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## **IMPACT OF FLY ASH PRODUCTION AND SOURCING CHANGES ON CHEMICAL AND PHYSICAL ASPECTS OF CONCRETE DURABILITY**

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# **Impact of Fly Ash Production and Sourcing Changes on Chemical and Physical Aspects of Concrete Durability**

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## **Abstract**

Changes in coal-fired power technology have recently been introduced, influencing emissions and efficiency, which may affect fly ash. Similarly, shortages of low lime fly ash, with power stations being taken out of service, mean recovery/processing of material from wet holding areas (e.g. stockpiles) is receiving attention. Previous research has considered the effect of these fly ashes on chloride ingress and carbonation of concrete. In the current study, chemical (sulfate attack and alkali-aggregate reaction (AAR)) and physical (freeze-thaw (salt) scaling and abrasion) processes causing concrete deterioration are investigated. These used laboratory tests and practical concrete mixes, with comparisons made against three reference fly ashes of different fineness, and data from earlier studies (late 1990s/early 2000s). The results indicate minor differences between fly ash concretes for sulfate attack and AAR, where small expansions were obtained. Although specific fly ash influences were not be identifiable, air-entrained concretes gave acceptable freeze-thaw scaling performance (0.45 water/cement ratio), while abrasion generally followed concrete strength. Similar effects were found to the earlier studies. The newer technologies and wet storage may influence fly ash characteristics, however, they follow typical behaviour for the concrete properties examined and suggest continued suitability for use.

## **INTRODUCTION**

Recent developments in coal-fired power generation have seen measures introduced, addressing emissions and efficiency [1], which could affect fly ash, the by-product of the process and widely used cement component (pozzolana) in concrete. These include low NO<sub>x</sub> methods with modified burning conditions (air/fuel supply; in-combustion), or injection of chemicals to the exhaust gases, with or without catalysts (post-combustion), and co-combustion combining coal with secondary fuels (for example, wood-based products) [2-4]. At the same time, the retirement of coal-fired power stations in some countries mean sourcing of material is beginning to change [5]. In future, options for this may include recovery from wet storage areas, e.g. stockpiles, and following processing [6]. It is, therefore, likely that fly ash from a wider range of technologies and origins will find use in concrete [7, 8].

The Authors recently investigated low lime fly ash from various power generation technologies [9], including those described above. This showed that while these can influence the physical and chemical properties, see Table 1, effects found for fly ash in concrete previously, e.g. fineness influences on water requirement and compressive strength, are generally maintained. Similarly, holding fly ash in wet storage, for example material moistened at around 10 to 20% by mass and kept in stockpiles, can cause agglomerates to develop, with products forming on particle surfaces, giving reductions in reactivity [8]. However, concrete mix adjustments, accounting for these effects, can enable target workability and strength properties to be achieved.

Given the important role of durability in concrete structures, earlier research by the Authors also investigated the effect of some of the fly ashes referred to above (from new technologies) on chloride ingress and carbonation of concrete [10]. This showed that the fly ashes generally followed behaviour noted previously for the material and processes. At equal compressive strength, chloride ingress rates increased with coarsening of fly ash, and reducing reactive alumina and glass contents in concrete. On this basis of comparison, fly ash properties did not appear to influence carbonation of concrete. Similar effects for these have also been found for equal strength concretes containing dry fly ash and following wet storage [11].

Concrete, however, can face a wider range of conditions [12, 13], causing chemical or physical effects (e.g. sulfates in the ground, alkali-aggregate reaction (AAR) (affected by constituent materials/moisture levels), freeze-thaw scaling in cold climates, and abrasion in industrial floors) leading to damage. For sulfate attack and AAR, fly ash may be expected to give benefits to concrete compared to that with Portland cement (PC), while for freeze-thaw scaling, mixed performance between these has been found, with abrasion mainly depending on strength and aggregate characteristics, rather than cement type [14, 15]. The behaviour corresponds to the chemical and physical effects associated with fly ash on the cementitious system and microstructure. Given the potential changes to fly ash that the technologies and wet storage may have (e.g. reactivity, carbon content), as suggested in Table 1, they could also affect the durability processes. A study was therefore set up to investigate this and extend the earlier research on chloride ingress and carbonation.

## **RESEARCH PROGRAMME**

Materials were obtained from the EU/UK, covering the various fly ashes referred to above. These include fly ash from (i) low NO<sub>x</sub> technology (in- and post-combustion), (ii) co-combustion (with different co-fuels), (iii) a power station stockpile and (iv) a stockpile and following processing. A range of practical concrete mixes, including those relevant to the durability processes being investigated, or meeting test requirements [16-18] were developed. The durability properties were investigated using (accelerated) laboratory methods to provide control and allow data to be obtained in a reasonable timescale.

The research programme enabled both individual and collective effects of fly ash on the durability properties of interest to be examined. Fly ash samples were only available following the introduction of the developing coal-fired technologies, or storage in the stockpile/processing. These data were, therefore, evaluated against

three reference fly ashes covering a range of fineness. In addition, comparisons were made with data from earlier studies carried out at the Authors' Institution during the late 1990s/early 2000s to determine whether established behaviour for the material occurred.

## **REFERENCE AND TEST FLY ASHES**

The fly ashes used, see Table 2, were all from bituminous coal, unless noted otherwise. Most power stations operate low NO<sub>x</sub> systems and hence some may have been from a combination of these and the techniques, or wet-storage conditions/processing, being investigated. Two of the reference fly ashes FA1 and FA2 were high fineness (Category S or close to this, fineness  $\leq$  12.0% retained on a 45  $\mu$ m sieve [19]) materials, with the former from a base-load station, while FA3 was an older, coarser, material produced during the 1990s. The NO<sub>x</sub> reduction fly ashes, FA4, FA5 and FA6, originated from post- (selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR)) and in-combustion (natural gas reburn) systems. The co-combustion fly ashes comprised coal and wood chips (FA7 and FA8, sampled in summer and winter; anthracite coal) or petroleum coke (FA9). The wet stored fly ashes were from a power station stockpile (STO), or were processed (PRO) (wet particle separation/carbon removal [20]) following this type of storage (different site to STO).

Details of the fly ash characterization methods used have been reported previously [9], with a summary of the data from these for the test materials, given in Table 3. The fly ashes had fineness between 9.6 and 49.5% (45  $\mu$ m sieve retention), i.e., within the limits of EN 450-1 ( $\leq$  40%), except STO which was coarser, reflecting probable agglomeration during wet storage [21]. While most had loss-on-ignition (LOI) below Category B ( $\leq$  7.0%) in EN 450-1, some were higher, FA6, FA7, FA8, FA9 and STO, and may reflect the burning conditions (FA6; [2]), coal and/or secondary fuel type (FA7, FA8, FA9 [4, 22] and wet storage effects STO [21]).

The chemical properties were typical for the coals used and within relevant Standard (EN 450-1) limits, where applicable: the sum of the main oxides ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ )  $\geq$  70%, CaO and alkali levels ( $\text{Na}_2\text{O}_{\text{eq}}$ )  $<$  4.6% and 4.0%, with sulfate levels  $<$  1.5%, except FA9 at about 2.5%, which may be due to the secondary fuel [23]. The fly ash mineralogy was typically as expected, although some components (e.g. quartz for FA4 and FA6) were comparatively high. All fly ashes had moisture contents of  $\leq$  0.6%, (tested on a moisture balance) before use (there is no limit in EN 450-1 [19] for this, but drying as a means of processing is referred to).

## **OTHER CONSTITUENTS FOR CONCRETE**

The PC (CEM I) was of Strength Class 52.5N to BS EN 197-1 [24] obtained in bulk, with a mean alkali content, ( $\text{Na}_2\text{O}_{\text{eq}}$ ) of 0.62% (used to calculate alkali contents in concrete for the AAR tests).

All aggregates met BS EN 12620 [25], with their physical properties given in Table 4 (particle densities between 2600 and 2650  $\text{kg/m}^3$  and water absorptions  $< 1.5\%$  (lab dry to saturated surface dry)). The aggregates for sulfate attack and abrasion were a local sand (0/4 mm) and gravel (4/10 and 10/20 mm). For AAR, Scottish greywacke fine (0/4 mm) and coarse aggregate (4/10 and 10/20 mm) were obtained. This aggregate combination is classified as highly reactive, for the process, according to BRE Digest 330 [26], although many (of greywacke type) can be variable in their behaviour.

The freeze-thaw scaling tests combined the local sand and Derbyshire magnesian limestone coarse aggregate (4/10 and 10/20 mm) from a related study [27]. A modified polycarboxylate ether superplasticizer (SP) was adopted in most concrete mixes to control water contents and workability. A commercial air-entraining admixture (AEA; tall oil, fatty acid/polyethylene glycol), was used in the freeze-thaw scaling test concretes. The admixtures both conformed to BS EN 934-2 [28].

## **CONCRETE MIXES AND SPECIMEN PREPARATION**

The concrete mixes, all containing 30% fly ash in cement, are given in Table 5. Those for sulfate attack and abrasion had a range of water/cement (w/c) ratios (free water content, 165  $\text{l/m}^3$ ). It was anticipated that these would give different levels of damage, while enabling interpolation for equal strength comparisons, as used previously [10]. The fine/total aggregate ratios were based on the BRE mix design method [29], with SP admixture doses from 0.3 to 0.9% by mass cement, adjusted to give 100 - 150 mm slump.

The AAR concretes followed the proportions given in BS 812-123 [17]. At equal volumes of cementitious material, the PC/fly ash contents by mass were less than those of PC, given the difference in particle densities for the two materials (PC, 3140  $\text{kg/m}^3$  and fly ash, approximately 2200  $\text{kg/m}^3$ ), with aggregate contents the same for the mixes. The concrete alkali content was raised to 7.0  $\text{kg/m}^3$   $\text{Na}_2\text{O}_{\text{eq}}$  by adding potassium sulfate, as described in BS 812-123 [17] and shown in Table 3. This was in addition to the alkali in PC, which at 0.62%  $\text{Na}_2\text{O}_{\text{eq}}$ , was below that referred to in the Standard. No alkali contribution was considered for fly ash,

given the 30% level used in cement, i.e. following technical guidance [26]. The SP was not included in these concretes, but compaction was achievable.

The freeze-thaw scaling concretes were air entrained, as indicated in Table 3, with a target air content of 5.0% by volume (tolerance +1.0%/-0.5%), 30% fly ash in cement and a free water content of 165 l/m<sup>3</sup>. The w/c ratios were 0.45 and 0.55, with a fixed SP dose of 0.3% by mass cement, and AEA added to achieve the target slump (mainly between 80 and 160 mm) and air content.

Concrete was prepared following BS 1881-125 [30] in a horizontal laboratory pan mixer. Air contents of the freeze-thaw scaling concretes were measured as described in BS EN 12350-7 [31]. The specimens were made following BS EN 12390-2 [32], with the initial 24 hours storage carried out in moist air at 20°C before curing/preparation for testing.

## **TEST METHODS**

### **Sulfate Attack**

An immersion test based on CEN/TR 15697 [33], with a 68 g/l Na<sub>2</sub>SO<sub>4</sub> solution at 20°C was used, which is about seven times the highest sulfate class in BRE Special Digest 1 [34]. Information suggests 1 to 2 years under these conditions should give significant results, with repeatability for this type of test (EU round robin tests) on mortar and at lower sulfate concentrations (than the current study) of 10 to 22% [33]. Three 75 × 75 × 300 mm<sup>3</sup> prisms, see photograph in Figure 1, with fixed-end studs were water cured at 20°C to 28 days. Lengths (by comparator, accurate to 0.002 mm) and masses (by balance, accurate to 0.1g) were then recorded before exposure. Care was taken to ensure the test solution, replenished 6 monthly, had access to all faces. Deterioration was evaluated by periodically comparing prism lengths and masses to initial values over 540 days, with the visual condition examined at the conclusion of the tests.

### **Alkali-aggregate Reaction**

AAR tests followed the BS 812-123 method [17], with precision data for the test indicating a spread at low expansion levels for four specimens of < 0.017%. The four 75 × 75 × 300 mm<sup>3</sup> prisms, see Figure 1, with fixed-end studs, were wrapped in cotton and secured in polythene tubing at 24 hours. Initial lengths were taken and the prism assembly sealed in polythene bags (with 5 ml of deionized water added) and stored in

plastic containers above water (RH > 96% [17]) at 20°C for 6 days. At 7 days, they were introduced to a 38°C chamber, with length measured (by comparator, as above) regularly over 365 days, and the results expressed with respect to the initial values. The specimens were also assessed visually at the end of the test period.

### **Freeze-thaw Scaling**

Freeze-thaw scaling tests adopted the slab method in CEN/TS 12390-9 [35], using 3 specimens. Repeatability data give a coefficient of variation of 17% for the test (at 1.0 kg/m<sup>2</sup> scaling). The 150 mm concrete cube specimens were water cured at 20°C for 6 days and stored at 20°C, 65% RH, thereafter, until starting the test. At 21 days, the specimens were cut perpendicular to the top surface and then sealed at 25 days with rubber sheet, except for the (cut) test face, see also in Figure 1. At 28 days a 3 mm layer of deionized water (67 ml) was poured on the test face, which was replaced with a similar salt water (3.0% NaCl) layer at 31 days. The specimens were thermally insulated on 5 faces, with polyethylene sheeting above the test face, and exposed to 56 freeze-thaw cycles ( $\pm 20^\circ\text{C}$  each day, at a controlled rate of temperature change). Loose, scaled material was removed at the required test times and weighed (using the balance referred to above), with results expressed in kg/m<sup>2</sup> concrete surface.

### **Abrasion**

Abrasion was measured using a modified British Cement Association method [36], which provides impacting, rolling and jolting actions that can occur on industrial floor slabs. Laboratory variability tests on similar PC concretes (single operator) gave a coefficient of variation of 6.1%. Following water curing of the slabs, 295 × 295 × 60 mm<sup>3</sup>, see details in Figure 1, at 20°C for 28 days and laboratory air storage for 14 days, ten points were marked on the abrasion path of the as-cast surface and initial measurements taken by digital gauge. The slab specimen was then positioned in the equipment frame and weighted rotating steel wheels loaded on the surface. The test ran for 15 minutes, with abrasion path depths then determined, and the mean result (from the 10 points), in millimetres, reported.

## **RESULTS AND DISCUSSION**

### **Sulfate Attack**

The results for PC and a selection of fly ash concretes (0.45 w/c ratio), following sulfate exposure are given in Figure 2. These follow expected behaviour, i.e. gradual increases in expansion with time (e.g. [37, 38]) and a



suggestion, in some cases, that effects will continue beyond the end of the exposure period. However, at this w/c ratio, expansions were in a relatively narrow range of around 0.01% or less by 540 days, i.e. suggesting little or no damaging effects.

A comparison between expansions at 540 days for the concretes at different w/c ratios is given in Figure 3. The results gave expansions  $\leq 0.02\%$  for the fly ash concretes, irrespective of w/c ratio, again suggesting little damage. Only PC concretes at 540 days, in particular 0.55 w/c ratio, gave noticeable expansion differences compared to the fly ash concretes. There is a suggestion of an optimum w/c ratio for least expansion, i.e. reflecting reactable material/microstructure effects, influencing sulfate solution access and damage, which for the sulfate concentration/concretes tested was 0.45.

Visually, signs of damage were found for PC concretes (greatest at 0.55 w/c ratio) with cracking, softening/loss of material at edges and corners, and whitish surface discoloration, typical for sulfate exposures [39]. Except for FA9 concrete (where the sulfate level in fly ash was higher), which gave local damage at a specimen corner, and white discoloration in some cases, most fly ash concretes showed little effect by 540 days. There was some agreement between expansion and specimen condition, but the former was less than might be expected, given damaging expansions found previously [40, 41]. It has been noted that expansion may be sensitive to cement type, including fly ash, during testing, with low values occurring despite undergoing deterioration [33].

The weight change results generally gave increases during storage, with values between 0.36 and 0.92% and typically  $< 0.45\%$  for PC and fly ash concretes respectively by 540 days, with the former highest at all w/c ratios during testing, see Table 6. Least weight gains were found at either 0.45 or 0.55 w/c ratio. These appear to reflect the reactable components and product formation at the cement rich concrete surface [42], with the microstructure influencing sulfate ingress beyond the outer layer [43]. There was little difference in weight change between fly ash concretes, although FA9 was slightly higher. The only concrete giving increases and then reductions in weight was PC at 0.55 w/c ratio, reflecting damage and material losses from the surface.

Previous work indicates improved performance may occur with low lime fly ash concrete in sulfate exposures [43]. Reductions in calcium hydroxide, dilution of PC aluminate phases, microstructure enhancement with fly ash [44] and benefits to the interfacial transition zone [45] are considered important factors influencing the

process. This has also been found with wood-based co-combustion fly ash, which gave similar expansions to coal-only material in mortar [46]. The pozzolanic potential has been noted [47] to maintain concrete strength in sulfate exposures, particularly at high fly ash levels and this may also affect behaviour.

Research has examined fly ash composition effects on sulfate behaviour, including Ca/Si ratio and SO<sub>3</sub> contents [45, 48] for material with a wider chemistry range and greater expansion levels, than noted here. While general relationships were noted in the analyses, there tended to be scatter. These were examined for the data in the current study, but there was little identifiable effect on behaviour. Another study indicates that finer fly ash (by processing) may reduce sulfate damage, due to greater calcium hydroxide reaction, limiting availability for sulfate reaction [49]. To examine this, data from the current and earlier studies [50] are compared in Figure 4. The equal strength concretes are shown against fly ash fineness (45 µm sieve retention). Although there are differences in sulfate concentrations, concrete strengths (see Figure 4) and relatively low expansion levels, these indicate minor variations with fly ash fineness and similar effects to the 1990s study.

### **Alkali-aggregate Reaction**

The AAR test results are given in Figure 5 and show gradual increases in expansion with time, tending to level off during the 365 day exposure period. At the end of this, the fly ash concrete expansions were all < 0.02%, indicating little or no damage, while PC concrete gave slightly greater expansions of approximately 0.035%. Although greywacke aggregates are classed as high reactivity in BRE Digest 330 [26], these can vary in their AAR behaviour [51], with only some potentially reactive [52]. From the expansion data, it appears that the aggregate combination has low reactivity [26]. Visually, no changes in specimen conditions were found by the end of the test period.

The use of fly ash in cement is known to have several physical and chemical effects on the properties of concrete. In the early stages during/following concrete mixing, dispersion of PC flocs (affecting early hydration) can occur [53, 54]. Soluble components in fly ash and pozzolanic reactions in the presence of lime, as well as the temperature and humidity, and the materials' fineness influence the pore fluid chemistry and resulting structure of concrete [53]. Chemical characteristics including, CaO/SiO<sub>2</sub> ratio, CaO and the alkali content of fly ash have been identified as important (with greater expansive effects due to AAR as these

increase) [55, 56]. Similarly, modifications to the microstructure including interfacial transition zones (affecting diffusion) [55], may be expected to impact on the damage occurring.

Literature suggests that high lime co-combustion biomass fly ash can reduce the expansive effects of the process (sawdust/switch grass [57]). With low lime co-combustion, using wood-based products, similar behaviour to coal-only fly ash has been found, imply similar mechanisms are involved. The effects of particle size noted, again suggest that pozzolanicity and particle packing are important [58]. Wet fly ash storage can lead to particle agglomeration, with possible alkali losses, particularly in excess water [59]. However, limited testing indicates little effect of site moistened fly ash on the process [52]. With wet-storage and processing, and thereby increasing finer fractions, there appears to be little influence on expansion.

Given the properties identified above as influencing the process, consideration was given to CaO/SiO<sub>2</sub>, CaO and alkali levels. As noted for sulfate attack, these parameters were within relatively narrow ranges and no correlations were found, with expansion. The fly ashes used had a range of fineness and influences of this on AAR expansion have been noted in some cases previously [60, 61]. The data from the study are compared with those from research carried out during the early 2000s at the Authors' institution [52]. This work also used the BS 812-123 [17] test and Scottish greywacke aggregate (different source) and is given in Figure 6. The earlier data included fly ash from a single source, which gave gradual increases in expansion with coarsening and time. While there were differences for the current research, perhaps reflecting between source/origin variations, similar type results, with minor expansions, and benefits in comparison to PC concrete were obtained between studies.

### **Freeze-thaw Scaling**

The results showing the AEA doses to achieve the target air content in concrete are given (0.55 and 0.45 w/c ratios) against fly ash specific surface area (SSA, by Nitrogen adsorption) in Figure 7. As the w/c ratio reduced, slightly less admixture was required per unit mass cement, which has been observed for fly ash previously [62]. The results demonstrate that there was an increase in admixture requirement with SSA of fly ash, agreeing with earlier work [63]. Studies have also shown that the SSA of the mineral component of fly ash is relatively constant at about 0.7 to 0.8 m<sup>2</sup>/g [64] and the remainder (of the SSA) corresponds to unburned carbon present (content and characteristics), where admixture is adsorbed and affects bubble stability. The results

also approximately followed LOI, for example concretes with FA7 and FA8, of highest LOI, had among the greatest AEA demands, but there were some variations between these, as found elsewhere [65], corresponding to the influences of the carbon characteristics on the process.

The effects observed with PRO fly ash, are similar to those of related research [66], which identified that wet-storage tends to give different effects with AEA adsorption (and admixture demand for a target air content), which seem to reflect surface chemistry/charge effects. Similar behaviour has also been observed on co-combustion fly ash with petroleum coke [67] and in that case appeared to reflect the dense nature of carbon present.

The freeze-thaw scaling results for the test concretes are given in Figure 8 and show gradual increases with time. Between the two w/c ratios, the data tend to level off more rapidly at lower scaling levels (and w/c ratio) for fly ash concretes, by about 28 days. Least scaling was found for the air-entrained PC concretes, at both w/c ratios (which had higher strengths), but with small differences between these. The ranges for fly ash concretes were 0.16 to 0.87 kg/m<sup>2</sup> at 56 cycles for 0.45 w/c ratio, and 0.60 to 1.81 kg/m<sup>2</sup> for 0.55 w/c ratio. Thus, all met the 1.0 kg/m<sup>2</sup> acceptable limit [68] at 0.45 w/c ratio, but some exceeded this at 0.55. There was no clear effect of the small differences in air content/cube strength (water cured, measured at 28 days, see Figure 8) between fly ash concretes, at a given w/c ratio, on the results.

Of the fly ash concretes, FA6 and FA7 (in-combustion low NO<sub>x</sub> and co-combustion) generally performed best with some of these exhibiting less scaling than those including the references (FA1 and FA2). The range of scaling results is perhaps surprising, since related work [69] examining the air void parameters (e.g. spacing factor) for a selection of the fly ash concretes (including FA1, FA2, FA8) suggests minor differences between these, which generally agrees with an earlier study from the 1990s [70]. The results may, therefore, relate to increased variability for freeze-thaw scaling of fly ash concretes [71].

Research investigating co-combustion fly ashes (petroleum coke) in concrete gave slightly better scaling resistance than coal only fly ash, but both poorer than PC concrete [67]. Studies on high lime fly ash (high level wood-based biomass in the fuel) gave greater scaling as the level in cement increased, but reduced with

entrained air content [72]. Wet laboratory-stored fly ash concrete has also been found to give comparable freeze-thaw scaling (equal strength/air content) to that with dry material [73].

A review of freeze-thaw scaling [74] suggests that it is fly ash influences on concrete behaviour that affect freeze-thaw scaling, e.g. level in cement, response to limited moist curing, rather than specific material properties. However, relationships with fly ash fineness have been noted previously [75] and a comparison between these and with respect to this earlier study (Ref. 75) is given in Figure 9, (equal strength, air-entrained). As shown, similar type effects, albeit with greater scatter in the current study, with reduced scaling for coarser fly ash are apparent. It is possible that coarser material could lead to less effective packing, creating space for pressure relief, which may be of benefit for scaling, however, this requires further investigation.

### **Abrasion**

A comparison is made between abrasion depths and cube strength for PC and fly ash concretes in Figure 10 (left). As expected, abrasion depth followed w/c ratio, reducing as this decreased from 0.55 to 0.45 for the concretes tested. The PC concretes gave higher cube strengths than those of fly ash and lowest abrasion depths at each of the w/c ratios. Strength differences of between 9.0 and 12.0 MPa were noted at 0.55 and 0.45 for the fly ash concretes, with variations in abrasion depth at each of these of 0.25 and 0.35 mm respectively.

Early research on abrasion suggests that fly ash affects the process as a result of its influences on concrete strength [76]. Increased abrasion resistance has also been noted with fly ash replacement of fine aggregate in concrete [77], which could be related to enhanced strength. Research [78], covering a selection of co-combustion fly ash concretes gave little difference in abrasion behaviour between these at equal strength. Increased abrasion (at equal strength) was also noted with fly ash levels greater than 15%, regardless of w/c ratio and age [79].

The relationship in Figure 10 (left) suggests that there is reasonable agreement between strength and abrasion depth for the concretes, with a similar relationship to that noted between different concretes in the literature [36]. However, abrasion is also sensitive to the near surface characteristics, composition and quality of the matrix in this region [36]. For example there are differences between the PC and fly ash concretes at almost

equivalent strength (around 42 to 45 MPa). Similarly, as noted above a range of results were obtained for the fly ash concretes.

In order to examine this, key fly ash properties are considered against abrasion depth in Figure 10 (middle) and (left). As indicated, although relationships are not strong, with coarsening of fly ash (increased 45  $\mu\text{m}$  sieve retention), which influences particle packing and reactivity, greater abrasion depths were noted. In addition, with increasing LOI (carbon) in fly ash, there was also a tendency for higher abrasion depth. This may reflect the friable nature of carbon [80] and its tendency, particularly at higher levels (which exceeded Standard limits in some cases), to rise to the concrete surface during production [81]. The results therefore suggest that the properties of fly ash can have an influence on the process.

A comparison is made between the data from the current study (at equal strength) and fineness, with those from the 1990s [82] in Figure 11. As indicated, there were relatively minor differences in abrasion depth with changing fly ash fineness at equal strength (40 MPa), which tends to reduce differences of the type noted in Figure 10 at equal w/c ratio, with similar type behaviour found to the earlier study. For the latter, the concretes were designed for equal 28 days strength, but were air cured from 7 days until testing at this age, which may explain the differences in depths between studies.

## **PRACTICAL IMPLICATIONS**

Developments in coal-fired electricity generation through changes to the burning conditions, fuel mixes and with emission reducing techniques, mean that fly ashes for use in concrete construction are increasingly likely to be produced by these means. Similarly, recovery and processing of material held in wet storage areas may complement fly ash supply given the withdrawal of coal-fired power stations. These provide environmental benefits, but at the same time may affect fly ash, which can offer technical benefits to concrete and contribute to sustainable construction. An understanding of their influences on the material and impact on the wider aspects of concrete in practice is therefore important with regard to the materials' continued use.

Concrete specifications for durability (e.g. [16]) do not distinguish between coal fly ashes, but require that they meet relevant material Standards [20]. As noted previously [82], and for fly ashes in the current study [9], changing fineness up to 40% retained on a 45  $\mu\text{m}$  sieve to BS EN 450-1 [20] can have a small influence on

strength. Comparisons of durability properties at equal strength, and air or alkali content, i.e. practical considerations, tended to give similar effects, for the various fly ashes, with those noted in earlier research and in comparison with PC. While confirmatory tests with normal type exposures should be carried out, the outcomes of the study and those of the related research covering chloride ingress and carbonation [10, 11], suggest that although fly ash production and sourcing are changing, established behaviour for the properties investigated in concrete may continue to be expected.

## CONCLUSIONS

Sodium sulfate immersion tests (high concentration) gave only minor expansions ( $\leq 0.02\%$ ) for fly ash concretes at various w/c ratios by 540 days, suggesting little or no damage, with lower levels than those of PC concrete. Differences in chemistry between fly ashes did not appear to influence behaviour, with minor effects of fly ash fineness noted. Weight changes were generally greatest with reducing w/c ratio and for PC concrete during exposure (with only the latter at high w/c ratio losing weight). White discoloration was noted for some concretes, with damage found on edges/corners of PC specimens.

A greywacke aggregate combination gave minor expansion levels for all fly ash concretes (high alkali content;  $\leq 0.02\%$ ) exposed to elevated temperature and relative humidity for 365 days, with no changes in specimen appearance noted. Again, little effect of fly ash chemistry or physical properties were identified in the data, with expansion levels less than those of PC concrete (approximately 0.04%). The aggregate combination type in concrete, which can sometimes give high reactivity, was classified as low reactivity/non-expansive according to BRE Digest 330 [26].

The AEA dose to entrain a target air content in concrete generally followed fly ash SSA, at a given w/c ratio, except for processed wet stored fly ash (PRO), which was less and may reflect moisture effects on particle surface charge. Freeze-thaw scaling of air-entrained concretes increased with exposure time, levelling off more rapidly, and giving reduced losses, at lower w/c ratio. All fly ash concretes lost  $< 1.0 \text{ kg/m}^2$  at 0.45 w/c ratio, with about half meeting this at 0.55 w/c ratio. It was not possible to identify specific effects associated with fly ash influencing damage. Air-entrained PC concrete gave lowest scaling of the materials tested.

Abrasion depth was found to reduce with w/c ratio and generally followed a single relationship with strength for the fly ash and PC concretes tested, with similar effects to those noted for the property previously. Changes in fly ash fineness (affecting particle packing and reactivity) and carbon (LOI) content (affecting the hardness of components at the concrete surface), appeared to have an influence on the observed effects for the property.

As found in earlier research on chloride ingress and carbonation, comparisons of the durability properties from the current and earlier studies generally gave similar type behaviour between these. While further research is required, the study provides information suggesting that the changes in production technology and sourcing of fly ash taking place are unlikely to greatly affect performance in concrete, compared to that typically found for the material.

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**Table 1** Summary of production and sourcing changes and possible effects on fly ash  
(based on literature)

<b>Production / Treatment of Fly Ash</b>	<b>Process Involved</b>	<b>Possible Effects on Fly Ash</b>
NOx Reduction	In-combustion: Changes in the combustion conditions at the power station, e.g. air-fuel ratios to reduce NOx.	Can increase fly ash coarseness and LOI. Chemistry can be affected, e.g. increased sulfate level, reduced glass content.
	Post-combustion: Injection of components, such as ammonia, with or without a catalyst to reduce NOx.	Appears to have little or no influence on the properties of fly ash except for possible contamination by ammonia.
Co-combustion	Produced during the firing of coal with partial replacement using materials such as wood chips, meat and bone meal.	Material dependent but can increase coarseness and LOI. Chemistry may also undergo some changes, sometimes including components from the co-fuel.
Stockpile Fly Ash	Moistened at levels of around 10 to 20% following production and stored in external holding areas.	Agglomerates and coarsening of fly ash may occur. Products can form on particles, with increases in LOI possible due to reactions. Bulk chemistry is essentially unchanged.
Processed Stockpile Fly Ash	Stored in wet holding areas. Removal of coarse fly ash particles and carbon within the material.	Increased fineness and reduction of carbon levels in the material. Chemistry may change slightly due to components present in different size fractions.

**Table 2** Fly ashes used during the study

<b>Fly Ash</b>	<b>Details of Production, Source or Standard Classification</b>
<b>FA1</b>	Category S (fineness < 12.0%, 45 µm sieve retention) base load power station
<b>FA2</b>	Category S (fineness < 12.0%, 45 µm sieve retention)
<b>FA3</b>	Produced during the 1990s
<b>FA4</b>	SNCR <sup>1</sup> NOx reduction technology
<b>FA5</b>	SCR <sup>2</sup> NOx reduction technology
<b>FA6</b>	In-combustion NOx reduction technology
<b>FA7</b>	Woodchip, co-combustion (Summer)
<b>FA8</b>	Wood chip, co-combustion (Winter)
<b>FA9</b>	Petroleum coke co-combustion
<b>STO</b>	Stockpile (storage history not known)
<b>PRO</b>	Stockpile processed (storage history not known)

<sup>1</sup>Selective catalytic reduction

<sup>2</sup>Selective non-catalytic reduction

**Table 3** Summary of characteristics for the fly ashes [9]

Characteristic	Fly ash										
	FA1	FA2	FA3	FA4	FA5	FA6	FA7	FA8	FA9	STO	PRO
<b>Physical properties</b>											
LOI, %	4.4	4.0	5.9	2.6	3.4	7.3	13.7	17.3	9.8	8.3	4.8
Fineness <sup>+</sup> , %	9.6	13.2	32.8	12.1	15.1	22.5	24.4	27.2	29.4	49.5	2.6
Water requirement, %	95	93	100	96	96	98	103	105	104	105	92
d50, $\mu\text{m}$	12.1	14.1	28.2	14.8	19.1	24.0	29.7	33.1	34.0	42.7	8.6
<b>Oxide composition, %</b>											
CaO	3.01	2.31	4.03	1.91	3.74	1.64	3.55	2.94	4.63	2.67	2.74
SiO <sub>2</sub>	48.29	49.81	43.40	51.42	47.07	45.74	42.86	41.98	39.41	43.81	48.28
Al <sub>2</sub> O <sub>3</sub>	20.12	22.31	23.28	17.34	19.93	16.55	20.92	20.82	21.07	23.42	23.98
Fe <sub>2</sub> O <sub>3</sub>	8.35	7.94	11.00	8.96	9.13	7.72	6.71	8.15	12.99	10.97	7.64
K <sub>2</sub> O	2.80	3.42	2.67	2.04	3.37	1.73	1.55	2.05	2.52	2.86	3.15
Na <sub>2</sub> O	2.01	1.33	1.71	1.74	1.44	1.24	0.84	0.75	1.19	0.90	0.74
SO <sub>3</sub>	0.97	0.89	1.40	1.45	1.24	1.08	0.80	1.24	2.55	0.97	0.55
<b>Mineral composition, %</b>											
Quartz	9.8	11.1	8.6	20.7	11.1	19.0	3.9	4.8	7.0	6.9	7.1
Hematite	2.2	2.3	3.2	2.4	2.7	1.7	1.4	1.5	2.6	3.4	1.8
Magnetite	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.4	0.1	0.0
Mullite	10.4	11.0	15.6	7.6	8.8	10.6	9.5	11.8	11.9	13.3	16.1
Glass/Others*	73.2	71.5	66.5	66.6	73.8	61.3	71.4	64.6	68.3	76.4	74.2

STO – stockpile

PRO – processed

<sup>+</sup> Percent retained on a 45  $\mu\text{m}$  sieve

\* not including LOI



**Table 4** Physical properties of the aggregates used in the study

<b>Aggregate Source</b>	<b>Size Fraction, mm</b>	<b>Particle Density (at SSD), kg/m<sup>3</sup></b>	<b>Water Absorption (lab dry to SSD), %</b>
North Fife sand and gravel	0/4	2630	0.8
	4/10	2600	1.4
	10/20	2610	1.3
Scottish greywacke sand and coarse	0/4	2650	0.8
	4/10	2600	1.0
	10/20	2630	1.2
Magnesian limestone coarse	4/10	2665	1.1
	10/20	2600	1.0
Trent Valley sand	0/4	2650	0.4

**Table 5** Mix proportions used for the various concretes

Mix	W/C ratio	Concrete Mix Proportions, kg/m <sup>3</sup>								Total
		Free water	Cement / Addition			Aggregate <sup>1</sup>				
			PC	Fly ash	Total	Sand	4/10	10/20	Total	
<b>Sulfate attack/Abrasion<sup>2</sup></b>										
PC	0.35	165	470	0	470	720	375	700	1795	2430
	0.45	165	365	0	365	790	380	710	1880	2410
	0.55	165	300	0	300	850	380	705	1935	2400
PC/Fly Ash	0.35	165	330	140	470	700	365	680	1745	2380
	0.45	165	255	110	365	775	375	695	1850	2375
	0.55	165	210	90	300	845	375	695	1915	2380
<b>Alkali-aggregate Reaction<sup>3</sup></b>										
PC	0.33	228	699	0	699	415	415	590	1417	2347
PC/Fly Ash	0.36	228	447	192	639	415	415	590	1417	2287
<b>Freeze-thaw Scaling<sup>4</sup></b>										
PC	0.45	165	365	0	365	730	370	685	1785	2315
	0.55	165	300	0	300	790	365	680	1840	2300
PC/Fly Ash	0.45	165	255	110	365	715	360	670	1745	2275
	0.55	165	210	90	300	780	360	670	1810	2275

<sup>1</sup> Aggregate values correspond to the SSD condition

<sup>2</sup> Superplasticizer used at quantities necessary to achieve 100 – 150 mm slump

<sup>3</sup> Potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) added to PC (7.5 kg/m<sup>3</sup>) and PC/fly ash (10.2 kg/m<sup>3</sup>) to give 7.0 kg/m<sup>3</sup> Na<sub>2</sub>O<sub>eq</sub> in concrete

<sup>4</sup> Superplasticizer used at fixed dose with air-entraining admixture added to achieve approximately 80 – 160 mm slump/5.0% air content

Aggregate combinations:

Sulfate attack/abrasion – North Fife sand/gravel

AAR – greywacke sand/coarse

Freeze-thaw scaling – North Fife sand/magnesian limestone coarse

**Table 6** Weight change of PC and PC/fly ash concretes at 540 days exposure (68 g/l Na-sulfate), %

<b>PC / Fly Ash</b>	<b>W/C Ratio of Concrete</b>		
	<b>0.35</b>	<b>0.45</b>	<b>0.55</b>
PC	0.86	0.36	0.92
FA1	0.34	0.15	0.17
FA2	0.30	0.17	0.32
FA3	0.34	0.25	–
FA4	0.25	0.22	0.21
FA5	0.38	0.16	0.03
FA6	–	0.23	0.27
FA7	0.39	0.26	0.16
FA8	–	0.17	0.14
FA9	0.49	0.28	–
Processed	0.22	0.09	0.16
Stockpile	0.46	0.22	–

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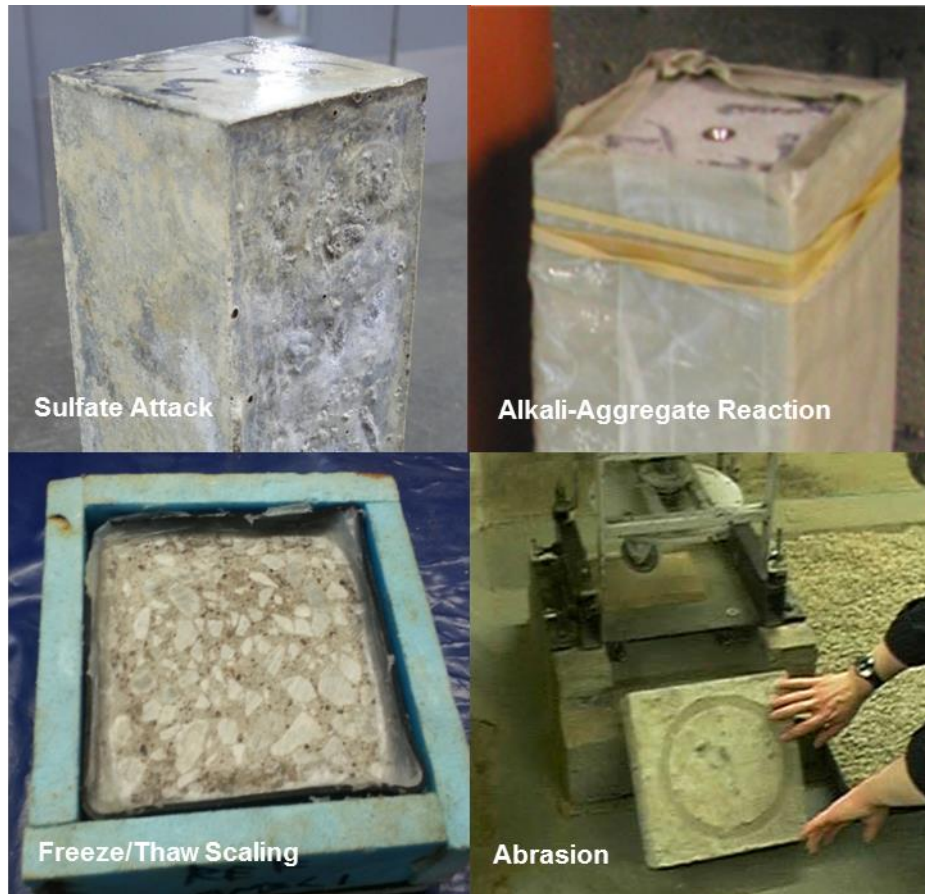
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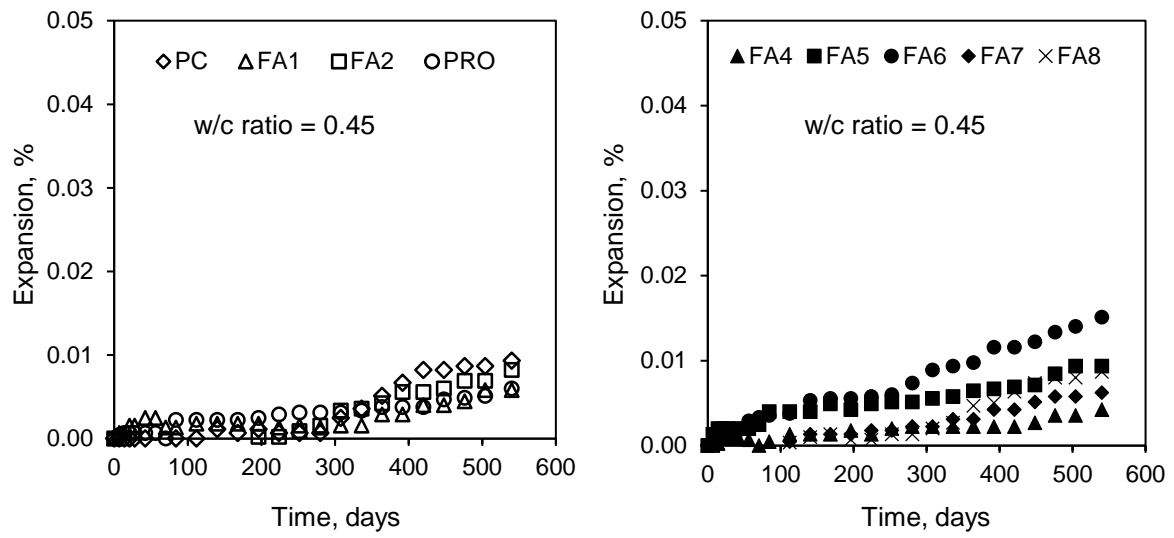
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Figure 10 Relationships between 28 days cube strength of PC and PC/fly ash concrete (left), fineness (45  $\mu\text{m}$  sieve retention, centre), Loss-on-Ignition (right) of fly ash and abrasion depth

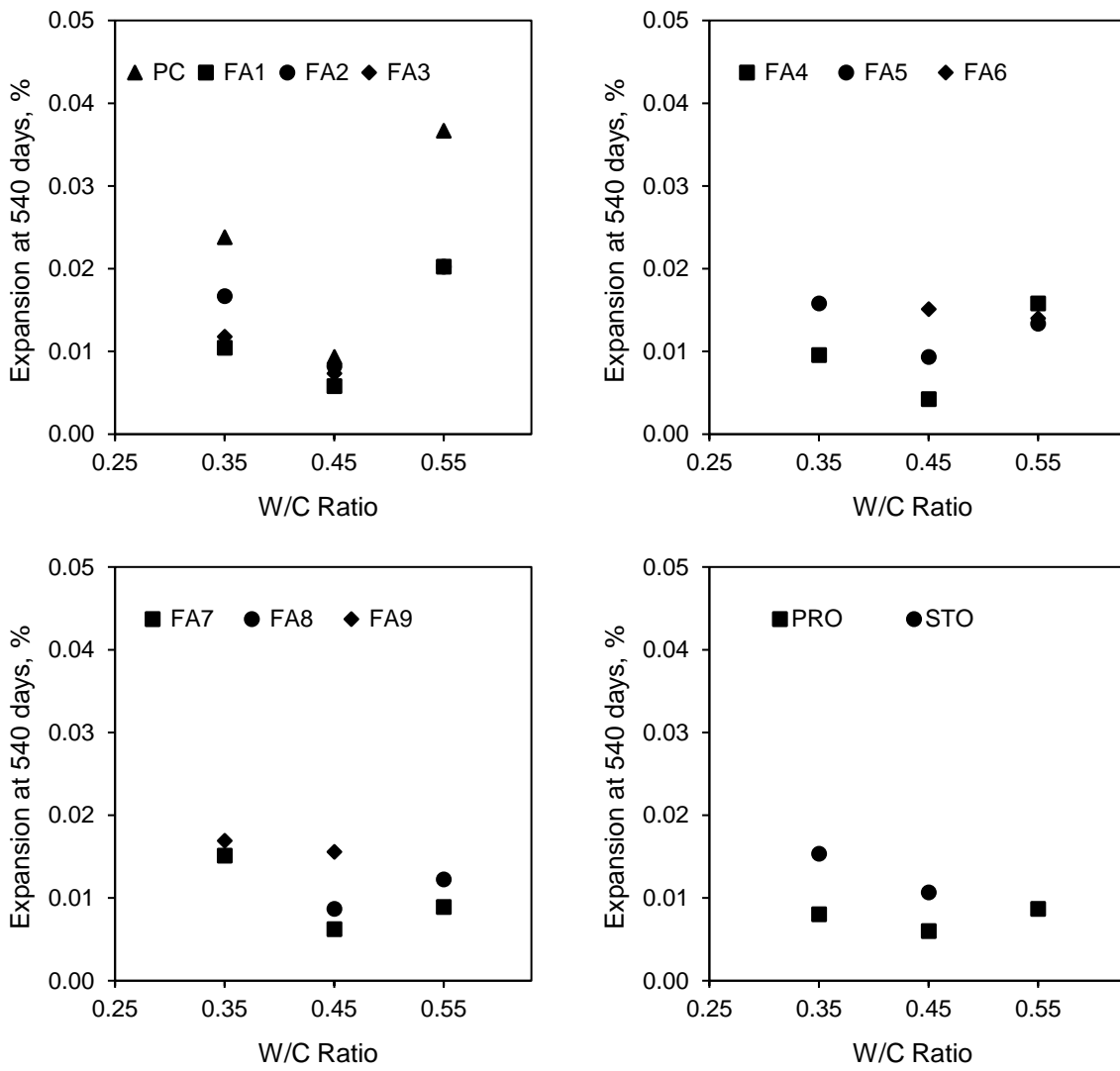
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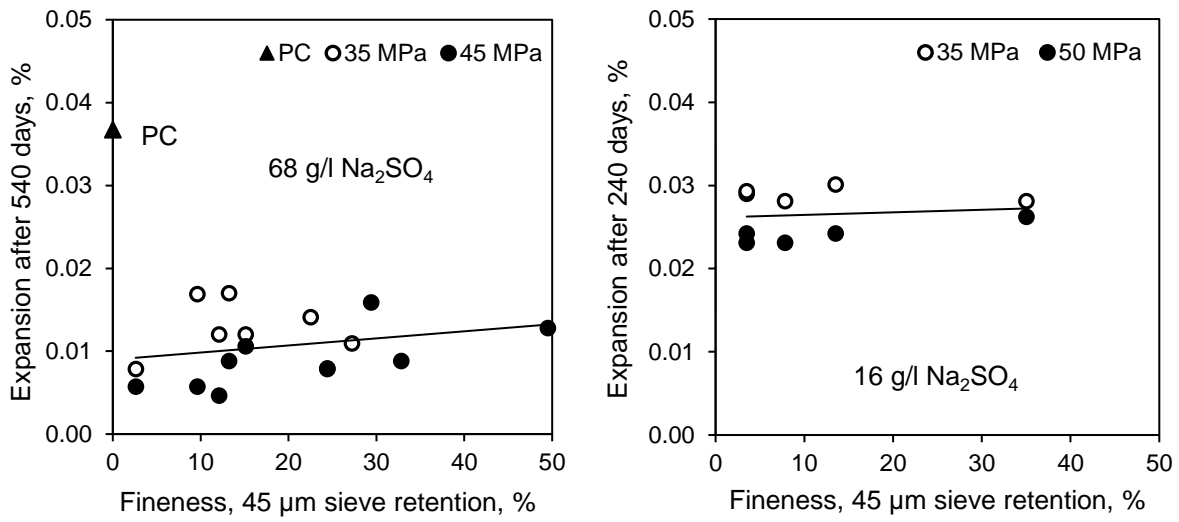
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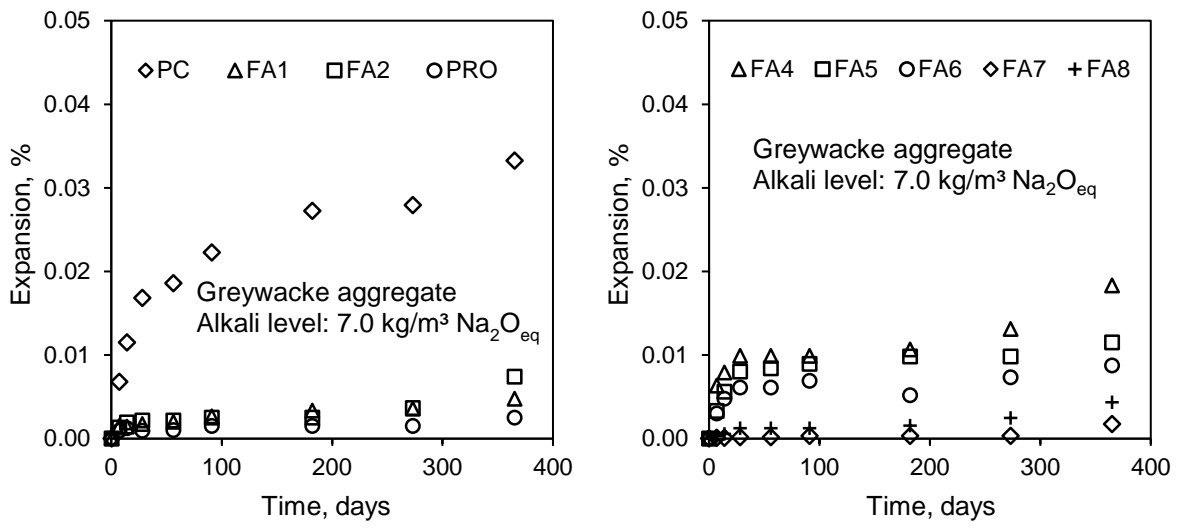


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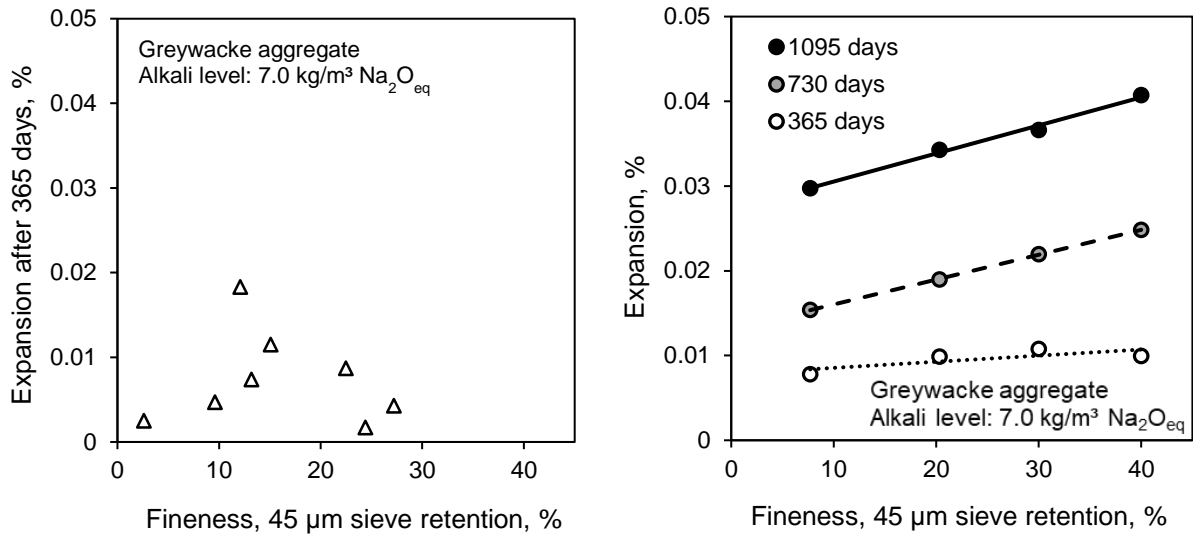


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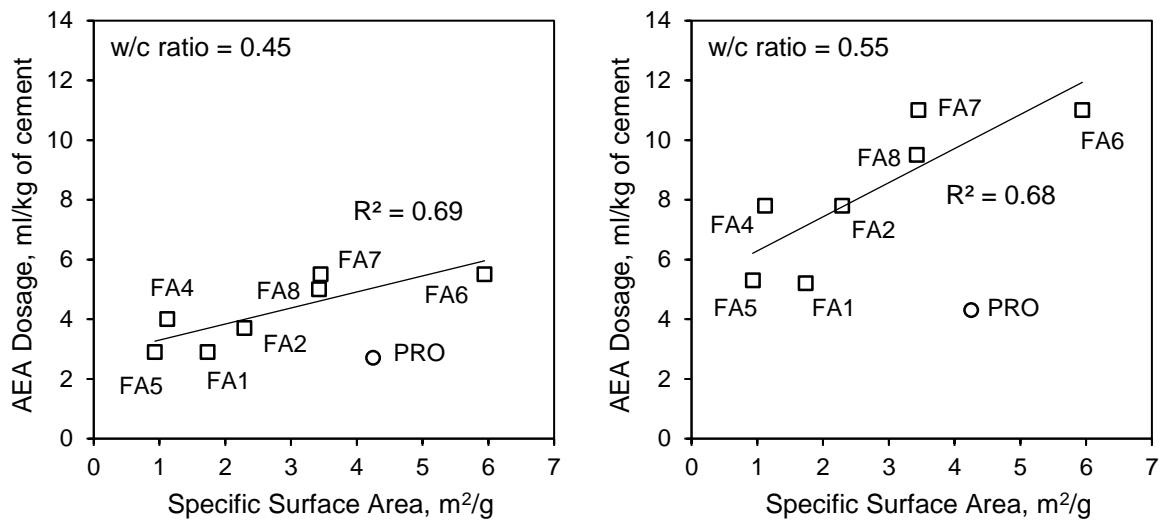




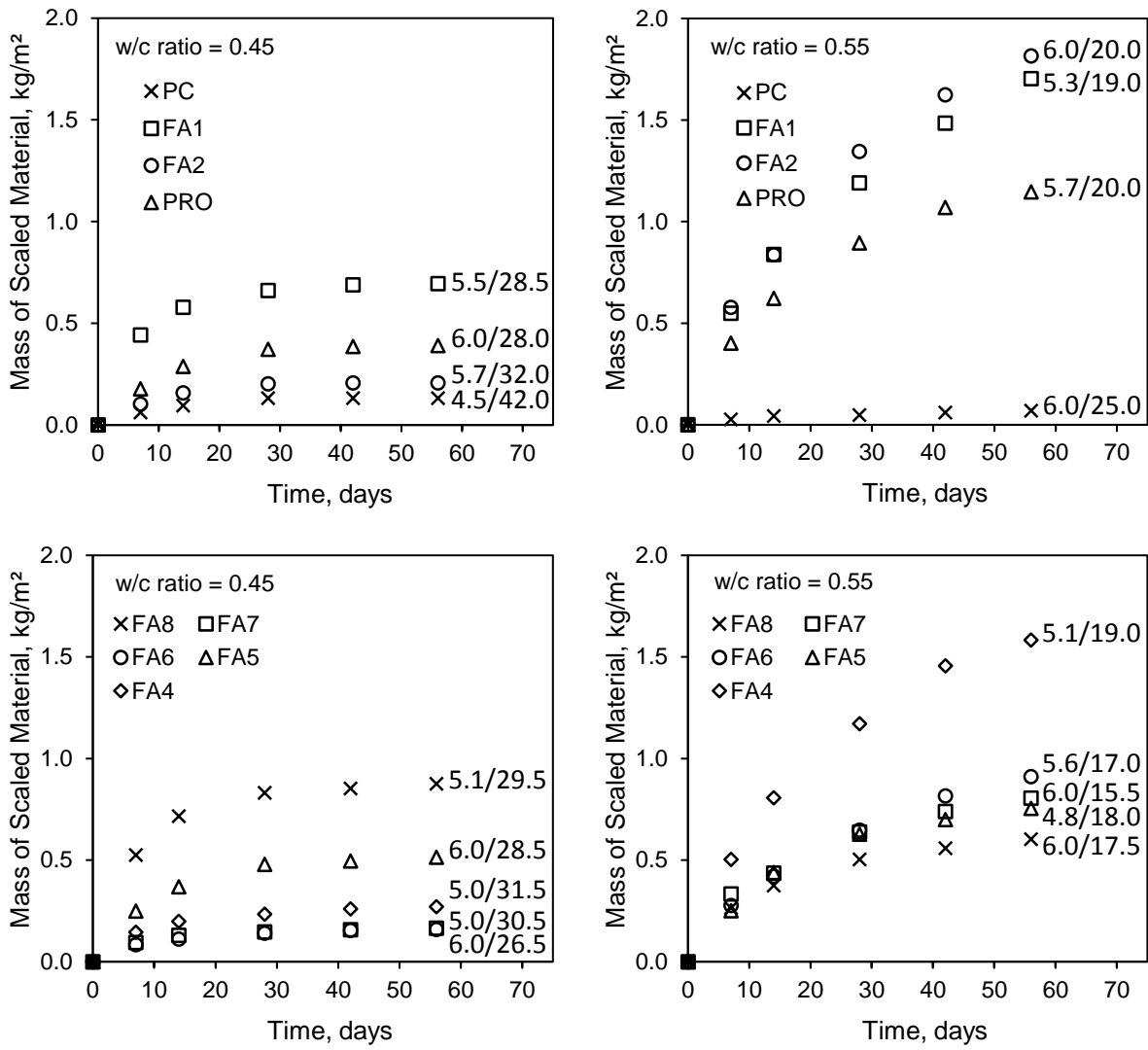
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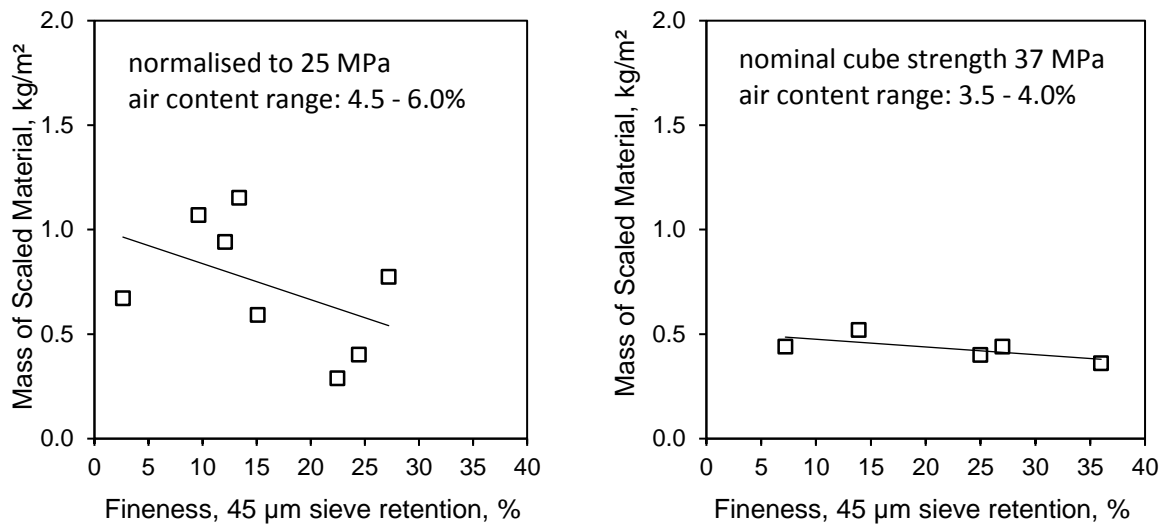
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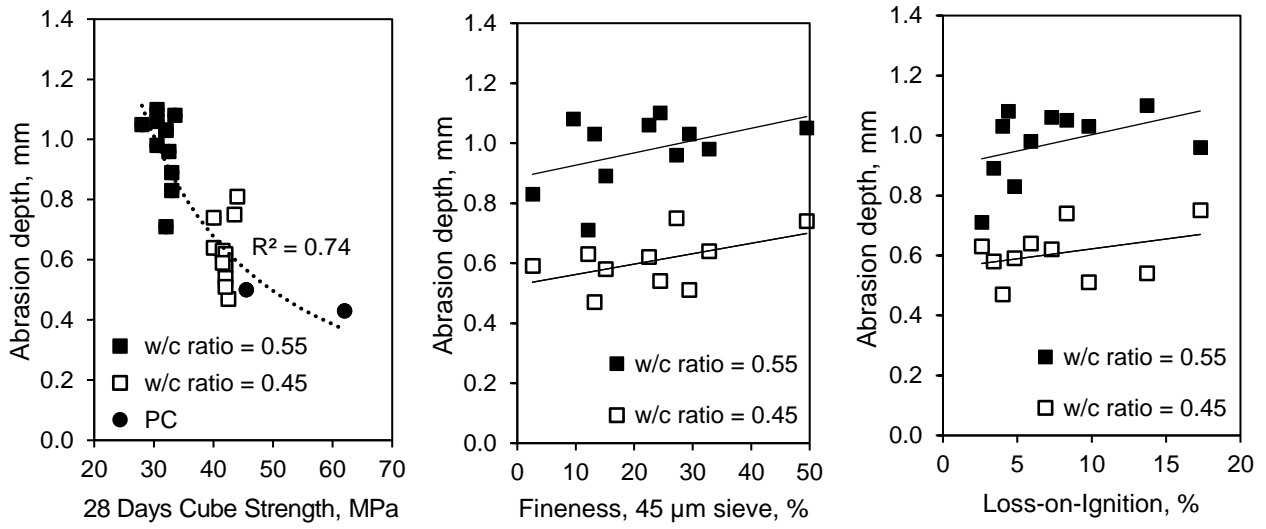
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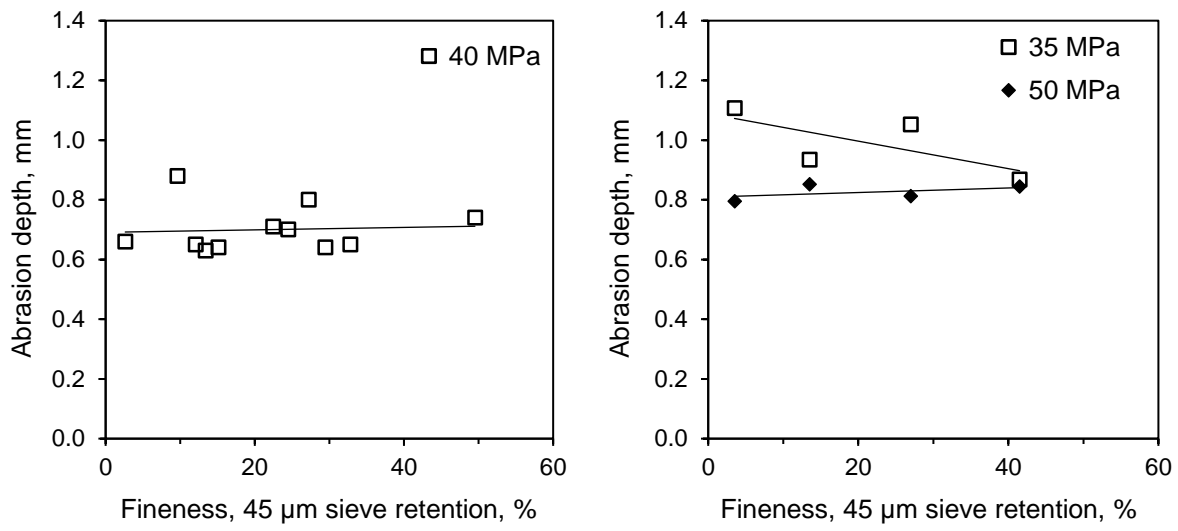
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