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Evaluation of Fly Ash Reactivity Potential Using a Lime Consumption Test

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Abstract

The reactivity of fly ash, for use in concrete, is normally evaluated in the UK/EU with the Activity Index test (on mortars at 28 and 90 days (BS EN 450-1)). The paper reports on the application of a lime consumption test, based on BS EN 196-5 (pozzolanic cement test), to determine this more rapidly. The method uses a Portland cement (PC) / fly ash slurry, stored for 8 or 15 days at 40°C, and measures OH^- and CaO concentrations of the filtrate. Seven fly ashes, including those produced using modern power station techniques (e.g. co-combustion, low NOx) and 3 PCs with different characteristics were tested. Early experiments established good repeatability for the test and that pozzolanic reactions mainly occur during the initial 8 to 15 days' storage. Similar behaviour for fly ash was noted to that in thermogravimetric analysis and Activity Index tests from related studies. Strong correlations were obtained for fly ash fineness and CaO consumed. While there was general agreement for CaO consumed and Activity Index, correlations were poor. Similar type effects occur for mortar (Activity Index) and concrete. The lime consumption test can assess fly ash reactivity, but should be combined with measurements of the materials' fineness.

1. Introduction

As with other constituents of concrete, a range of properties are normally tested to establish the suitability of fly ash as an addition (Lamond and Pielert, 2006; BSI, 2012; ASTM, 2012). These include, (i) physical characteristics such as fineness, particle density and water requirement, (ii) various aspects of the materials' chemistry, for example loss-on-ignition (LOI), the sum of the main oxides, alkali and SO_3 contents, and (iii) pozzolanic reactivity. Some of these can be traced to the early days of fly ash use in concrete (Anderson et al, 2008), while others have been introduced with experience gained, or changes in electricity generation technology, e.g. co-combustion (BSI, 2012), that have taken place.

The majority of tests for evaluating fly ash can normally be carried out in a relatively short period of time. For example, fineness is measured within 24 hours, while many other properties can be determined in a similar or shorter time-scale (McCarthy et al, 2013). The exception to this is the measurement of fly ash reactivity, since this tends to occur in the period post 7 to 14 days (at temperatures of around 20°C; Fraay et al, 1989; Papadakis, 1999) and can continue for several months or longer thereafter (Massazza, 1998; Concrete Society, 2011), depending on curing conditions. As a result, longer-term testing is frequently adopted to enable this to be evaluated.

Reactivity measurements frequently use mortar as the test medium (Gava and Prudêncio, 2007a, 2007b; Bentz et al, 2011), replacing part of the Portland cement (PC) by fly ash (with standard sand also in the mix). The approach in BS EN 450-1 (BSI, 2012) is carried out on equal w/c ratio mortar (variable flow), while other Standards make comparisons at equal flow (variable w/c ratio; e.g. ASTM C618 (ASTM, 2012)). Tests in compression are made at specific times and the PC/fly ash to PC mortar strengths (expressed as a percentage), compared against required values (75 and 85% at 28 and 90 days in BS EN 450-1 (BSI, 2012); 75% at 7 or 28 days in ASTM C618 (ASTM, 2012)). Clearly, there would be advantages to fly ash production control, not least early availability of information, if the time required to assess its reactivity was shorter.

Literature reviews (McCarthy et al, 2013; Snellings and Scrivener, 2016) indicate that several methods, following various approaches, have been considered to evaluate pozzolana / fly ash reactivity. One technique recently identified with potential (Donatello et al, 2010) is the lime consumption test in BS EN 196-5 (BSI, 2011a), taking 8 or 15 days and normally used to evaluate pozzolanic cements. While comparisons between methodologies for different pozzolanic materials have been questioned (Cava and Prudêncio Jr, 2007a), correlations have been noted between lime consumption and strength for individual pozzolanas (Massazza, 1998). This has also been found in preliminary studies on a range of fly ashes, using BS EN 196-5 (BSI, 2011a) / BS EN 450-1 (BSI, 2012) mortar tests at the University of Dundee (McCarthy et al, 2013). Given the initial promise, a study was carried out to more fully evaluate this method as an alternative to mortar-type tests for determining fly ash reactivity.

2. Programme of Research

The programme of research was divided into two parts. The first was concerned with investigating several issues associated with the lime consumption test and its use with fly ash. A single PC and fly ashes covering a range of properties were used. These included materials produced from modern power station technologies, e.g. co-combustion (coal with secondary fuels), low NOx methods (reduce NOx emissions) and supercritical steam generation (improve process efficiency; Baxter, 2005; Beer, 2007; Franco and Diaz, 2009). Tests were carried out to determine the repeatability of the method and period necessary for fly ash reactions to approach completion. Comparisons between the lime consumption results and related data from thermogravimetric (TG) and Activity Index test data (i.e. other means of assessing reactivity) for fly ash, were also made.

The second part was concerned with the potential of the lime consumption test as a more rapid alternative to mortar-type methods currently used for evaluating fly ash reactivity. This included additional PCs to that used during the first part of the study. Relationships between lime consumed for different PC/fly ash combinations and Activity Index were investigated. Concrete compressive (cube) strength tests were carried out on selected materials as part of the reactivity assessment. The practical implications of the study were also evaluated. It should be recognised that while the term 'fly ash reactivity' is used for the methods described in the Paper, they in fact provide a measure of the reactivity of PC/fly ash.

3. Materials

Three PCs and seven fly ashes were selected, giving a range of materials to evaluate the lime consumption test. Details of the PCs (from the supplier), which all met the requirements of BS EN 197-1 (BSI, 2011b) are given in Table 1. PC1 was most widely used during the study, with PC2 and PC3 introduced to investigate material effects in Part 2. The specific surface area (Blaine) of these increased in the following order, PC3, PC1 and PC2, while, their corresponding strength classes were 42.5 N, 52.5 N and 52.5 R, i.e. meeting the requirement (of 42.5 or higher) for the Activity Index test, according to BS EN 450-1 (2012).

The main characteristics of the seven fly ashes investigated are given in Table 2. The materials were (with one exception) produced at different power stations under various conditions. These include base-load (full-capacity) combustion (Fly Ash 1), co-combustion (wood chip; Fly Ash 2), supercritical steam generation (Fly Ashes 3 and 4), co-combustion produced at the same station as Fly Ash 2, but under base-load conditions (wood chip; Fly Ash 5) and low NOx technology using selective non-catalytic reduction (SNCR; Fly Ash 6) and selective catalytic reduction (SCR; Fly Ash 7). Initial work (McCarthy et al, 2014) suggests that fly ash from these newer technologies has only minor influences on behaviour in cementitious systems, compared to conventionally produced material.

The LOI of the fly ashes ranged from 1.4 to 17.3 %, with fineness (45 μm sieve retention) from 9.6 to 29.6%. The CaO contents were all ≤4.5%, with the sum of the main oxides between 68 and 78%. The alkali contents (Na_2O_{eq}) ranged from 1.9 to 4.2%. The mineral compositions were in the typical range, with Fly Ashes 3 and 7 at the upper and lower end for glass / others respectively. The data indicate that some fly ashes had properties outside BS EN 450-1 (BSI, 2012) limits. For example, Fly Ashes 2 and 5 exceed 9.0% for LOI, while Fly Ashes 3 and 4 were slightly less than 70% for the sum of the main oxides.

CEN standard sand to BS EN 196-1 (BSI, 2016) was used in the Activity Index mortar tests. For the concretes, a coarse gravel in 10/20 and 4/10 mm sizes and a medium grade sand (North Fife), meeting the requirements of BS EN 12620 (BSI, 2013a) were adopted. Their particle densities (saturated surface dry) and water absorptions (laboratory dry to saturated surface dry) were 2600, 2610 and 2630 kg/m³ and 1.3, 1.2 and 0.8% respectively. A superplasticizing admixture, based on a modified polycarboxylic ether to BS EN 934-2 (BSI, 2009a) was used in the concretes to enable control of the mix water content and consistence.

4. Test Procedures and Sample Preparation

Lime Consumption

The procedure was based on the BS EN 196-5 method (BSI, 2011a; with slight differences in reagents used / number of duplicate tests made). The reference contained 20.0 g of PC, with 15.0 g of PC / 5.0 g of fly ash adopted for test mixes (i.e. matching Activity Index proportions). These were added to 100 ml of de-ionised water in a plastic bottle, which was shaken vigorously by hand, before storing in a controlled chamber at 40°C for the required time (8 and 15 days in the Standard). Following these periods, the mix was filtered and the solution tested for OH^- and CaO contents, i.e. neutralisation with dilute nitric acid (0.1 M), followed by the addition of a single bead of potassium hydroxide to the neutralised filtrate, and titration with EDTA (disodium-dihydrate salt of ethylenediamine tetra-acetic acid) solution (0.025 M) in the presence of murexide indicator.

An auto-titrator (Metrohm Titrino 719) was used, with a 20 ml exchange unit, which could dispense reagents at 2 µl increments, with end points established instrumentally (by pH and photometric electrodes). Single samples were tested, with repeats carried out selectively for confirmation. A plot of OH^- against CaO is normally made from the data and if the point lies below the lime saturation line, at either 8 or 15 days, the PC/pozzolana combination passes the test.

The results from the tests are mainly presented in the paper as the difference in CaO between PC and PC/fly ash with respect to that in PC as a percentage, referred to as CaO consumed in PC/fly ash. In comparing CaO levels, it is evident that CaO in PC/fly ash corresponds to fly ash influences on PC hydration, e.g. dispersion of flocs /

provision of hydration sites (Dhir, 1986), PC dilution by fly ash, as well as lime consumed. Thus, the CaO in PC/fly ash is the net result of these effects. Such influences are likely in PC/fly ash mortar, and expression of the data in the terms indicated is similar to that used for Activity Index.

Activity Index

The Activity Index tests followed the method described in BS EN 450-1 (BSI, 2012). The mortar comprised 450 g PC (337.5 g PC / 112.5 g fly ash in the test mixes), 225 g water and 1350 g of CEN standard sand. The mortar was mixed using an orbital mixer, as described in BS EN 196-1 (BSI, 2016). This was used to prepare prisms of 40 mm × 40 mm × 160 mm size.

After water-curing at 20°C, samples were tested in compression (2 measurements on each 40 mm × 40 mm × 160 mm prism) using a jig, inserted into the compression testing machine, as described in the Standard. Six tests (three prisms) were used during Part 1, with three tests (1.5 prisms) in Part 2, for each material combination at 28 and 90 days. The Activity Index at these test ages was expressed as the strength ratio of PC/fly ash to PC mortars as a percentage (as described in BS EN 196-1 (6 half prisms) or mean of the tests (3 half prisms)).

Concrete Cube Strength

Concrete was prepared in a horizontal laboratory pan mixer, following BS 1881-125 (BSI, 2013b). The concretes comprised 330 kg/m³ PC (reference mix) or 231 kg/m³ PC, 99 kg/m³ fly ash (test mixes), 165 *l*/m³ water and a fine to total aggregate ratio of 0.42. Superplasticizing admixture was used at doses between 0.45 and 0.55% by mass cement (PC and addition), to achieve a slump in the range 130 ± 20 mm. The target plastic densities were 2400 and 2375 kg/m³ for PC and PC/fly ash concretes respectively.

To assess the reactivity of fly ash in concrete, 100 mm cubes were cast following mixing and cured in water at 20°C for the required period of time. Cube strengths were measured at 28 and 90 days (BSI, 2009b), i.e. corresponding to Activity Index test times, with three specimens used at each age. The PC/fly ash concrete strengths (mean of the tests) were expressed as a percentage of those obtained for PC.

5. Lime Consumption Tests and their Use with PC/Fly Ash Combinations

Test Repeatability

Initial tests were carried out to investigate the variability of the lime consumption test. Fly ashes 1 and 2 (fineness, 9.6 and 24.4% retained on the 45 μm sieve) were used with PC1, and testing carried out at 8 and 15 days. The results from the measurements of OH^- and CaO for the materials and test ages are given in Table 3. These indicate that the OH^- concentrations were higher for Fly Ash 1 than Fly Ash 2, reflecting its greater alkali content (see Table 2) and release during the test. The opposite was found for the CaO contents, with Fly Ash 1 giving lower levels than Fly Ash 2, corresponding to differences in their consumption and fineness (noted to provide a good indication of fly ash reactivity; Fernandez-Jimenez and Palomo 2003; Soutsos et al, 2016).

The standard deviation for the OH^- concentrations ranged from 0.60 to 1.43 mM, with that for the CaO contents between 0.14 to 0.41 mM. There was no consistent effect for the different fly ashes tested, however, lower variability was noted at the 15 day test age. This perhaps relates to the increased time for dissolution / reactions to take place between samples and that they are tending towards limiting values, reducing measurement differences. The results obtained during the tests were similar to, or slightly higher than the repeatability data given for the method in BS EN 196-5 (BSI, 2011a; standard deviation for OH^- = 0.5 mM and CaO = 0.2 mM). These indicate acceptable variability levels for laboratory testing, and methodology for investigation of the technique as a means of evaluating fly ash reactivity.

Calcium Oxide / Hydroxyl Ion Relationship

The test results, shown as described in BS EN 196-5 (BSI, 2011a), i.e. OH^- concentration against CaO content, are given in Figure 1. The data for PC are above the solubility curve at 8 and 15 days, with a reduction in CaO noted by the later age (and increase in OH^-). This has been found for PC previously with the test (Sear, 2001; Snelling and Scrivener, 2016). It has been suggested that calcium, e.g. from C-S-H gel, may pass through the filter when separating solids from the solution, increasing CaO recorded (Donatello et al, 2010). While this is possible, the chemistry of the system is also complex with various effects occurring / ions present. Clearly, lime will develop with time, while also tending towards the saturation line. However, it appears that this idealised equilibrium condition may not be achieved for PC, at least during the test period.

According to BS EN 196-5 (BSI, 2011a) the PC/pozzolana combination satisfies the pozzolanicity test if the result lies below the lime saturation line by either 8 or 15 days. As indicated, with the exception of Fly Ash 4 (which was the coarsest of those tested), the combinations passed the test by 8 days, with all achieving this by 15 days. Between test ages, it is apparent that there was a general shift downwards and to the right in the data, relating to the CaO consumed as noted above and increased availability of alkali in solution from PC and fly ash.

For the fineness values 10 to 30% retained on the 45 µm sieve, the range for CaO at 8 and 15 days was 2.06 and 1.62 mM, corresponding to quantities of EDTA solution of 19.4 and 17.8 µl for each 1.0% change in sieve retention. This appears to give adequate differences for the fly ashes being investigated and sensitivity with the test (and equipment), as a means of quantifying the materials' reactivity.

Test Period

In order to examine general behaviour and the period until the majority of lime has been consumed, tests were made at various intervals up to 20 days (including 8 and 15 days, given in the Standard). The results for the fly ashes, shown as relative CaO levels (i.e. CaO in PC/fly ash / CaO in PC), are given in Figure 2. As indicated, Category S fly ash (45 µm sieve retention ≤ 12%) to BS EN 450-1 (BSI, 2012) gave lower relative CaO levels than those of Category N (45 µm sieve retention between 12% and 40%), corresponding to their greater fineness. These also show small differences between PC and PC/fly ash combinations at 4 days (of about 5 to 15%), which increased to 8 days. Beyond this, small changes in relative CaO levels occurred until the conclusion of tests at 20 days.

The results can be understood by comparing with TG data from tests on mortar (water cured at 20°C; mass change in nitrogen atmosphere over 450 to 510°C range, during a rise to 1000°C at 20°C/min.) from a previous study (Dhir et al, 1996) using fly ash of varying fineness from a single source (Category S and N) shown in Figure 3. The increase in CaO content up to 7 days corresponds to lime production during early PC hydration, with minor effects of fly ash reactions during this period. Between 7 to 14 days, reductions due to CaO consumed by fly ash are apparent, which continue thereafter until the end of testing at 56 days. The increases in CaO consumed with finer fly ash and sensitivity of the test to material properties are also evident.

As might be expected, the relative CaO results correspond to those of the TG data. It is unclear whether the relative CaO level at 4 days in Figure 2 represents the peak value for the materials. However, for the conditions used, the test ages provide a good indication of the main period of fly ash reactivity. Indeed, the data suggest that the 8 and 15 day test ages are reasonable for evaluating this, i.e. corresponding to the period where changes in relative CaO level have noticeably reduced. In addition, the fine and coarse fly ashes gave differences of approximately 5% or greater, again indicating sensitivity of the test to material properties.

Comparisons of CaO Consumed with Activity Index

Data showing typical Activity Index results with time to 180 days from a related study (Sadiqul Islam, 2012), for a selection of fly ashes from various sources and of different fineness (with PC, 52.5N) is given in Figure 4. As indicated, at 7 days the Activity Index was between 75 to 85%, increasing to 85 to 95% by 28 days and then approximately 100 to 110% by 90 days, with little further increase by 180 days. The 7 day results correspond to the period of little fly ash contribution to strength. Thereafter, with fly ash reactions, differences reduce with respect to PC, eventually matching and exceeding this. The results suggest that 90 days is necessary to fully evaluate fly ash reactivity and the test is sensitive to fly ash properties.

The results in terms of CaO consumed for the PC/fly ash mixes, over 20 days, are shown in Figure 5. The data between Figures 4 and 5 indicate similar type behaviour. As noted above, reductions in rates of CaO consumption had mainly occurred by about 15 days, which generally relates to 90 days in the Activity Index tests. The wider spread of data in the lime consumption test also suggests increased sensitivity to material effects, than for mortar strength measurements.

Given the outcomes of Part 1, which indicate acceptable precision and agreement with other methods of assessing fly ash reactivity, the research progressed to examine the potential of the lime consumption test method to assess reactivity for a wider range of material combinations and as a more rapid alternative to Activity Index tests.

6. Lime Consumption Tests to Assess Fly Ash Reactivity

In this part of the study, two additional PCs were used with the fly ashes. Results showing CaO consumed against fly ash fineness for the three PCs are given at 8 and 15 days in Figure 6. As indicated, similar behaviour was obtained for all PCs, with CaO consumed reducing with fly ash fineness (increasing 45 μm sieve retention), and small variations in gradients noted. As expected, between the two test ages, there were increases in CaO consumed by about 10 to 15%, with more noticeable changes for PC3. For the different PCs, all gave R^2 for fly ash fineness against CaO consumed at both test ages between 0.69 and 0.95, increasing in the following order, PC3, PC1 and PC2.

It has been noted previously (Dhir et al, 1993) that the use of rapid hardening PC can increase early strength of fly ash concrete, which may reflect early availability of lime and its influence on fly ash reactions, while in the longer term, a less reactive PC in combination with fly ash may give higher strength. These early effects were not apparent in the data, perhaps occurring prior to testing at 8 days. However, greater differences in CaO consumed were noted at the later test age with PC3. Other work (Sadiqul Islam, 2012) has also found higher Activity Index values for fly ash with lower strength class cement.

The Activity Index results for fly ashes with PC1 are shown against fineness in Figure 7. As indicated, all fly ashes passed the BS EN 450-1 limits of 75 and 85% at 28 and 90 days respectively. This was marginal at the early age, in some cases, but greater at the later test time. The comparison of Activity Index results with fineness, suggests slight reductions with increasing sieve retention at 28 days and more noticeable effects at 90 days. However, neither gave strong correlations, albeit R^2 was higher by the later test age. Similar type behaviour was noted with the tests for PC2 and PC3, with relatively low R^2 values also mainly obtained (except for PC2 at 28 days, with R^2 approximately 0.7).

If a comparison is made between the relationships for fineness and CaO consumed (Figure 6) and fineness and Activity Index (Figure 7), these are much stronger for the former. This suggests that testing in a slurry, as for the lime consumption test, gives increased sensitivity to the reactivity of fly ash than in mortar. The behaviour may be due to more intimate contact between lime and fly ash particles, since its migration may be restricted by the denser developing hardened structure in mortar (Massazza, 1998). It appears that this may also affect the influence of particle size on reactivity and measured effects of fly ash, and why there is a stronger relationship between CaO consumed and fineness than with Activity Index.

A comparison between CaO consumed with Activity Index for PC1 and the 7 fly ashes at 28 and 90 days is shown in Figure 8. At both test ages for the lime consumption test (8 and 15 days), the relationship was poor with 28 day Activity Index. However, by 90 days, R^2 of around 0.60 was noted at 8 and 15 days. The results again suggest the need for longer-term testing with Activity Index to establish fly ash reaction potential. As noted above, 8 days appears to be sufficient to establish reactivity with the lime consumption test, with little improvement in the relationship by extending this.

A similar effect is noted in Figure 9, where a comparison is made between the properties for the different PC / fly ash combinations. The trend suggests some agreement between these, but poor correlations and significant scatter for the wider range of cement combinations. It therefore appears that CaO consumed / mortar strength relationships change for the same fly ashes with different PCs. This agrees with previous data (Dhir et al, 1998), which gave a range of concrete strengths for the same fly ash when combined with various PCs and may relate to differences in microstructure, availability of lime and their effects on fly ash reactions. The results suggest that the measurement of CaO consumed and correlation with Activity Index for fly ash may not be possible.

In order to further investigate lime consumption and mortar behaviour, concrete tests were also carried out. The PC1/fly ash cube strengths with respect to the PC1 reference concrete, at both 28 and 90 days, are shown in Figure 10. The data indicate similar effects to those noted previously in tests comparing concrete strength and fly ash fineness (Dhir et al, 1998; Chindaprasirt et al, 2005). While the ranking between mortar and concrete relative strengths changed between 28 and 90 days, (with greater increases for mortar), both gave reductions in this at similar rates compared to fly ash fineness at the two test ages. The gradients for concrete were therefore less than those for CaO consumed and fineness, suggesting corresponding effects with the developing hardened structure to those for mortar, and reduced influence of material properties on behaviour.

7. Practical Implications

The results indicate that there is only general agreement between CaO consumed and Activity Index (mortar tests) for evaluating fly ash reactivity. This agrees with views expressed in the literature between pozzolanic materials (Massazza, 1998; Snelling and Scrivener, 2016), where differences in CaO consumed / strength behaviour have been noted and translation between these parameters has been questioned. However, given the strong relationships noted between fly ash fineness and CaO consumed, it is possible that this could provide an approach for more rapidly assessing fly ash reactivity.

To examine this, the results from all PC/fly ash combinations are plotted for Activity Index and CaO consumed against fly ash fineness in Figure 11. As indicated, and noted earlier, changes in fly ash fineness could not always be related to Activity Index and there was scatter in the data. As a result, the single point pass or fail values used in BS EN 450-1 (BSI, 2012) at the different test ages (75% and 85% at 28 and 90 days respectively), seems a reasonable approach for this type of test and data, irrespective of the fineness of fly ash.

As indicated, there is a gradual reduction in CaO consumed as fly ash becomes coarser at 8 and 15 days in the data (see Figure 11), with R^2 between these of 0.72 or greater at both ages. A potential approach to assess fly ash reactivity could then be to measure the fineness of the material (45 µm sieve retention) and CaO consumed. On establishing fineness (normally measured routinely during material testing), the reactivity could then be assessed in terms of CaO consumed for the material being investigated. This would then ensure that for given physical properties, the fly ash achieved a required level of reactivity.

The differences between the mean Activity Index for the materials tested and limits for this in BS EN 450-1 (BSI, 2012), gave values of 8% and 12% at 28 and 90 days (Figure 11). With further research and more data, it should be possible to establish practical limits for CaO consumed, based on the relationship noted with fineness. Limits for 5 and 10% are shown below the regression lines in Figure 11 to illustrate the form that these could take and potential approach that may be followed as a means of more rapidly assessing reactivity of fly ash.

8. Conclusions

Repeatability tests made for the method based on BS EN 196-5 indicate that measurements carried out according to this lime consumption technique with fly ash gave standard deviations less than 1.43 and 0.41 mM for OH^- concentrations and CaO contents, respectively. This provides an acceptable level of precision for the test and with regard to its evaluation of fly ash reactivity.

The lime consumption tests indicate that the main effects occurred during the first 8 to 15 days of the contact period. Thereafter there were only small changes up to 20 days. This was observed for the range of fly ashes tested. The data profiles for the tests were similar to those found previously for thermogravimetric analysis and Activity Index data, with sensitivity noted in all cases with respect to fly ash properties.

Strong relationships were obtained between fly ash fineness and CaO consumed at 8 and 15 days. This was noted for all PCs tested. These were much stronger than corresponding relationships between fineness and Activity Index, although there were improvements for this between 28 and 90 days, suggesting that extended test periods are necessary to evaluate reactivity of the material under standard curing conditions.

Poor relationships were found for CaO consumed and Activity Index, suggesting differences in behaviour between the slurry and developing hardened mortar structure, and indicating that estimation of mortar strength directly from the more rapid lime consumption test for fly ash may not be possible.

A comparison of concrete cube strength results (PC/fly ash against PC at 28 and 90 days) and Activity Index with fineness indicated similar type relationships. While comparable behaviour was found between lime consumption and fineness, the relationship showed greater sensitivity (increased gradient) to the effects of particle size on fly ash reactivity. This again may indicate that the hardened structure development affects fly ash reactions, compared to the slurry in the lime consumption tests.

It is suggested that limits for CaO consumed, corresponding to the fineness of fly ash could be established. A measure of both properties could then be made to evaluate the particle size of fly ash and in relation to this associated reactivity. With further work, this offers potential as a more rapid means of assessing fly ash reactivity, and an alternative to Activity Index mortar tests.

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Table 1 Typical characteristics of PCs used during the study (from Supplier)

CHARACTERISTIC	PORTLAND CEMENT		
	PC1	PC2	PC3
Oxide composition, %			
CaO	63.8	64.3	65.0
SiO_2	20.7	19.8	20.8
Al_2O_3	4.7	5.0	5.5
Fe_2O_3	2.7	2.4	2.4
MgO	1.1	2.0	2.4
K_2O	0.6	0.6	0.7
Na_2O	0.2	0.4	0.4
Cl	0.1	0.1	0.1
SO_3	3.1	2.8	3.3
LOI	2.1	2.4	0.8
Clinker Compounds, %			
C_3S	60.1	56.9	57.4
C_2S	17.1	19.9	18.6
C_3A	7.2	9.8	9.7
C_4AF	7.2	7.4	-
Physical Properties			
Specific surface area (Blaine), m^2/kg	470	490	325
Strength class	52.5N	52.5R	42.5N

Table 2 Characteristics of fly ashes used during the study

CHARACTERISTIC	FLY ASH						
	FA1	FA2	FA3	FA4	FA5	FA6	FA7
Physical properties							
LOI, %	4.4	17.3	2.4	1.4	13.7	3.4	2.6
Specific surface area*, m^2/kg	1740	3430	1810	860	3450	930	1120
Fineness+ (45 µm sieve), %	9.6 (S)	27.2 (N)	20.0 (N)	29.6 (N)	24.4 (N)	15.1 (N)	12.1 (S)
d10, µm	1.8	3.4	3.6	3.8	2.6	2.5	2.1
d50, µm	12.1	33.1	31.1	30.8	29.7	19.1	14.8
d90, µm	57.5	117.6	132.8	122.7	94.0	77.4	78.8
Sub-10 µm quantity, %	44.5	23.6	22.3	23.2	26.9	32.7	39.8
Oxide composition, %							
CaO	3.0	2.9	4.5	4.2	3.6	3.7	1.9
SiO_2	48.4	42.0	44.0	44.4	42.9	47.1	51.4
Al_2O_3	20.1	20.8	16.3	16.0	20.9	19.9	17.3
Fe_2O_3	8.4	8.2	7.9	8.5	6.7	9.1	9.0
MgO	1.6	1.2	1.4	1.4	1.1	1.7	1.6
MnO	0.1	0.1	0.1	0.1	0.1	0.1	0.1
TiO_2	1.0	0.9	0.8	0.9	1.0	1.1	1.0
K_2O	2.8	2.1	1.8	1.9	1.6	3.4	2.0
Na_2O	2.0	0.8	1.7	2.9	0.8	1.4	1.7
P_2O_5	0.5	0.9	0.4	0.3	0.9	0.8	0.2
SO_3	1.0	1.2	0.7	0.9	0.8	1.2	1.5
Mineral composition, %							
Quartz	9.8	4.8	5.6	10.7	3.9	11.1	20.7
Hematite	2.2	1.5	2.4	3.0	1.4	2.7	2.4
Magnetite	0.1	0.2	0.2	0.2	0.1	0.2	0.1
Mullite	10.4	11.8	5.6	6.2	9.5	8.8	7.6
Glass / Others	77.6	81.8	86.2	79.9	85.1	77.2	69.2

*measured by nitrogen adsorption (BET)

+(S) and (N) fineness category to BS EN 450-1. Category S ≤ 12% on 45 µm sieve; Category N between 12 and 40% on 45 µm sieve

Table 3 Lime consumption repeatability test results (mM unless indicated otherwise)

Time	**8 days**				**15 days**	
Fly ash	FA1		FA2		FA1	
No. of Repeats	OH^-	CaO	OH^-	CaO	OH^-	CaO
1	58.73	7.59	54.36	9.33	60.93	5.80
2	55.57	7.76	54.23	9.19	61.58	5.92
3	55.76	7.22	52.81	8.25	60.03	5.85
4	54.84	7.31	52.48	8.58	60.72	5.65
5	56.03	7.44	52.50	8.65	61.63	5.66
6	57.43	7.35	53.03	8.92	60.70	6.01
Mean	56.39	7.44	53.23	8.82	60.93	5.82
Standard deviation	1.43	0.20	0.85	0.41	0.60	0.14

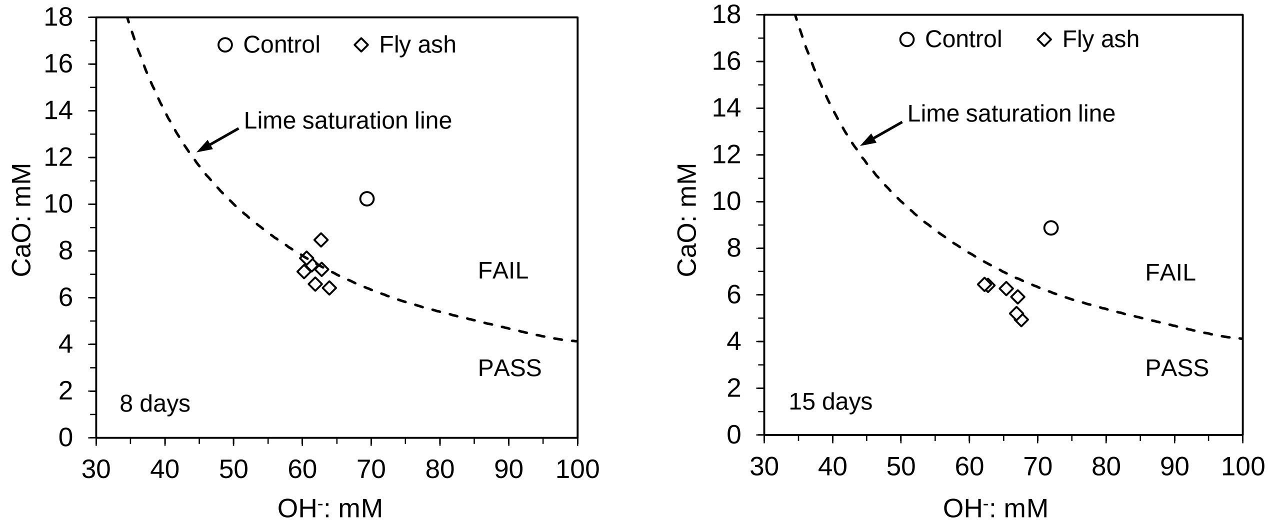

Figure 1 Comparison of OH^- and CaO concentrations at 8 and 15 days with regard to lime saturation line (broken) for PC1 and PC1/fly ash combinations (as per BS EN 196-5)

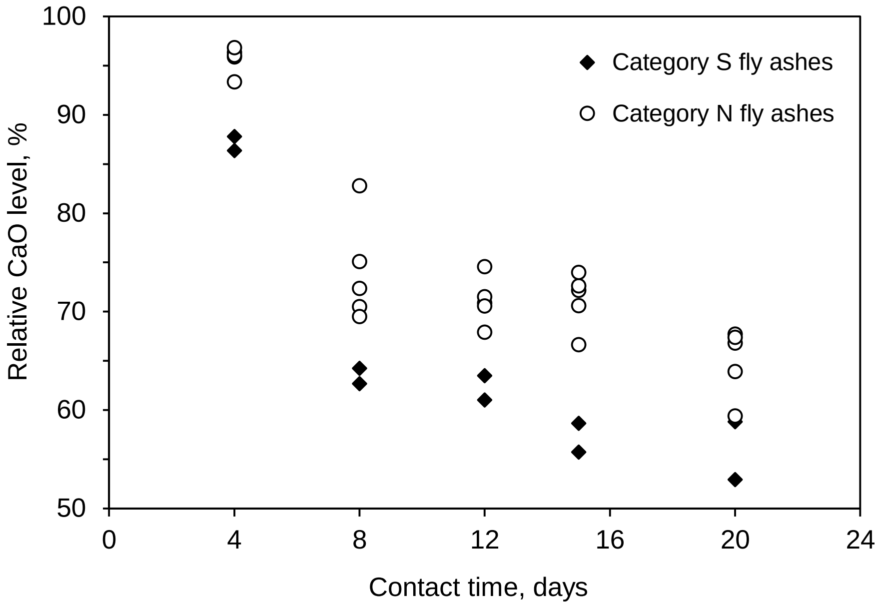

Figure 2 Changes in relative CaO level (CaO in PC/fly ash / CaO in PC) with time for PC1/fly ash combinations (Category S: fine and Category N: coarse)

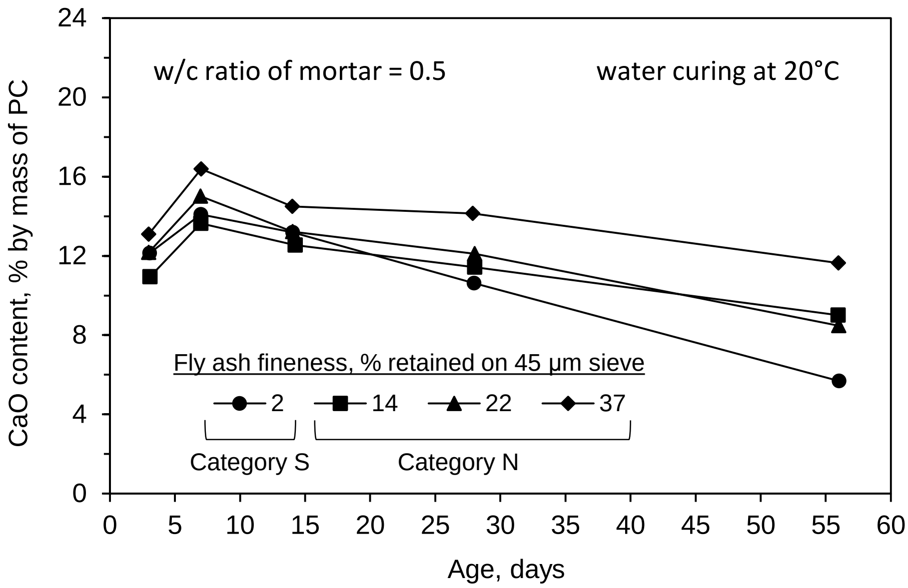

Figure 3 Changes in CaO in PC/fly ash mortars with time by thermogravimetric analysis (fly ashes of varying fineness from single source; Dhir et al, 1996)

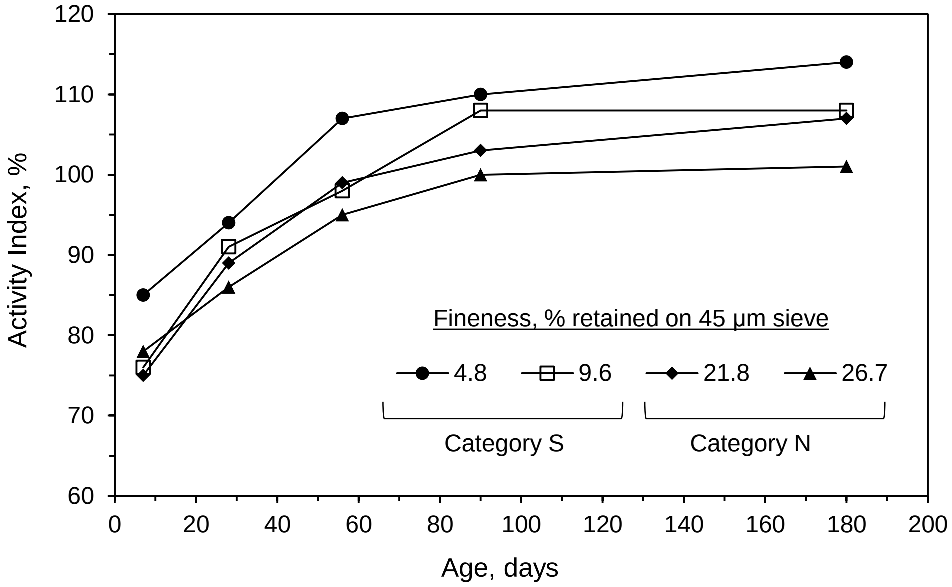

Figure 4 Changes in Activity Index for PC/fly ash combinations with time (fly ashes of varying fineness from different sources; Sadiqul Islam, 2012)

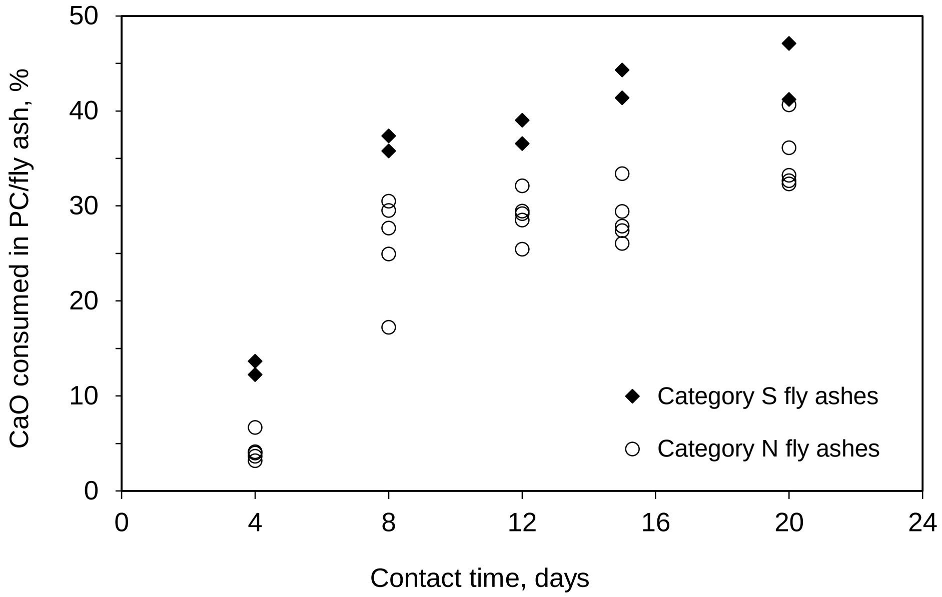

Figure 5 Changes in CaO consumed with time for PC1/fly ash combinations (Category S: fine and Category N: coarse)

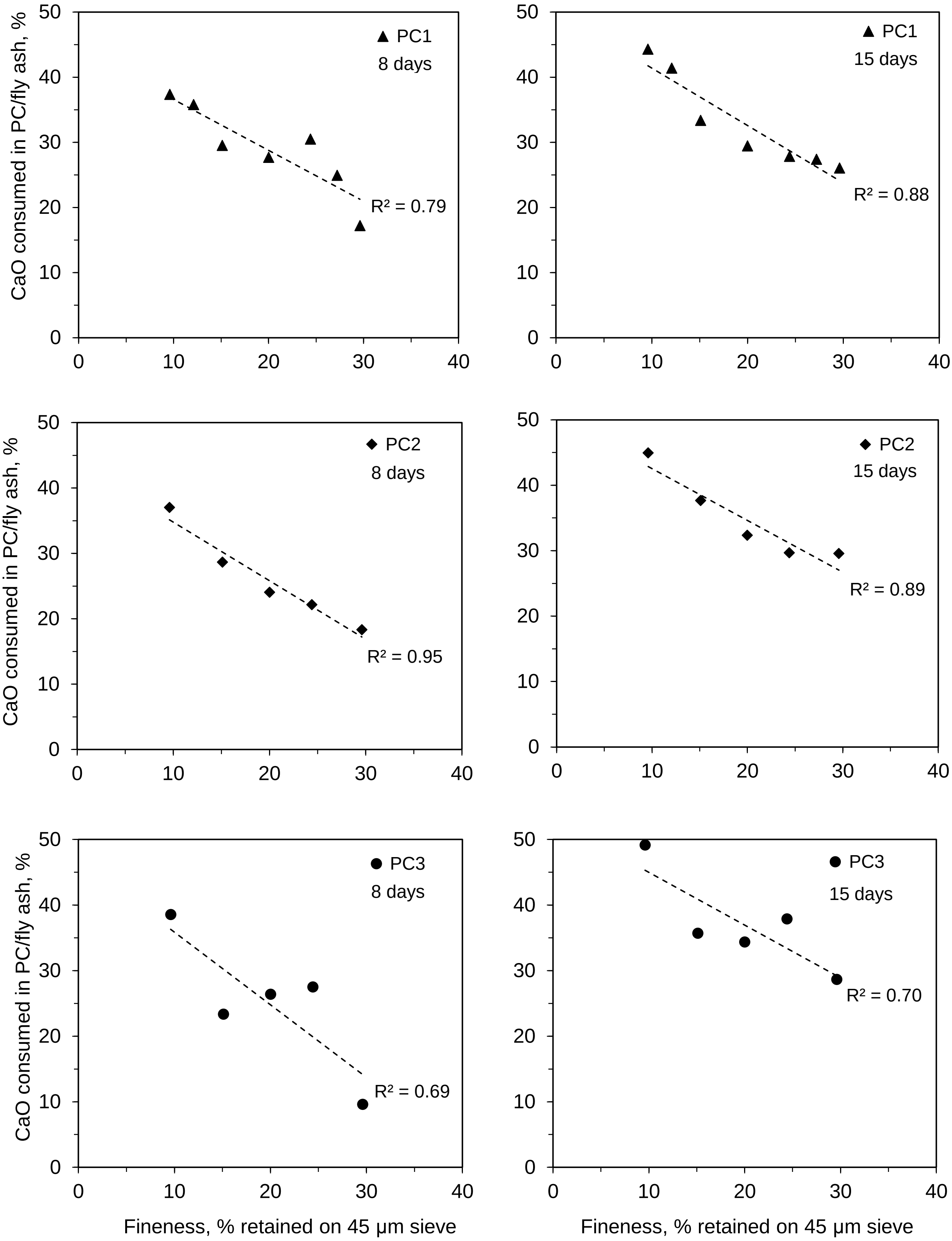

Figure 6 Comparison of fineness with CaO consumed at 8 and 15 days in PC/fly ash combinations with PC1, PC2 and PC3

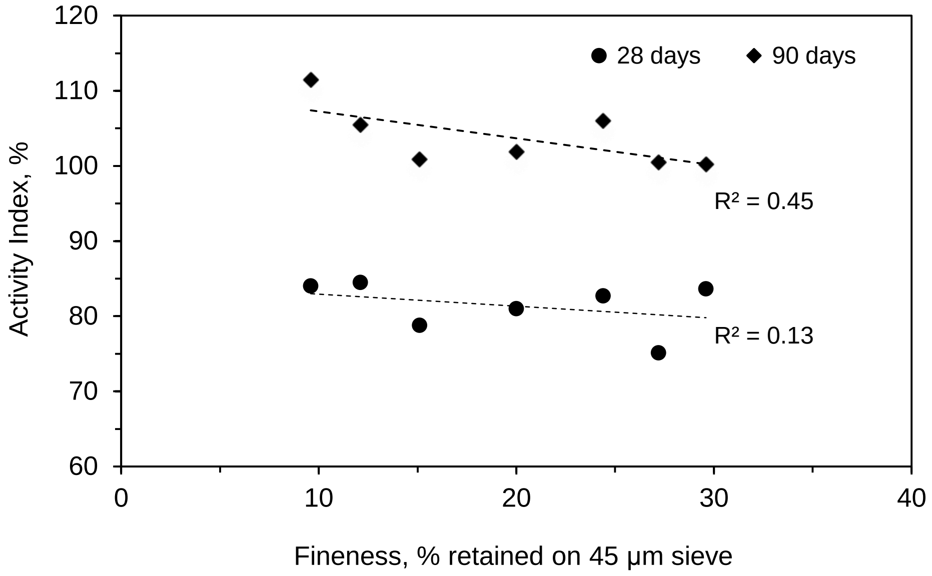

Figure 7 Relationship between fly ash fineness and Activity Index at 28 and 90 days for PC1/fly ash combinations

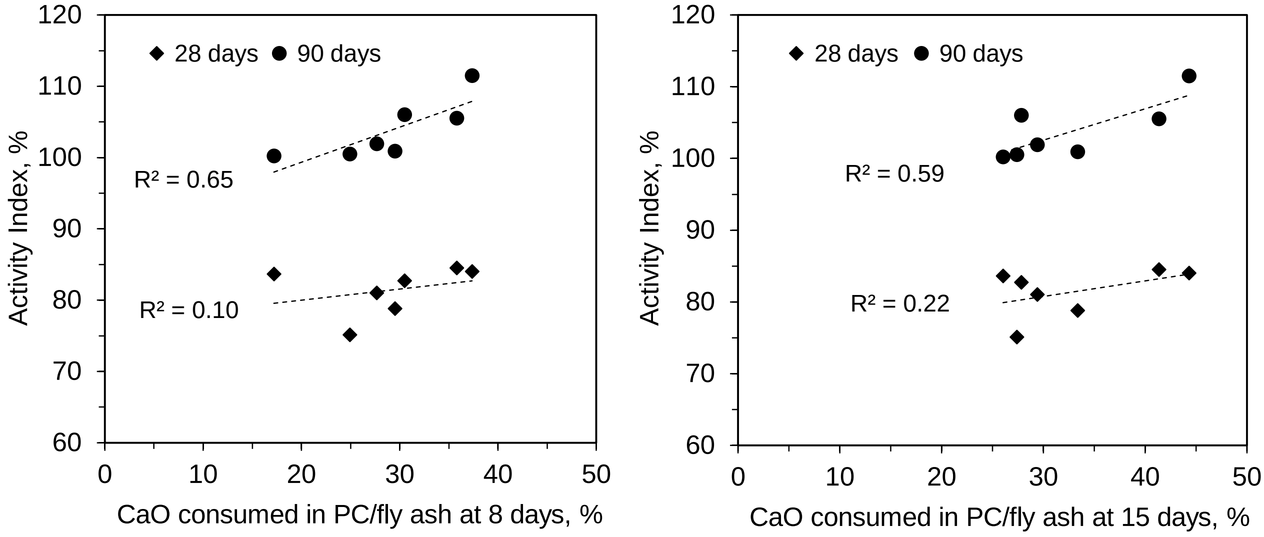

Figure 8 Relationships between CaO consumed at 8 and 15 days in PC1/fly ash combinations with Activity Index at 28 and 90 days

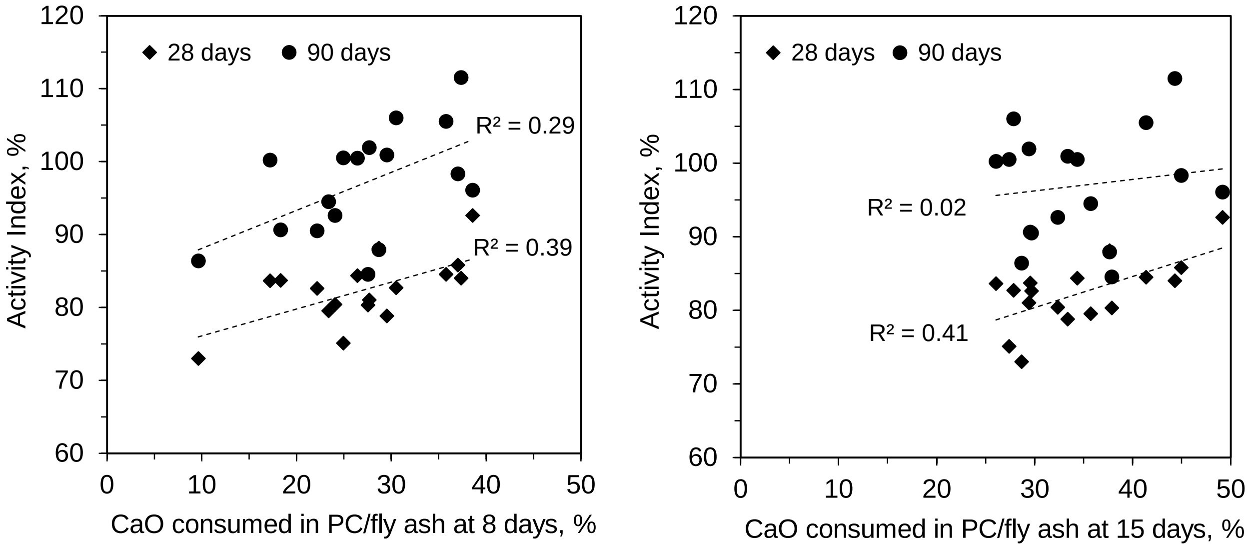

Figure 9 Relationship between CaO consumed in all PC/fly ash combinations at 8 and 15 days with Activity Index at 28 and 90 days

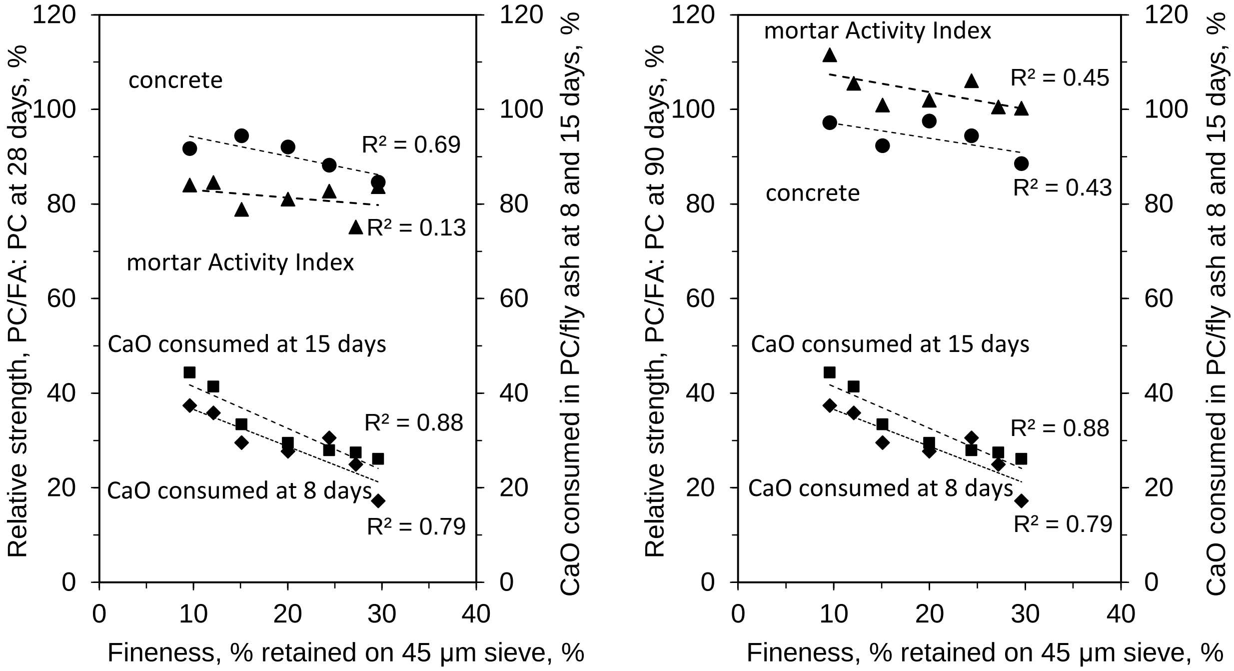

Figure 10 Relationships between fly ash fineness and relative strength of PC1/fly ash combinations at 28 and 90 days for mortar and concrete, and CaO consumed at 8 and 15 days

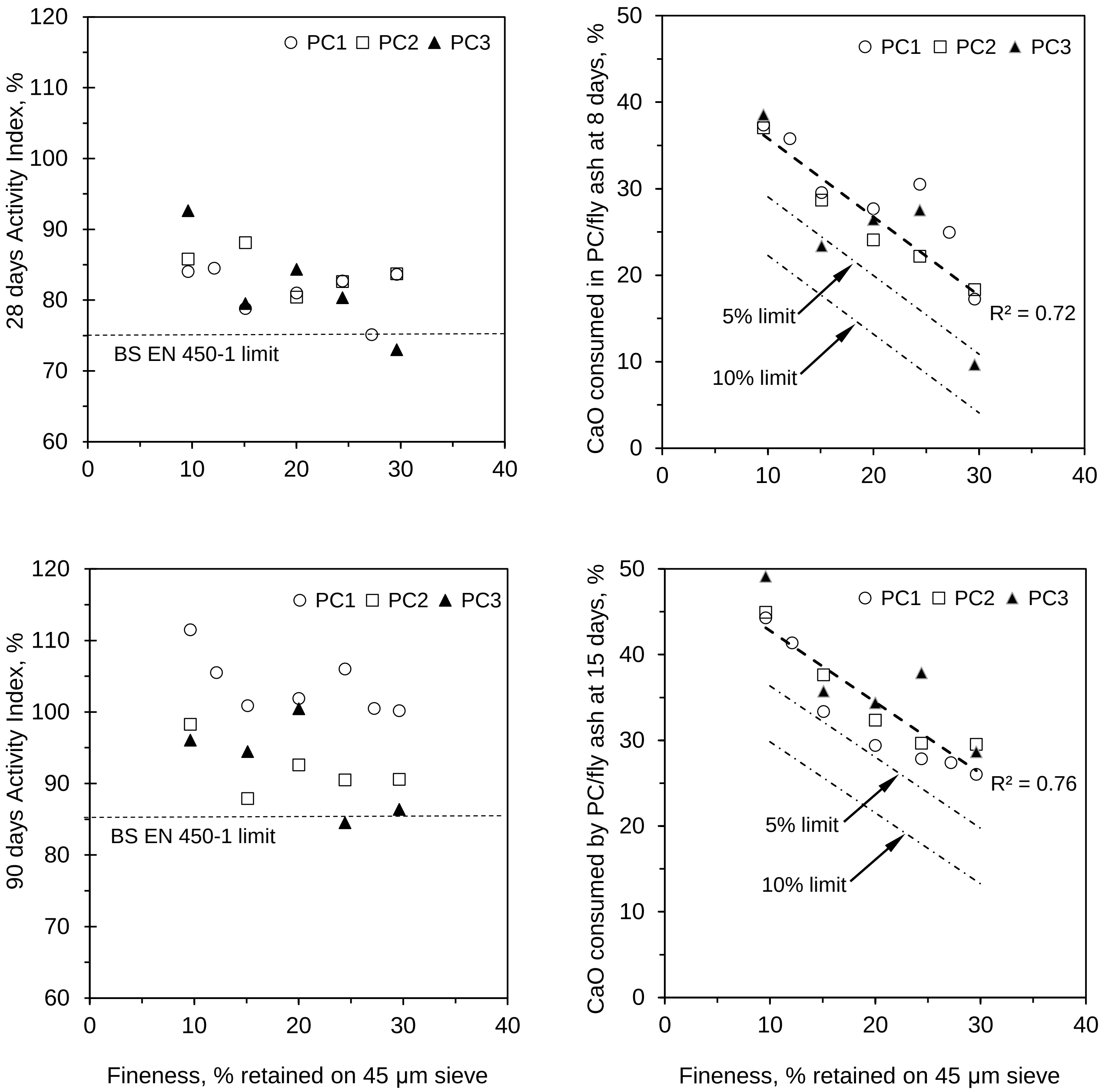

Figure 11 Relationships between fly ash fineness and Activity Index at 28 and 90 days, and CaO consumed at 8 and 15 day of/in all PC/fly ash combinations