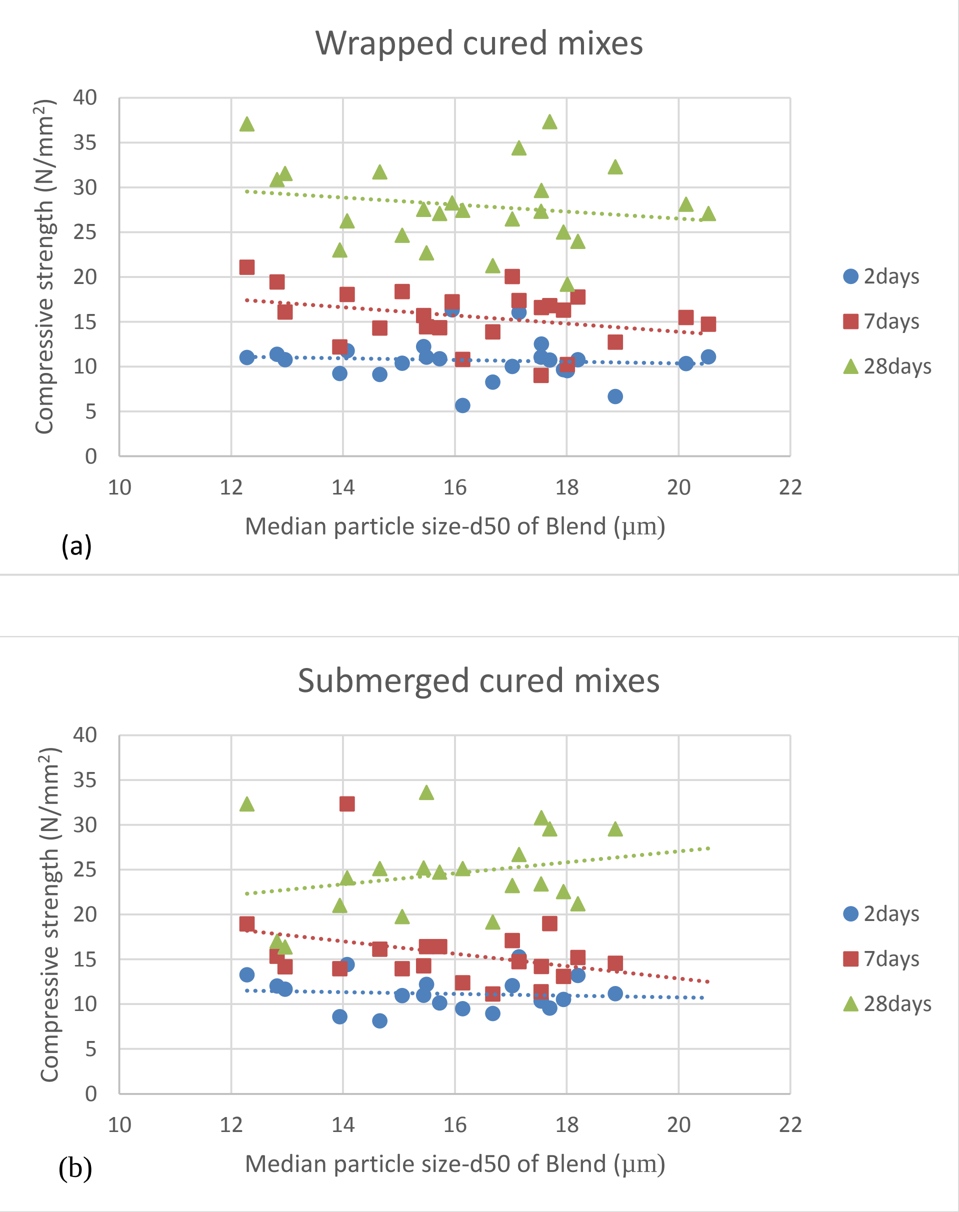


Figure 13: Compressive strength of paste samples for varying median particle size of blend for (a) wrapped curing and (b) submerged curing

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