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Corrosion of Reinforcement in Concrete Containing Wet-Stored Fly Ash

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ABSTRACT

The study described was concerned with moistened fly ash as a cement component in concrete and its influence on carbonation and chloride-induced corrosion. Five laboratory-moistened fly ashes (10% by mass) and samples from two power station stockpiles (moistened at 10 to 30% by mass) were examined, with several material/storage variables investigated. Initial tests quantified moisture effects, which indicate agglomeration of fly ash and a tendency for this to increase with free lime content, storage period and temperature. Concretes were compared at equal slump (75 mm) and 28 day (cube) strength. Air (intrinsic) permeability and water absorption were slightly greater (high free lime, 0.9%), or lower (low free lime < 0.1%) with moistened fly ash in concrete (compared to that with dry material), and where there were benefits, these increased with longer storage. For carbonation and chloride diffusion, moistening of low free lime fly ash gave similar or slightly enhanced results. In the case of high free lime fly ash, wet-storage gave increased chloride diffusion. This seemed to be due to the effects that higher free lime content has on wet fly ash (increased agglomeration, reduced fineness/reactivity) and their influences on the durability process. Carbonation tended to reduce with low storage temperature, while chloride diffusion gave little change. Reinforcement corrosion associated with these was similar between dry and moistened low free lime fly ash concretes. While paste experiments suggest some differences in chemistry between dry and wet-stored fly ash systems and their response to carbon dioxide and chloride exposures, these didn't seem to have a noticeable effect on concrete resistance to the processes.

1. INTRODUCTION

Fly ash from electricity generation, used as a cement component in concrete, provides several technical (e.g. reduced water requirement, increased particle packing, enhanced long-term strength and aspects of durability) and environmental (e.g. take up of by-product material and reduced embodied CO_2) benefits [1-5]. In most cases, fly ash as with other additions for concrete is used dry (N.B. silica fume can be supplied as a slurry [6]). Indeed, limits on moisture level/prescriptive details are/have been given for this in many Standards [*e.g.* 7-9]. For example, 3.0% is used in ASTM C618 [8], while the current edition of EN 450-1 [9] includes drying of fly ash (i.e. processing) before use. Reference to moisture conditions appears to be made, since in this form, handling and transportation of fly ash can become difficult [10, 11]. This is important, as wetting and storage of fly ash are often necessary to achieve a balance between production, dry holding capacity and demand [2].

One approach involves mixing fly ash with water at around 10 to 20% by mass (sometimes referred to as conditioning) and stockpiling. Studies suggest that, depending on the properties of the material, site conditions and period of storage, effects occurring can range from minor changes in fly ash, to dissolution of certain components/product formation at particle surfaces [12-14]. It has been noted [2, 15] during compaction of fly ash that (following water addition), cohesive forces initially develop in the material, with sulfate-based products subsequently forming and with time, and in the presence of free lime, pozzolanic reactions occur.

Early research in the laboratory using sealed storage (up to 18 months) and moisture levels of 1 to 40% noted roughening of particle surfaces (sulfate-based product formation) and agglomeration [16]. This coarsening of fly ash (changes in 45 µm sieve retention/particle size distribution (by laser analysis)) was found to increase with time, but at a reducing rate (with minor changes after the initial 6 months storage), and free lime contents. Greatest agglomeration (coarsening) was also noted at moisture contents of about 10% to 20%, with lower and higher levels appearing to limit chemical effects or cause some particle dispersion.

At a practical level, handling trials suggest that, while the flow properties of fly ash are modified, providing factors including (i) the quantity of material stored (affecting compaction), (ii) the holding time and (iii) the use of external vibration are considered, moistened fly ash can be kept in and discharged from a suitably designed aggregate hopper, enabling concrete production [17]. Research also indicates that wet storage of fly ash can affect aspects of concrete performance (fresh properties and strength), however, these can be accommodated by adjustments to the concrete mix proportions [18]. Recent estimates note that about 50 Mt of wet-stored fly ash are accessible for recovery from storage areas (mainly at power stations) in the UK [19] and establishing suitability for its use in concrete could offer an alternative option for sourcing material.

The influence of fly ash on chloride ingress and carbonation, and resulting reinforcement corrosion in concrete, have been examined in many investigations over the last few decades, given their damaging effects on structures [*e.g.* 20-31]. The influence of fly ash in concrete on these processes, compared to that of Portland cement (PC), is mainly due to physical and chemical effects including, changes in microstructure, lime consumption and binding capacity. Between dry low lime fly ashes covering a range of properties, small differences in carbonation and chloride ingress in concrete have been noted when these have been proportioned at equal strength [26, 32]. Given the influences of moistening and storage on fly ash, it is possible that material in this form could affect these aspects of concrete durability. The current paper describes a research project carried out to investigate this.

2. MATERIALS

2.1 Fly Ashes
Seven low-lime UK fly ashes were used, providing a range of characteristics. These include five dry samples (from different sources and of various properties), moistened and stored in the laboratory, and two from site

stockpiles. A summary of the test methods used to investigate the fly ash characteristics is given in Table 1 [33-35], while Table 2 gives the physical and chemical properties of the five dry fly ashes (before moistening).

Fly Ashes 1, 2 and 3 had different fineness and low free lime contents (< 0.1%, using the EN 451-1 test [35]). Fly ashes 4 and 5 had high loss-on-ignition (LOI), (10.6%; Fly Ash 4) and free lime content (0.9%; Fly Ash 5). For all materials, the sum of the main oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) exceeded 70%, with CaO less than 5.0%, and alkalis (Na_2O_{eq}) and sulfates between 0.6 and 4.7%, and 0.2 and 1.7% respectively. The mineral compositions are typical of those for the coal used. Fly Ash 6 was from a stockpile set up for the project at the power station supplying Fly Ash 3, while Fly Ash 7 had also been moistened and kept in the main stockpile at this power station, providing longer-term stored material.

2.2 Other Concrete Constituents

The other constituents, normally used in ready-mix concrete production, were sourced from UK material suppliers. The PC (CEM I) was of Strength Class 42.5 N. The aggregates were natural gravel in 20 and 10 mm sizes and a medium grade sand. Their particle densities and water absorptions (laboratory dry to saturated surface dry) were 2590, 2590 and 2630 kg/m³ and 1.0, 1.0 and 0.7%, with laboratory drying carried out before preparing concrete. Tap water was used for concrete, with a polymeric sulfonate-based, superplasticizing (SP) admixture enabling the target slump (75 mm)/mix water contents to be controlled.

3. MOISTENING AND STORAGE OF FLY ASH AND THEIR EFFECTS

Moistening and storage of fly ash in the laboratory followed methods described previously [16]. Fly ash was mixed with tap water at 10% (by dry mass) in a 25 litre pan mixer for 4 minutes. Hand mixing at 2 minutes and on completion was also carried out. This was lightly compacted and sealed in polythene bags/air-tight containers and stored at 20°C (main condition), or 5°C, for 1 and 6 months. To examine water property effects, Fly Ashes 1 and 3 were also moistened with seawater (North Sea (Montrose, Scotland), chloride content 18,600 ppm, pH 8.2) and stored for 6 months at 20°C. Given the moisture and chloride contents, and fly ash levels used, the chloride contribution to concrete, in this case, would be around 0.010% by mass.

Fly Ash 6 (same source as Fly Ash 3) was moistened at the power station (10 - 30%) with potable water and stockpiled in a 2.0 m mound (flat top/steep sides) at an external location. At 1 and 6 months, 25 kg samples

were taken at 1.0 m depth, and the pile made good for further storage. Fly Ash 7, similarly moistened, had been in the main stockpile at this site for 6 years, before sampling and testing.

The effects of moistening and storage period on fly ash are summarized in the Appendix. The data for selective fly ashes, given in Table A1, indicate reduced fineness and slightly increased LOI (likely to reflect decomposition of sulfate-based hydration products during ignition, rather than changes in carbon [16]), compared to dry material, and these effects developed with storage period. Laser particle size analyses indicates fewer fine particles in moistened fly ash in some cases, with greater quantities of coarser fractions (suggesting agglomeration). Little change in bulk oxide or main mineral compositions was found. However, calcium sulfate reaction products were noted in some materials, as found previously [16]. Fly Ash 5, high free lime, generally gave greatest changes (fineness, LOI) with wet storage.

While the fineness and LOI results in Table A2 indicate slightly smaller changes by moistening and storage at 5°C than with tap or seawater at 20°C, the differences in particle size distribution, oxide composition and mineralogy seem unlikely to relate to moistening and storage effects, and the results may reflect sample variation. Site stockpile material (Fly Ash 6) gave similar physical and chemical properties to that moistened in the laboratory. The results with longer-term stored stockpile fly ash (Fly Ash 7), may reflect changes in power station operating conditions and coal source with time.

Scanning electron microscope images for fly ash (single source) from a related study are shown in Figure 1 and include dry, laboratory moistened and stored, and that from a power plant stockpile. This illustrates the effects that may occur with wet storage, i.e. changes at particle surfaces, formation of secondary phases (sulfate-based), roughening of particles and agglomeration. In general, the results agree with effects noted in earlier studies, see Reference 16, where the mechanisms are also reviewed.

4. MIX PROPORTIONS AND SPECIMEN PREPARATION

While processing or beneficiation is an option to take account of wet storage effects on fly ash [36], this can be achieved by modifying concrete mixes as referred to above (*e.g.* changing w/c ratio), and was the approach followed during the study. It was decided to make comparisons at equal slump (75 mm)/28 day cube strength,

and to consider concrete strength classes that may be used in practice for the particular exposures being investigated, i.e. 35 MPa for carbonation and 35 and 50 MPa for chloride [37].

The above were achieved by (i) using SP admixture to control fresh properties and (ii) following a normalisation procedure (for equal strength), similar to that described previously [38]. This involved preparing concretes over a range of w/c ratios for the PC/fly ash combinations, with coarse aggregate contents fixed and minor adjustments made to fine aggregate to maintain concrete yield. Small reductions in water contents (5 to 10 l/m^3) were adopted with coarser fly ash, as followed in an earlier study [32]. The w/c ratio to achieve the strength at which the assessments were to be made was established. At least two w/c ratios for each PC/fly ash concrete and property (carbonation rates, chloride diffusion, etc) being considered were tested. The results from these were normalised to the w/c ratio identified for the strength at which the comparison was to be made.

An example showing the mixes for dry Fly Ash 1 is given in Table 3 for 35 and 50 MPa strength classes, while the w/c ratios for dry/moistened fly ashes are shown in Table 4. At equal strength, lower w/c ratios were generally required for coarser and moistened/stored fly ash. With seawater and 5°C storage, slightly higher w/c ratios than those with tap water at 20°C were used. There were minor changes in SP dose for the target slump between dry and wet-stored fly ash concretes.

A horizontal pan mixer was used to prepare concrete and followed the method described in BS 1881-125 (dry aggregates) [39]. Adjustment was made during batching (water and aggregate contents) and to the mixing procedure (including a period with aggregate/water covered in the mixer) enabling aggregates (which were added in a laboratory dry condition) to absorb water. Fly ash was used wet and hence this was also taken into account during batching (following moisture content measurements (by oven drying)), to give quantities (water and fly ash) equivalent to those in dry fly ash concretes. Moisture contents of 1 to 2% below that added to fly ash in the laboratory (10%) were typically recorded after storage (Tables A1 and A2), appearing to reflect combined water and changes in LOI noted above.

After casting and 24 hours under damp hessian/polythene at 20°C, specimens were water-cured at the same temperature to 28 days, before preparation for testing.

5. TEST PROCEDURES

5.1 Concrete

Air (intrinsic) permeability and water absorption (initial surface absorption (ISA)), i.e. transportation properties, were investigated to provide a measure of the concrete microstructure. Air permeability was measured following the method in Reference 40 and involved testing 50 mm Φ oven-dried (105ºC) cores (cut to 50 mm length), from 100 mm cubes, parallel to the trowelled face. Tests used a tri-axial cell, circumferential pressure of 2.1 MPa and a range of inlet pressures (0.2 to 0.8 MPa in 0.15 MPa increments), with steady-state flow rates recorded. A solution to Darcy's Law [40] was followed to determine air permeability, with two specimens tested per mix. ISA was measured, as described in BS 1881, Part 208 [41]. Two 150 mm oven-dried concrete cubes were tested for each mix on a cast surface, using a Perspex cap, under a 200 mm head of water. The rate of water uptake, measured on one side of the equipment using a capillary tube, after reducing the head in the main reservoir, was recorded at 10 minutes (ISA-10).

Carbonation was tested on 100 mm cubes (1 per age), following the BS 1881-210 [42] exposure conditions, i.e. 4.0% CO_2, 55% relative humidity (RH), 20°C. Several studies have used or examined the effects of accelerated testing on cement/fly ash systems (e.g. [27, 30, 43]). Research suggests that ettringite, aluminates and portlandite carbonate independently of exposure concentration [44]. However, at higher CO_2 levels, the ratio of reaction products can be different to those formed when these are lower [30] and variations in porosity [44], which may change between cement combinations [43] have been noted. However, there appears to be no evidence [30] that these have any significant effect on overall carbonation rate. Given the reactivity between CSH products and CO_2 may change for different additions, it has been suggested that accelerated tests are best restricted to comparisons where these are the same [45], which was the approach followed in the current study. For the type of accelerated system used, good agreement with real exposure conditions has been noted [38], with variability tests in the laboratory giving a coefficient of variation of 9.0% for similar concretes.

After curing, specimens were kept in air at 55% RH, 20°C for 14 days, before sealing and exposure to the above conditions for 30 weeks. These were periodically removed, split, and broken surfaces sprayed with pH indicator (phenolphthalein). The mean distance from the cast surface to the internal colour change, at 5 locations on the exposed surface was taken as the carbonation depth.

Chloride diffusion was measured on concrete in two-compartment uPVC cells. The specimens of 100 mm $\varnothing$ $\times$ 25 mm (from 300 mm cylinders) and test set up enabled control of (i) thickness of concrete in relation to maximum aggregate size and (ii) chloride concentration upstream and measurements downstream. Laboratory tests considering variability for the test, with similar concretes, gave a coefficient of variation of approximately 5.0%. Two saturated specimens per mix were sealed in the 1 litre cells, which were filled with distilled, de-ionised water, saturated with $Ca(OH)_2$. The cells were partially immersed in 5.0 M NaCl solution at 20°C and chloride build-up in the interior recorded by ion-selective electrode until reaching a constant rate of change with time. A solution to Fick's First Law was used to calculate the chloride diffusion coefficient [46].

Reinforcement corrosion tests used 100 mm concrete cubes, with 10 mm Φ high yield steel at 25 mm depth from the surface (and a cast-in counter electrode, 25 mm from the specimen base). The grit blasted bars had a screw/insulating wire for electrical connection at one end, with pitch epoxy resin applied at both ends to isolate this/define the test area ($\approx$ 1900 mm^2). Specimens were sealed with silane primer/paraffin wax, except the exposed (trowelled) face, following 14 or 3 days in air (55% RH, 20°C) after curing, for carbonation and chloride tests respectively. The exposure conditions used were (i) 4% CO_2, 55% RH, 20°C until the carbonation front reached 35 mm depth ($\approx$ 52 weeks), then 95% RH, 20°C for 20 weeks, or (ii) 3 hours wetting in 2.4 M NaCl/9 hours drying at 20°C for 52 weeks.

A schematic illustration of the corrosion potential and polarization resistance test arrangement (Ag/AgCl reference electrode, potentiostat with IR compensation and ramp unit) is shown in Figure 2, with measurements made periodically during the 20 weeks, 95% RH, 20°C period for (i) and throughout for the conditions used in (ii). The steel was polarized to $\pm$10 mV of the corrosion potential at a rate of 0.1 mV/sec to measure polarization resistance. A B-value of 26 mV for the Tafel slopes was used in the Stern-Geary equation [47] to determine the corrosion current.

5.2 Paste

Tests on paste samples (25 $\times$ 30 $\times$ 40 mm for carbonation; 70 $\times$ 70 $\times$ 70 mm for chloride) to examine chemical effects associated with moistened fly ash (Pastes: 0.5 w/c ratio, 30% fly ash in cement and water-cured at 20°C for 28 days) were made following, (i) 5 weeks in 4.0% CO_2, 55% RH, 20°C conditions, or (ii) 2 weeks in 1.0 M NaCl solution at 20°C. For (i), thermogravimetric analysis was used to determine $Ca(OH)_2$ in the paste

(mass change in samples in a nitrogen atmosphere over a temperature range 450 to 510°C, during a rise to 1000°C at 20°C/min) before and after exposure. Calcium carbonate, forming during carbonation [48], was measured by X-ray diffraction, with qualitative assessments made from peak intensities.

In the case of (ii), the latter was used to evaluate Friedel's salt, which reflects chloride binding [49]. Additional tests for chloride binding were carried out, based on the procedure described by Tang and Nilsson [50]. The core of the 70 mm specimens were crushed, dried in a desiccator and sieved until achieving a specific particle size range (0.2 to 2 mm). Following vacuum drying, a 25 g sample was exposed to 30 ml of 1.0 M NaCl solution for 2 weeks (sealed and stored at room temperature). Its chloride concentration was determined using a copper disc evaporation method and X-ray fluorescence spectrometry [51]. Chloride binding capacity was calculated using the equation in Reference 50.

6. RESULTS AND DISCUSSION

6.1 Air (intrinsic) Permeability and Water Absorption

The air permeability and water absorption results at 28 days for 35 MPa concrete with dry and moistened fly ashes are given in Table 5. These indicate that dry fly ash fineness and LOI had little influence on the transportation properties, however, they were slightly lower (enhanced) with Fly Ash 5 (high free lime). Moistening and storage gave progressive reductions in air permeability and water absorption of concrete for most fly ashes, with values after 6 months up to 50% and 30% lower respectively, compared to dry material. However, Fly Ash 5 gave slight increases with moistening and had among the highest values of the wet fly ash concretes. Moistening and storage with seawater, or at 5°C and site stockpile Fly Ash 6 gave values slightly above and below those of concrete with laboratory moistened materials stored at 20°C.

Whilst improved properties might be expected with dry fly ash of increased fineness in concrete, comparisons at equal strength gave little difference to those with coarse material. The behaviour for moistened fly ash may relate to bleeding rates in concrete, which have been found to reduce with increasing storage time [18] and can affect paste/aggregate (interfacial) properties [52]. This effect, the action of aggregates during mixing (attrition) on wet fly ash and the equal strength comparison may offset influences of agglomerated material and any changes in reactivity [18]. The results, however, suggest that greater effects in the material (e.g. increased agglomeration) may negatively affect transportation properties, as noted with high free lime fly ash.

6.2 Carbonation Rates

The carbonation results for Fly Ashes 1 to 3 are shown with exposure period in Figure 3. These follow typical trends, i.e. increasing depth with time, but at gradually reducing rates [26, 38]. Between dry fly ashes, slightly lower carbonation was obtained for fine material, particularly at later ages, but there was no consistent effect and the result range was narrow. The concretes with dry Fly Ashes 4 and 5, Figure 4, also gave little difference in carbonation compared to Fly Ash 2. These agree with earlier research on carbonation using dry fly ash in concrete for the effect of (i) free lime content [53] and (ii) varying fineness and LOI at equal strength [26, 32].

For moistened Fly Ashes 1 to 3, there was no clear influence of fineness or storage period on carbonation, with small differences generally noted. Similar effects were found for Fly Ashes 4 and 5, as shown in Figure 4. Given the transportation properties which indicate enhancements with wet-stored fly ash, the results suggest an influence of moistening on chemical resistance to carbonation. However, with the comparison at equal strength, the net result appears to give little difference between wet and dry stored fly ash.

Concrete with fly ash moistened by seawater, stored for 6 months, gave slightly less carbonation at 30 weeks than tap water, as shown in Figure 5. The transportation properties of the concretes were similar, suggesting other factors influence behaviour. It has been noted that chloride in cement paste may increase alkali levels, as for high alkali cement, which has been found to give greater carbonation [54, 55]. Carbonation tests with chloride and chloride/sulfate in concrete have also given increased rates, but contamination levels were higher than in the current study [56]. Other research suggests that chloride present gives changes in hydroxyl ion consumed and RH in the pores, with reductions in carbonation rate [57]. Given the conflicting effects, this is an area requiring further investigation.

After 30 weeks, concretes containing moistened Fly Ashes 1 and 3 stored for 6 months at 5°C also had carbonation depths a few mm less than those wet-stored at 20°C, see Figure 5. Small differences were noted in transportation properties between these. The results may be related to temperature effects on fly ash reactivity, similar to curing temperature influences on fly ash concrete strength [58], giving less change during moist storage, and thereby influence on concrete properties. It seems that the balance of physical and chemical effects associated with this give slightly better resistance to carbonation.

Carbonation of concrete containing site stockpiled Fly Ash 6 was, with a few exceptions, less than those of laboratory stored material, as shown in Figure 6 (which could relate to differences in temperature and moisture condition history), and generally comparable to dry fly ash concrete. Six year stockpile material, Fly Ash 7, also had little influence on carbonation resistance, giving similar results to the other concretes. Thus, short or longer-term wet storage of fly ash, in equal strength concrete does not appear to affect carbonation resistance.

6.3 Chloride Diffusion

Chloride diffusion coefficients of 35 MPa concretes for Fly Ashes 1 to 3 are given in Figure 7(a). Dry fly ash concretes had values of between 4.0 to 5.0 x 10^{-13} m²/s. The data indicate good chloride resistance for the concretes and give agreement with previous studies on chloride diffusion in terms of (i) values obtained for the fly ash level in cement/strength class used and (ii) the effect of fly ash with variable fineness and LOI in equal strength concrete [20, 32].

In most cases, moistening of Fly Ashes 1 to 3 gave lower chloride diffusion than dry materials in concrete. Tests on 60 MPa concretes (not shown) gave values less than 1.0 x 10^{-13} m²/s, with little difference between dry and wet-stored materials. Factors associated with fly ash likely to be influenced by moistening and affecting chloride resistance include, fly ash reactivity, surface characteristics and influences on microstructure [59]. With the enhanced transportation properties noted above (air permeability and absorption) for wet fly ash, it may be that the chemical resistance to chloride (chemi-sorption/binding) between dry and wet-storage is not significantly different.

The chloride diffusion coefficient of dry fly ash concrete increased slightly with Fly Ash 4 (high LOI), as shown in Figure 7(b) for 35 MPa concrete compared to Fly Ash 2, which could reflect the reduced mineral component in this material. For concrete with dry Fly Ash 5 (high free lime), reductions were obtained compared to Fly Ash 2, which is different to another study where this had little effect on chloride resistance [53]. The results of Fly Ash 2 and 5 concretes, however, both agree with the transportation properties in terms of ranking. Moistening of Fly Ash 4 gave chloride diffusion values both above and below dry material, and general agreement with most of the other fly ashes. The increases with Fly Ash 5 suggest that with minor changes in transportation properties, wet storage may affect chemical resistance to chloride.

In some cases, chloride diffusion was slightly higher for concrete with fly ash moistened by seawater compared to those with tap water or dry material, see Figure 8 (35 MPa concretes, Fly Ashes 1 and 3, 6 months stored). The transportation properties gave small differences for concrete between moistening solutions. The data may reflect the chloride already present in concrete, and ability of fly ash to then resist further ingress. Similar behaviour has been found with internal chloride and its effect on rates of external chloride ingress [60].

The results given in Figure 8, also show the effect of moistened fly ash storage temperature (5 and 20°C) on chloride diffusion for 35 MPa concretes, with values slightly less than dry fly ash concretes and similar to 20°C wet storage. It appears that the effects occurring in fly ash with low temperature storage, unlike carbonation, had little subsequent effect on chloride diffusion (e.g. chloride binding), which may reflect the different factors influencing the two processes.

For a given fly ash storage period (1 and 6 months) and concrete strength (35 MPa), site stockpile Fly Ash 6 gave similar or slightly higher chloride diffusion, compared to that stored in the laboratory, as shown in Figure 9. Longer-term storage for 6 years (Fly Ash 7) did not seem to affect this, with chloride diffusion coefficient comparable to those with dry and shorter-term stockpile-stored material.

6.4 Reinforcement Corrosion

Corrosion potential and current measurements are shown with exposure period (95% RH and 20°C conditions) for 35 MPa carbonated concrete in Figure 10 (a) and (b), respectively. For wet and dry Fly Ashes 1 and 3, initial reductions in corrosion potential were noted during the first 4 weeks, with values suggesting the occurrence of corrosion by this time. Continued exposure to 20 weeks generally had little further influence on this or corrosion currents, which were recorded from 4 weeks. It has been noted [48], that the RH of the environment and moisture content of concrete are important factors influencing carbonation-induced corrosion. Material effects, including fineness and moistening of fly ash appear to have less influence.

Corrosion results for 50 MPa concrete, containing Fly Ashes 1 and 3, exposed to wetting/drying with chloride solution are shown in Figure 11 and gave similar trends to the carbonation tests. In this case, greatest changes in corrosion potential occurred during the first 2 weeks, with fly ash fineness or moistening/storage having little effect, and values suggesting corrosion was occurring by this time (and from 4 weeks for corrosion

current). Previous research suggests [61] that for a given chloride content at the location of steel, corrosion occurring relates to the chloride diffusion coefficient, since this reflects the prevailing environment, concrete microstructure and chemistry. In this case, the corrosion data also give general agreement with the chloride diffusion tests above, suggesting little effect of fly ash moistening and storage on the process.

7. CHARACTERIZING MOISTENED FLY ASH INFLUENCES ON THE PROCESSES

A combination of physical and chemical effects are likely to influence carbonation and chloride ingress in fly ash concrete. The transportation properties indicate differences between dry and moistened fly ash concrete, while the carbonation and chloride diffusion data suggest some chemical influences. Paste experiments to examine moistening effects on aspects of the processes were, therefore, carried out.

The data from thermogravimetric analysis on water-cured pastes, for selective fly ashes are shown in Table 6. These suggest an increase in calcium hydroxide with (dry) coarser fly ash and moistening/storage period, reflecting reducing reactivity (i.e. less lime consumed) and this was slightly greater for high free lime material. The results from tests for calcium hydroxide after 5 weeks exposure to carbonation are shown in Figure 12 (a). Depletion in $Ca(OH)_2$ was noted in all cases (compared to Table 6), with greatest relative reductions in pastes containing moistened fly ash, however, slightly higher residual levels were present in this material.

Figure 12 (b) gives the quantities of calcium carbonate measured in the paste samples. This indicates highest levels in those with moistened fly ash, which increased with storage period. These may reflect either the higher level of $Ca(OH)_2$ available to react during carbonation, or that a greater degree of carbonation occurred. However, it is unclear if the effects for the concrete transportation properties also apply to the paste samples, or if increased calcium hydroxide in the pores affects the progress of carbonation. The results suggest there are differences between wet and dry fly ash systems, in terms of their chemistry and response to carbon dioxide. However, the net effect in concretes of equal strength indicate little influence on carbonation resistance.

The Friedel's salt results on paste (2 weeks in 1.0 NaCl solution) are shown in Figure 13. For dry fly ash, this was highest for Fly Ash 5, which with the transportation properties above corresponds to low chloride diffusion. While moistening and storage of Fly Ashes 1 and 3 gave similar or slightly higher Friedel's salt compared to dry fly ash, reduced counts were noted for Fly Ash 5, which increased with storage period. The

results for chloride binding are given in Table 7 and suggest reductions with wet storage, in particular at 6 months, but less apparent effect of fly ash properties. As wet storage gives enhanced chloride resistance for Fly Ashes 1 and 3, this suggests, as noted previously [23], that physical effects have a greater influence than chemical. In the case of Fly Ash 5, the results with moistening and storage suggest that with increases in transportation properties and reductions in Friedel's salt (and binding), greater chloride diffusion in concrete may occur.

8. CONCLUSIONS

Moisture addition to fly ash and storage gave coarsening of material and slight increases in LOI, which developed with time. These effects increase with high free lime fly ash, but tend to be slightly less with low temperature exposure. Minor changes in bulk oxide composition and mineralogy occurred. Seawater moistening gave little difference compared to tap water, with similar behaviour between material stored in stockpiles and that in the laboratory for the same period of time.

Concretes were compared at equal slump and 28 day cube strength. Moistening and storage of fly ash mainly gave gradual reductions in air permeability and ISA-10 of concrete with values up to 50% and 30% lower respectively than dry material by 6 months storage. Low temperature storage and seawater moistening gave little difference in behaviour to tap water at 20°C. While dry high free lime fly ash gave lowest transportation properties in concrete, these had slight increases with moistening and storage.

In general, carbonation rates and chloride diffusion of concrete were similar, irrespective of whether fly ash was wet or dry. Chloride diffusion was slightly higher with moistened high free lime Fly Ash 5. Minor effects were noted using seawater to moisten fly ash (reduced carbonation, increased chloride diffusion) and with low storage temperature (reduced carbonation) on these properties. The short and longer-term stored fly ash from power station stockpiles gave general agreement with that wet-stored in the laboratory.

Corrosion potential and current measurements used to assess corrosion of reinforcement due to carbonation and chloride were not significantly different between wet or dry fly ash (for the low free lime materials examined in this case). These gave similar behaviour for the properties to that found in other studies examining dry fly ash in concrete.

Paste experiments were carried out to examine the effects of moistening fly ash on aspects of behaviour. The results indicate some influences of this on consumption of $Ca(OH)_2$, and $CaCO_3$ and Friedel's salt formation and chloride binding. These could be used to deduce effects occurring with the materials in concrete, during chloride ingress and carbonation, however, this represents an area where further research is required.

Overall, the results suggest that the use of wet-stored fly ash gives similar behaviour for the properties studied, compared to dry fly ash, in equal strength concrete. It is necessary for this to be assessed under normal exposure conditions.

9. ACKNOWLEDGEMENTS

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Table 1. Summary of test methods used for characterizing fly ash in the study

PROPERTY	METHOD/ STANDARD	SPECIMEN DETAILS	TEST ARRANGEMENT
Fineness/Particle size distribution	BS EN 451-2 [33]	1.0 g powder sample/ 45 µm sieve	Wet-sieving carried out for 1 minute under fixed pressure. Residue after oven drying compared to original sample mass.
	Laser particle size analysis+	1.0 g powder sample in 50 ml of water dispersed in ultrasonic bath.	Particle size distribution determined from scattering of collimated laser beam passing through the sample and using equipment software.
Loss-On-Ignition (LOI)	BS EN 196-2 [34]	1.0 g powder sample in a crucible	Ignition of sample carried out at 950°C for 1 hour. Change in mass compared to initial sample mass.
Free calcium oxide content	BS EN 451-1 [35]	1.0 to 1.5 g sieved powder sample	Acid digestion in boiling solution for 1 hour and titration to determine CaO quantity.
Bulk oxide composition	X-ray fluorescence+	Pressed homogenised powder pellet	X-ray fluorescence spectrometer with Cu Kα source.
Mineralogical composition	X-ray diffraction+	Homogenised powder sample	X-ray diffractometer with Cu Kα source. Reference made to standard samples. Area under main peak of mineralogical trace measured using commercial software.

+ Tests followed in-house methods as indicated

Table 2. Properties of dry fly ashes used in study

PROPERTY[#]	FLY ASH 1	FLY ASH 2	FLY ASH 3	FLY ASH 4	FLY ASH 5
Physical and LOI					
Fineness*	4.8	14.6	29.6	25.2	17.3
LOI	5.2	7.5	3.7	10.6	4.0
<6 µm	24.2	33.0	24.7	23.4	44.5
6-13 µm	21.0	17.2	14.3	17.3	20.6
13-26 µm	24.9	14.4	14.2	19.7	14.7
26-45 µm	18.4	14.1	14.5	17.9	9.0
45-75 µm	9.3	12.8	16.3	14.2	7.2
75-125 µm	2.2	7.7	13.3	7.2	3.9
>125 µm	0	1.0	2.7	0.5	0.1
Oxide Composition					
SiO_2	41.3	51.3	52.0	45.8	48.5
Al_2O_3	30.3	23.7	27.2	24.8	22.9
Fe_2O_3	5.0	6.9	6.7	9.8	11.1
CaO	4.5	2.1	2.1	2.7	4.4
Free lime	<0.1	<0.1	<0.1	-	0.9
MgO	0.5	0.8	0.6	0.4	1.4
P_2O_5	<0.1	<0.1	<0.1	<0.1	0.4
TiO_2	1.7	1.5	1.5	1.6	0.9
SO_3	0.2	0.2	0.3	0.3	1.7
K_2O	0.7	3.6	3.5	2.9	3.6
Na_2O	0.1	2.3	2.1	0.9	1.1
Mineral Composition					
Quartz	2.4	2.4	2.4	2.6	1.8
Mullite	6.3	1.6	2.5	3.2	2.2
Magnetite	0.8	0.4	0.6	1.0	2.2
Hematite	7.7	1.9	3.1	4.7	2.8
Glass/others[x]	78	86	88	74	87

[#] Percent by mass, except for particle size distribution (by volume)
*Retained on 45µm sieve
[x] Not including LOI

Table 3. Example of concrete mix proportions for Fly Ash 1, kg/m^3 unless noted otherwise

STRENGTH CLASS, MPa	W/C RATIO	PC	DRY PFA	FREE WATER	SP, % total cement	AGGREGATES		
						20 mm	10 mm	Sand
Dry								
35	0.50	230	100	165	0.50	810	410	645
50	0.37	310	135	165	0.80	810	410	555
1 Month$^+$								
35	0.48	240	105	165	0.50	810	410	625
50	0.36	320	140	165	0.60	810	410	505
6 Months$^+$								
35	0.46	250	110	165	0.50	810	410	600
50	0.36	320	140	165	0.90	810	410	500

[+] wet-storage period
Target slump of concretes, 75 mm

Table 4. Water/cement ratios to achieve equal strength in dry and moistened fly ash concretes

CONCRETE MIX	35 MPa[x]			50 MPa		
	DRY	1 MONTH	6 MONTHS	DRY	1 MONTH	6 MONTHS
Fly Ash 1	0.50	0.48	0.46	0.37	0.36	0.36
Fly Ash 2	0.52	0.48	0.47	0.40	0.36	0.35
Fly Ash 3	0.48	0.43	0.46	0.36	0.33	0.34
Fly Ash 4	0.45	0.48	0.45	0.35	0.36	0.34
Fly Ash 5	0.46	0.45	0.44	0.35	0.33	0.33
Fly Ash 6	-	0.47	0.46	-	0.34	0.33

Minor adjustments in water content were made between concrete containing fly ash of different fineness

[x] Fly Ash 7 : 0.48; Seawater, 6 months, Fly Ash 1 : 0.50, Fly Ash 3 : 0.49;

5°C stored, 6 months, Fly Ash 1 : 0.48, Fly Ash 3 : 0.49.

Table 5. Air permeability and initial surface absorption (10 minutes, ISA-10) of test concretes
(Concrete strength class, 35 MPa)

CONCRETE MIX	AIR (INTRINSIC) PERMEABILITY*+ x 10^{-17} m^2			ISA-10*+, $ml/m^2/sec$		
	Dry	1 Month	6 Months	Dry	1 Month	6 Months
Fly Ash 1	4.7	3.4	2.5	0.35	0.27	0.26
Fly Ash 2	3.8	2.8	1.9	0.31	0.30	0.24
Fly Ash 3	5.0	3.9	2.3	0.33	0.25	0.23
Fly Ash 4	4.8	3.4	3.3	0.32	0.26	0.24
Fly Ash 5	3.2	3.8	3.8	0.28	0.30	0.29
Fly Ash 6	-	1.9	2.0	-	0.29	0.25

*Seawater, 6 months, Air (intrinsic) permeability Fly Ash 1 : 2.9, Fly Ash 3 : 2.1; ISA-10 Fly Ash 1 : 0.28, Fly Ash 3 : 0.25
+ 5°C stored, 6 months, Air (intrinsic) permeability Fly Ash 1 : 2.1, Fly Ash 3, 2.1; ISA-10 Fly Ash 1 : 0.30, Fly Ash 3 : 0.26

Table 6. Calcium hydroxide in paste (w/c ratio, 0.5; 30% fly ash in cement; g per100 g of PC) following 28 days water curing

PASTE MIX	FLY ASH CONDITION / MOISTURE STORAGE PERIOD		
	DRY	1 MONTH	6 MONTHS
Fly Ash 1	14.8	18.1	19.9
Fly Ash 3	17.5	18.2	19.5
Fly Ash 5	16.3	20.0	20.7

Table 7. Chloride binding capacity in paste (w/c ratio, 0.5; 30% fly ash in cement; Exposure, 2 weeks 1.0 M NaCl, 20°C; mg/g of sample)

PASTE MIX	FLY ASH CONDITION / MOISTURE STORAGE PERIOD		
	DRY	1 MONTH	6 MONTHS
Fly Ash 1	28.9	22.5	21.8
Fly Ash 3	25.5	28.0	20.8
Fly Ash 5	27.9	29.1	21.6

|	FLY ASH CONDITION / MOISTURE STORAGE PERIOD		
PASTE MIX	DRY	1 MONTH	6 MONTHS

(a)
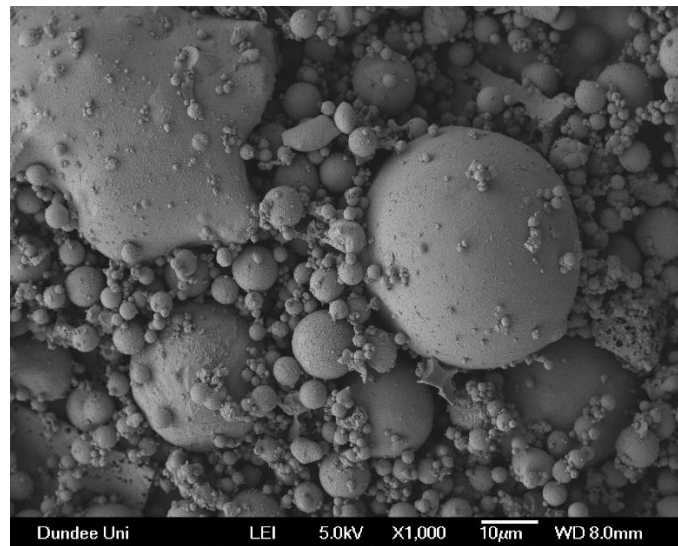
(b)
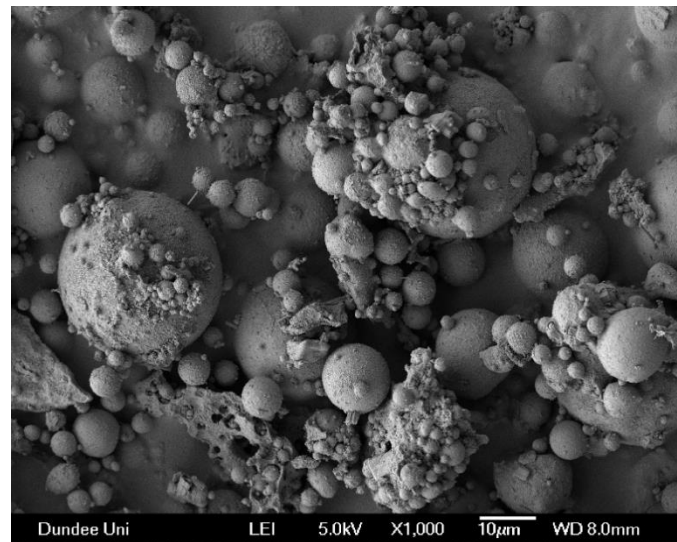
(c)
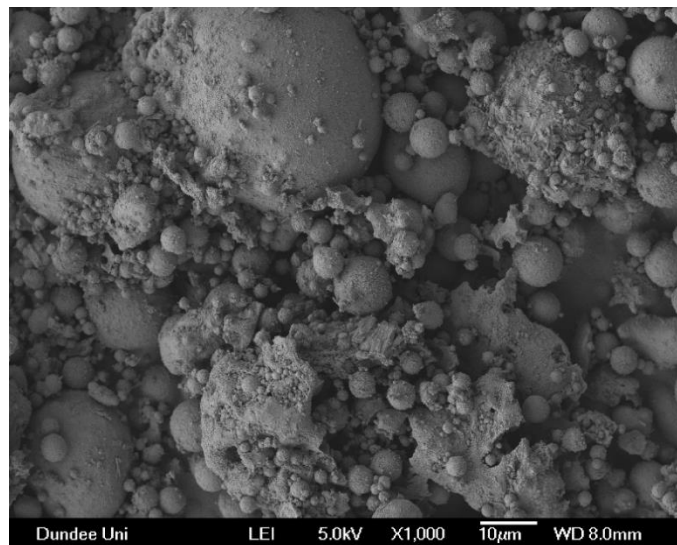
Figure 1. Scanning electron microscopy images showing the morphology of (a) dry,
(b) wet stored laboratory (10% moisture/6 months stored) and (c) power station stockpile fly ash
(Courtesy of Mr T A Hope, University of Dundee)

WE, CE : 10 mm ɸ reinforcement bars
RE : Ag/AgCl reference electrode

Screen

Ramp unit set at
0.1 mV/second

Reinforced concrete
cube test specimen

RE

Potentiostat
with IR
compensation

WE

CE

Voltmeter

Specimen polarized to
± 10 mV of corrosion potential

Earth

WE – Working electrode, CE – Counter electrode
RE – Reference electrode
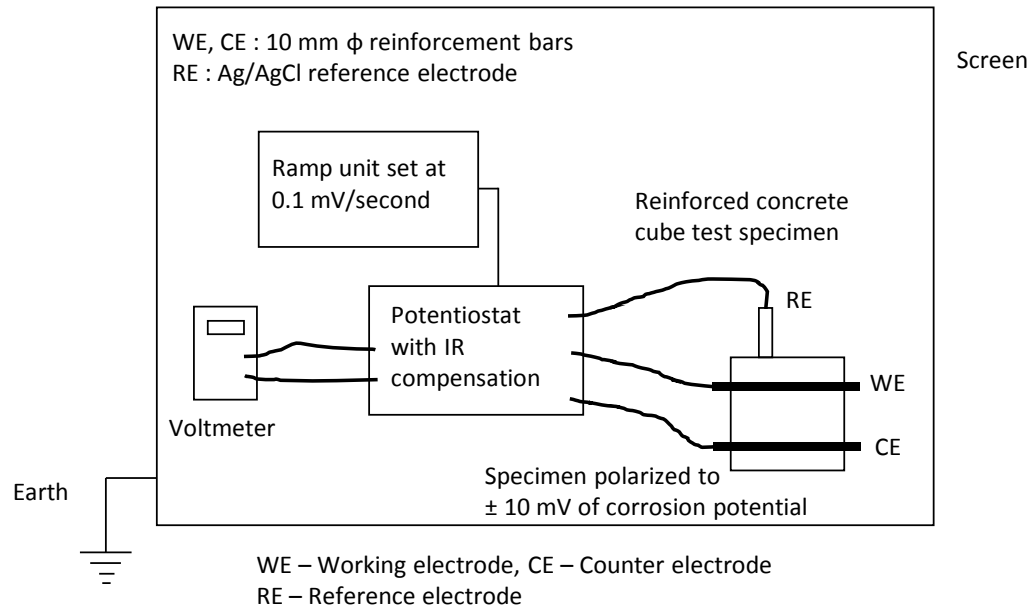
Figure 2. Schematic illustration of corrosion testing equipment
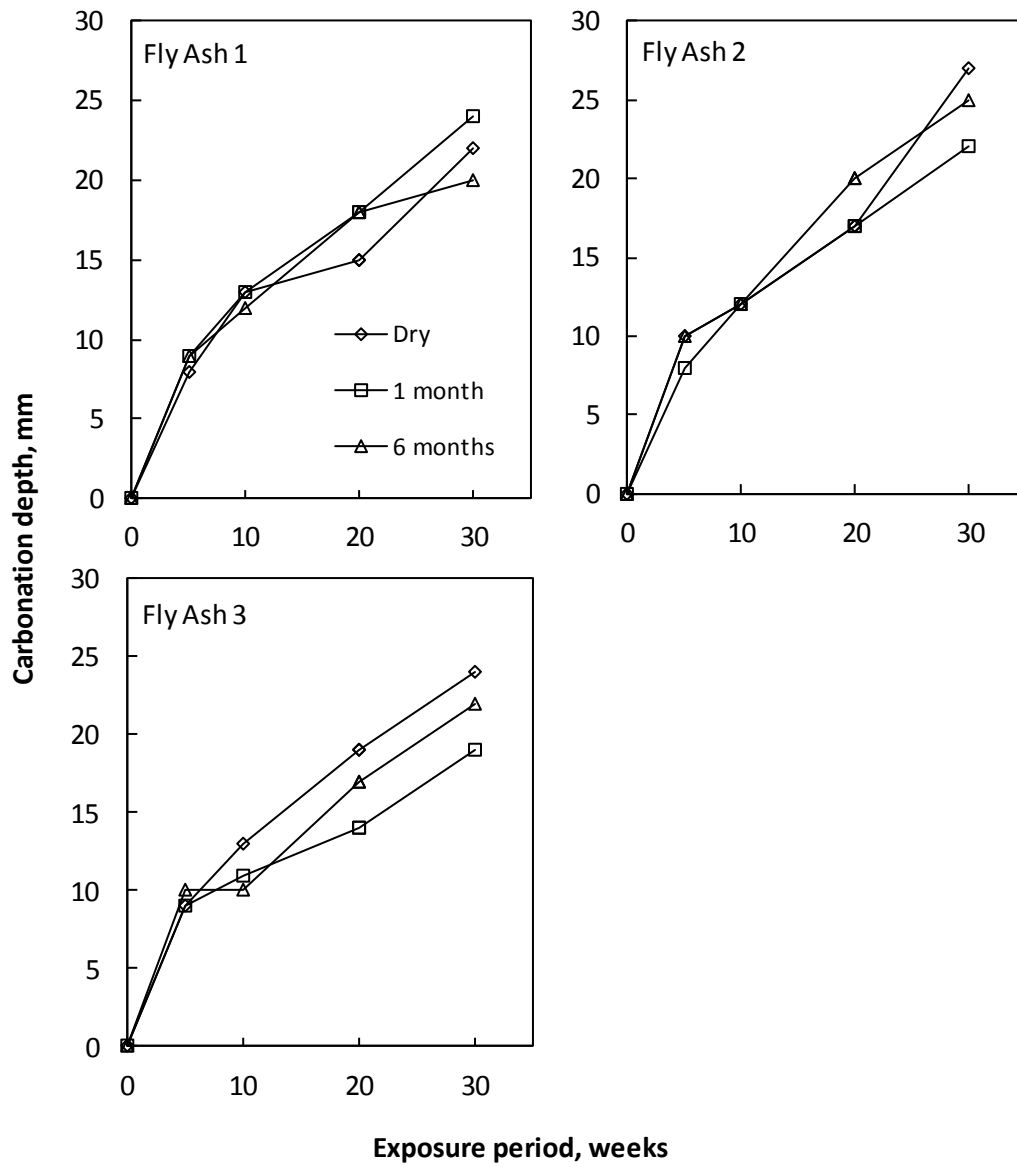
Figure 3. Effect of fineness and wet-storage on carbonation in moistened fly ash concretes
(Concrete strength class, 35 MPa; Exposure, 4.0% CO_2, 55% RH, 20°C)
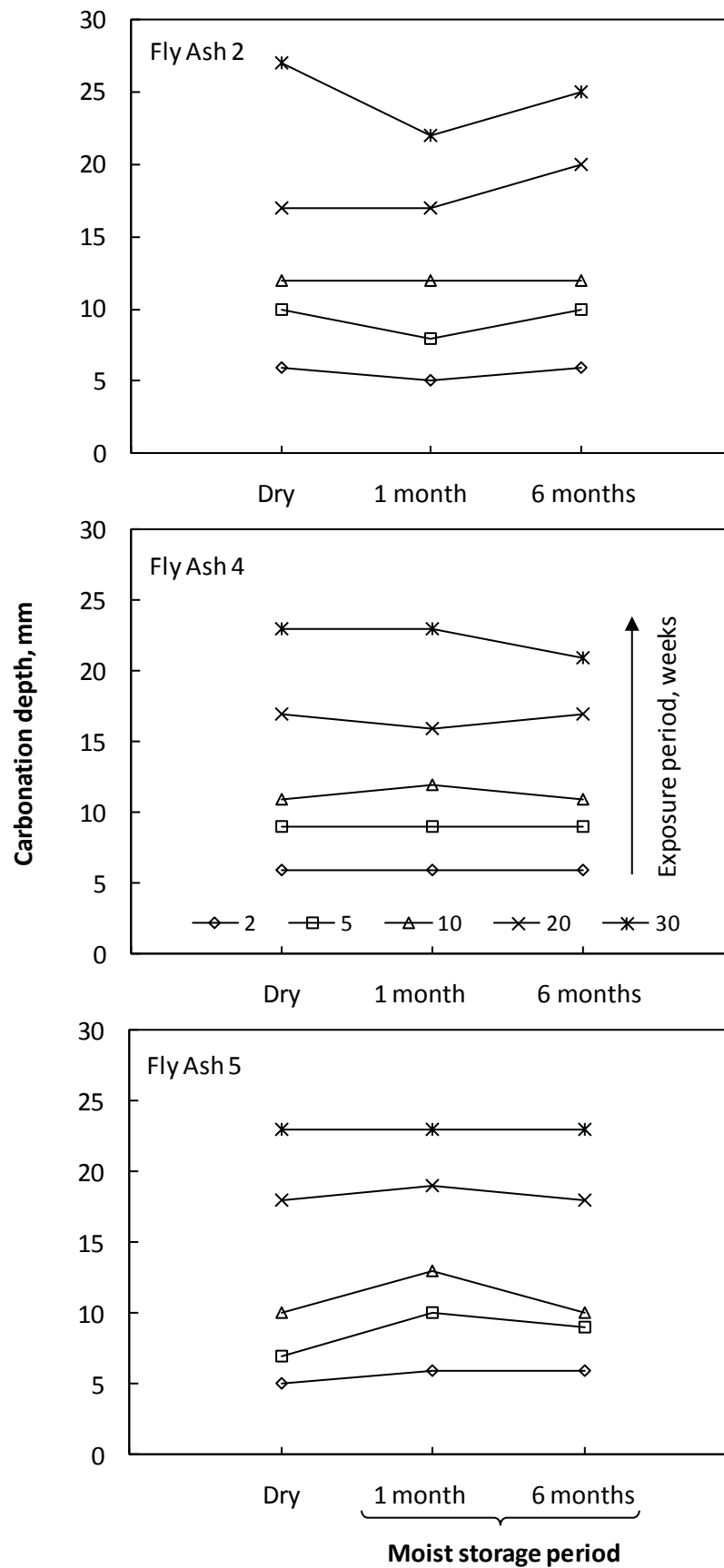
Figure 4. Effect of LOI (Fly Ash 4) and free lime content (Fly Ash 5) on carbonation
of moistened fly ash concretes (Concrete strength class, 35 MPa;
Exposure, 4.0% CO_2, 55% RH, 20°C)
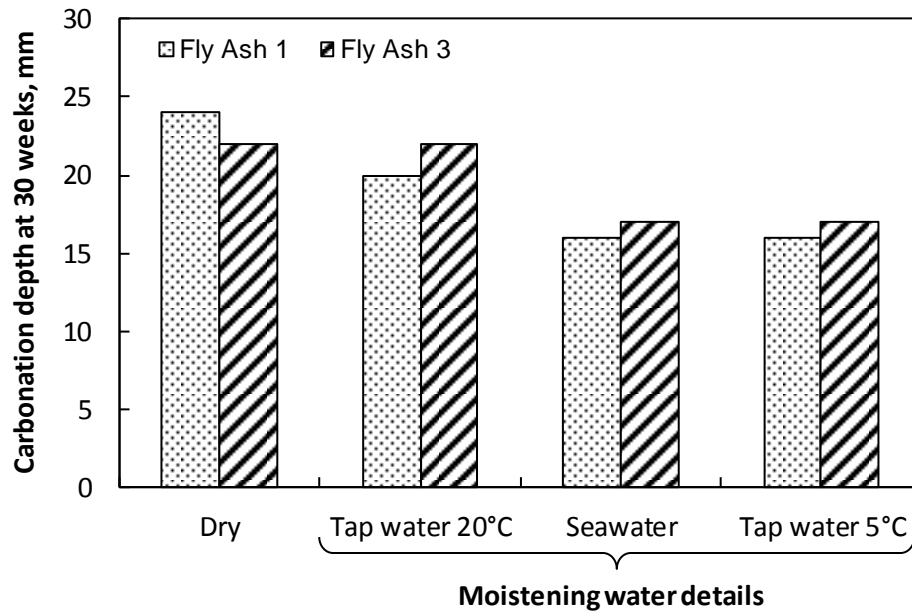
Figure 5. Effect of water properties and storage temperature on carbonation depth of moistened fly ash concretes (6 months stored; Concrete strength class, 35 MPa; Exposure, 4.0% CO_2, 55% RH, 20°C)
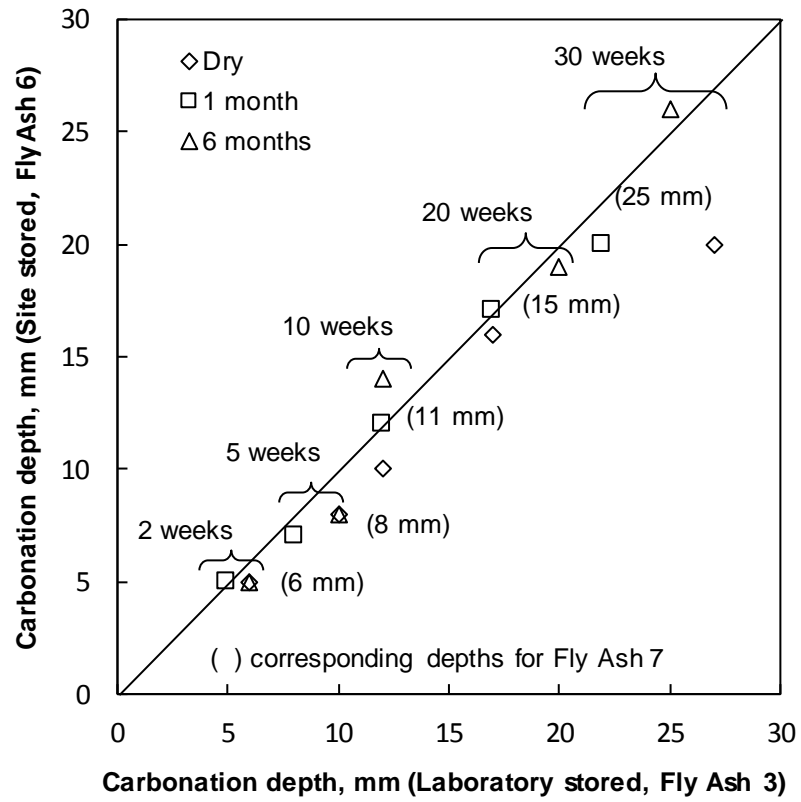
Figure 6. Comparison of carbonation depths in laboratory and site stored moistened fly ash concretes (Concrete strength class, 35 MPa; Exposure, 4.0% CO_2, 55% RH, 20°C)
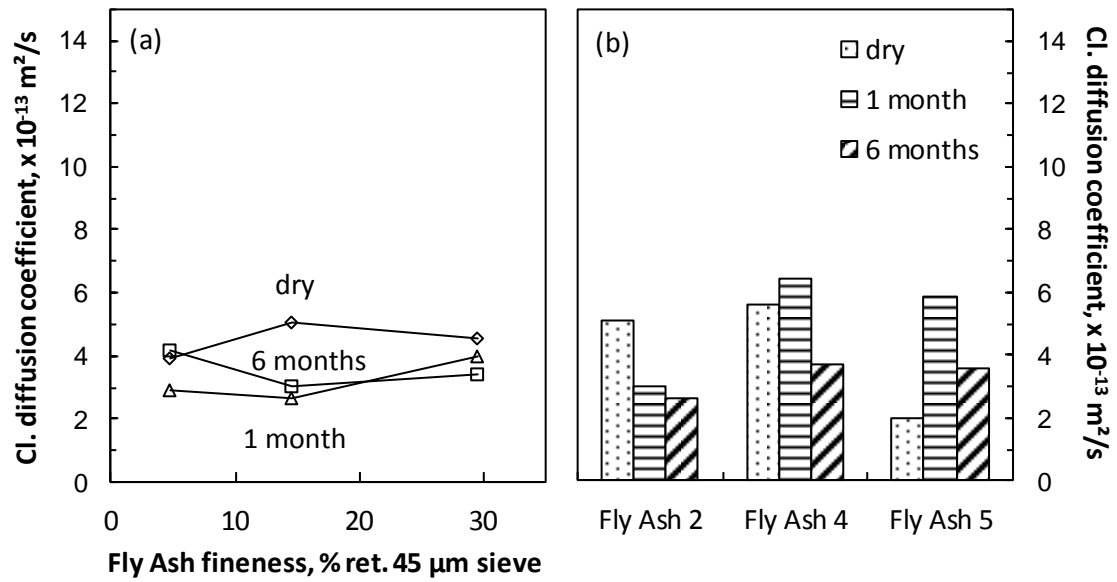
Figure 7. Effect of (a) fineness and (b) LOI (Fly Ash 4) and free lime content (Fly Ash 5)
on chloride diffusion coefficients of moistened fly ash concretes
(Concrete strength class, 35 MPa)
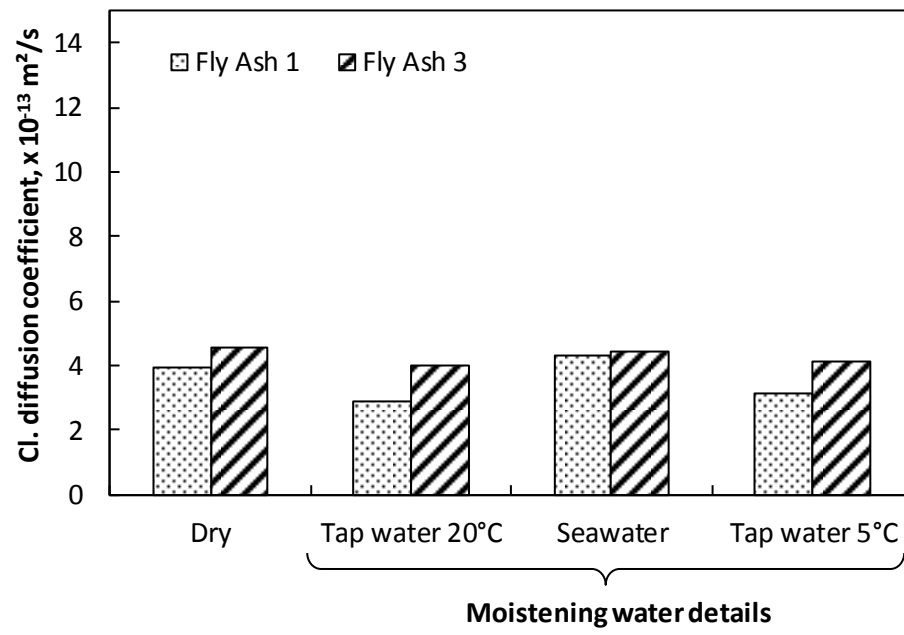
Figure 8. Effect of water properties and storage temperature on chloride diffusion coefficients of moistened fly ash concretes (6 months stored; Concrete strength class, 35 MPa)
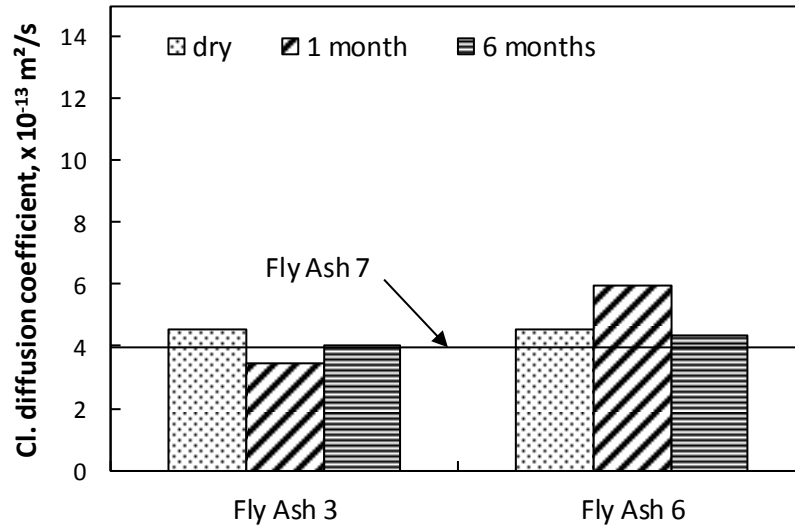
Figure 9. Comparison of chloride diffusion coefficients for laboratory (Fly Ash 3)
and site (Fly Ash 6) stored moistened fly ash concretes (Concrete strength class, 35 MPa)
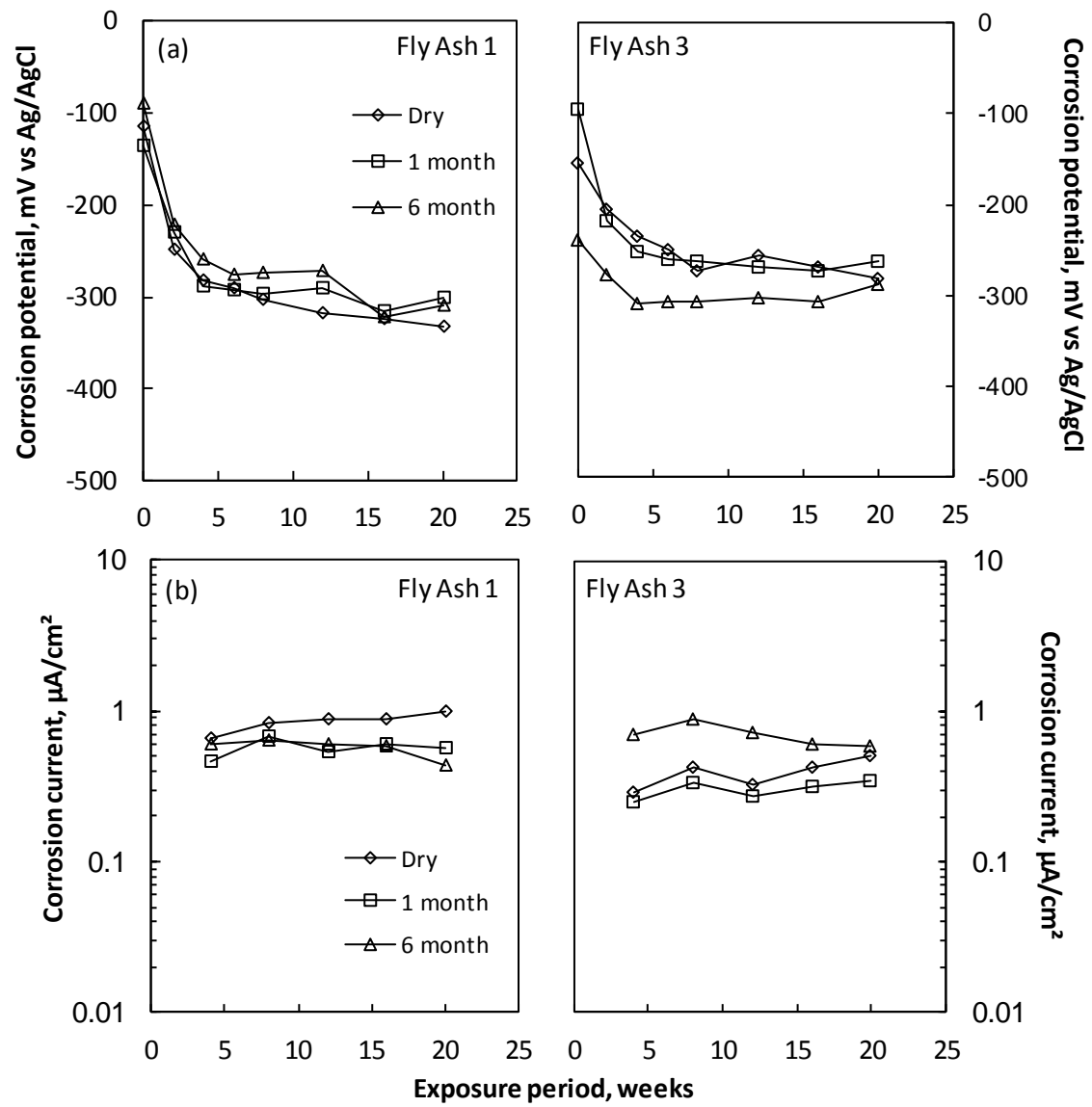
Figure 10. Effect of wet-storage on (a) corrosion potential and (b) corrosion current of carbonated moistened fly ash concretes (Concrete strength class, 35 MPa; Exposure, 95% RH, 20ºC)
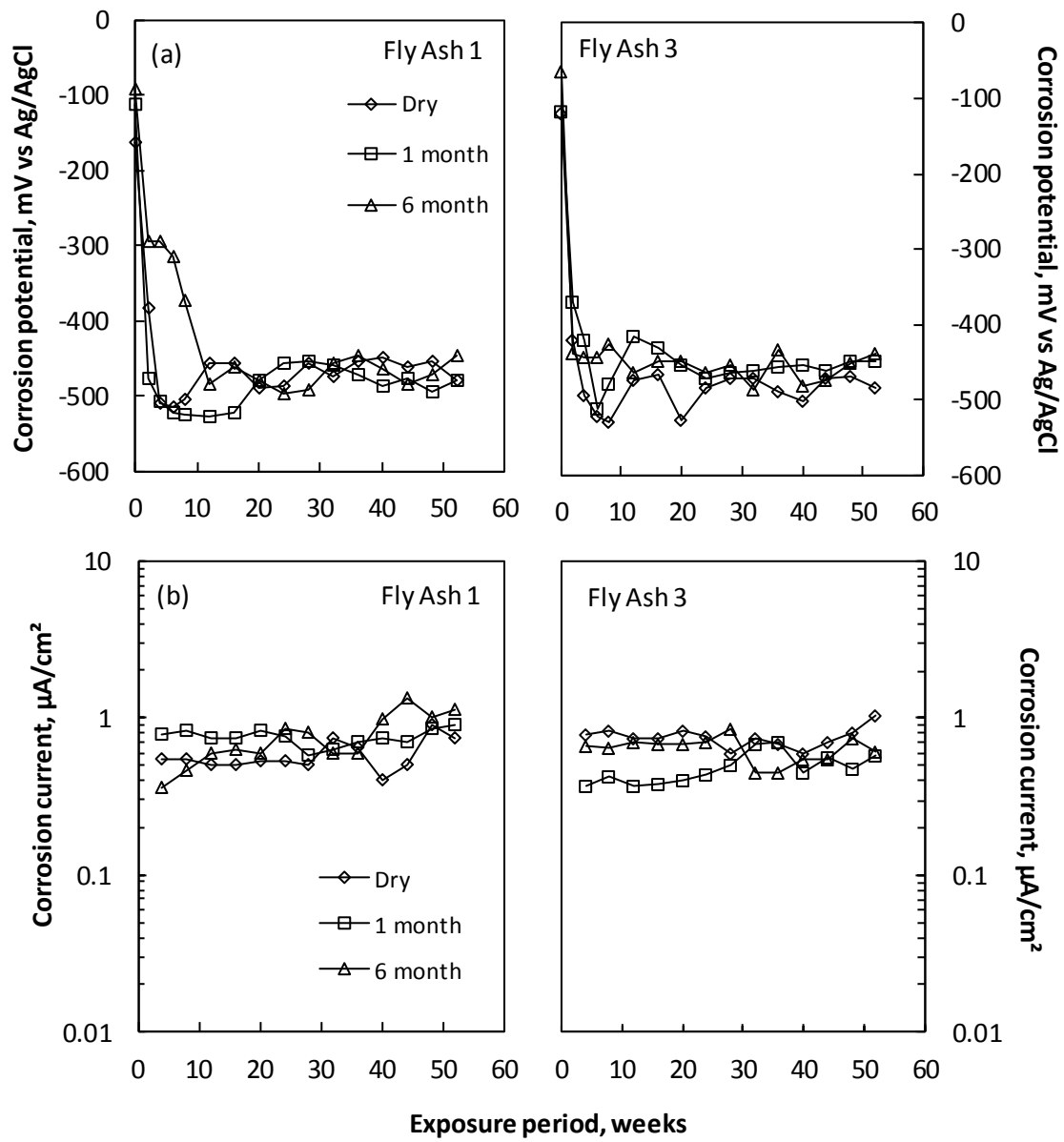
Figure 11. Effect of wet-storage on (a) corrosion potential and (b) corrosion current of chloride-exposed fly ash concretes (Concrete strength class, 50 MPa; Exposure, 3 hours wetting 2.4 M NaCl/ 9 hours drying, 20ºC)
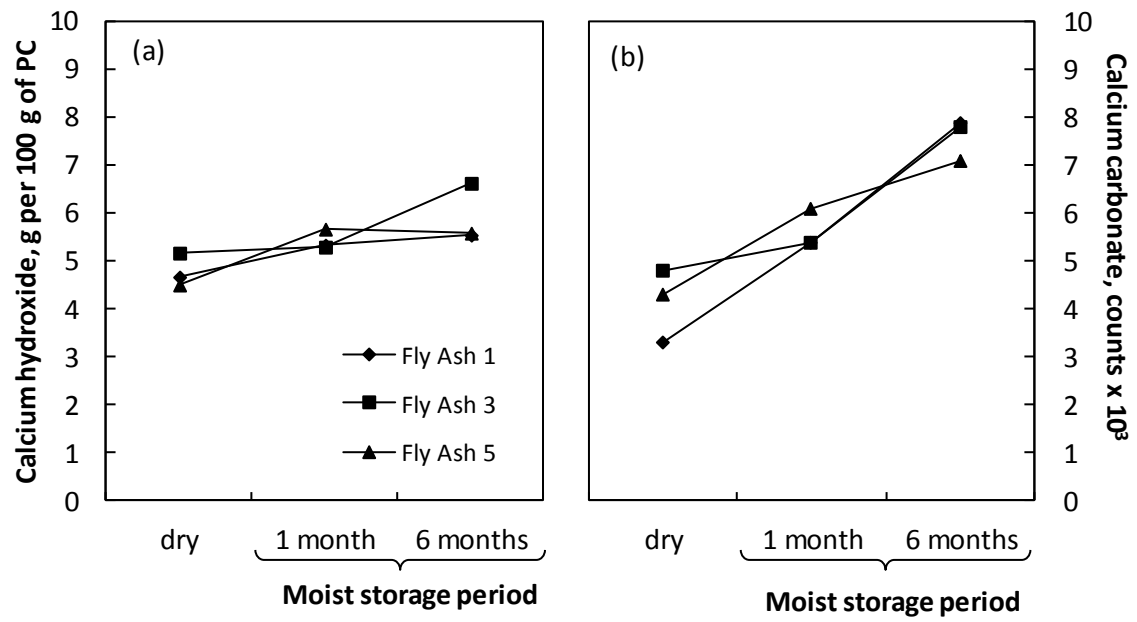
Figure 12. Effect of wet-storage on (a) calcium hydroxide and (b) calcium carbonate in fly ash paste following carbonation (w/c ratio, 0.5, 30% fly ash in cement; Exposure, 5 weeks 4.0% CO_2, 55% RH, 20°C)
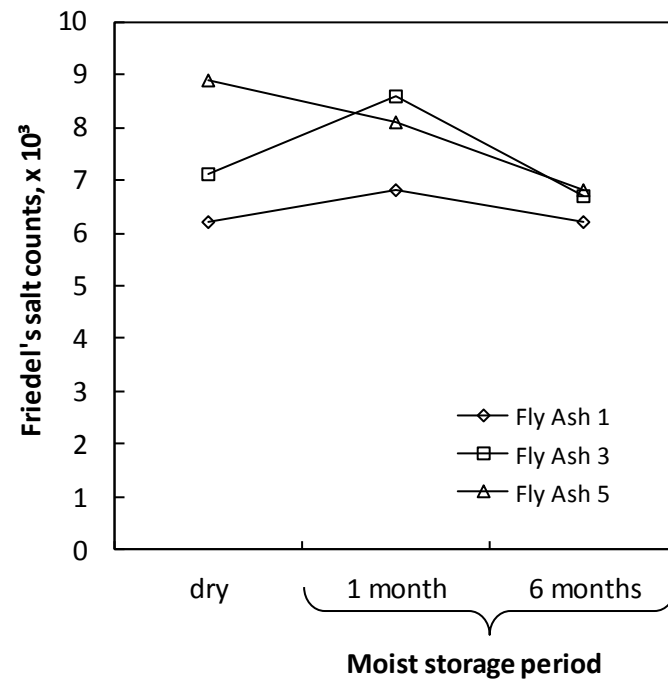
Figure 13. Effect of wet-storage on Friedel's salt in fly ash paste following chloride exposure (w/c ratio, 0.5, 30% fly ash in cement; Exposure, 2 weeks 1.0 M NaCl, 20ºC)

APPENDIX

Table A1. Effect of moistening (10%) and storage period (months (m) at 20ºC) on fly ash properties

| PROPERTY[#]	FLY ASH 3			FLY ASH 4			FLY ASH 5		
	Dry	1m	6m	Dry	1m	6m	Dry	1m	6m
Physical and LOI									
Fineness*	29.6	32.1	40.1	15.1	20.4	34.8	17.3	63.4	70.2
LOI	3.7	3.8	3.9	10.6	10.8	10.9	4.0	4.1	4.9
Moisture Content	-	9.1	8.6	-	8.5	8.4	-	8.5	8.4
<6	24.7	25.1	25.1	23.4	22.5	18.9	44.5	36.3	30.4
6-13	14.3	15.5	15.8	17.3	19.3	18.6	20.6	21.3	18.0
13-26	14.2	15.3	15.5	19.7	22.2	23.0	14.7	18.3	16.1
26-45	14.5	15.0	14.2	17.9	20.0	20.1	9.0	11.9	13.6
45-75	16.3	15.6	15.3	14.2	13.0	14.4	7.2	7.9	11.6
75-125	13.3	11.3	12.1	7.2	2.9	5.1	3.9	4.1	8.4
>125	2.7	2.3	2.0	0.5	0	0	0.1	0.2	1.9
Oxide Composition									
SiO_2	52.0	52.0	50.4	45.8	46.6	44.9	48.5	48.4	46.7
Al_2O_3	27.2	27.3	28.1	24.8	25.4	25.2	22.9	22.7	23.2
Fe_2O_3	6.7	6.4	6.5	9.8	8.4	9.1	11.1	11.0	11.2
CaO	2.1	1.8	1.8	2.7	2.3	2.7	4.4	4.3	5.7
MgO	0.6	0.6	0.4	0.4	0.6	0.3	1.4	1.8	1.4
P_2O_5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TiO_2	1.5	1.4	1.4	1.6	1.4	1.5	0.9	1.0	0.8
SO_3	0.3	0.4	0.6	0.3	0.5	1.0	1.7	1.6	1.4
K_2O	3.5	3.6	3.9	2.9	3.0	3.2	3.6	3.7	3.6
Na_2O	2.1	2.5	3.0	0.9	0.9	1.2	1.1	1.1	0.8
Mineral Composition									
Quartz	2.4	2.0	2.6	2.6	3.2	3.2	1.8	2.5	2.1
Mullite	2.5	2.3	2.5	3.2	3.4	3.3	2.2	2.1	1.8
Magnetite	0.6	0.5	0.5	1.0	0.9	0.8	2.2	2.3	2.1
Hematite	3.1	3.0	2.6	4.7	4.4	4.8	2.8	2.9	2.9
Glass/others[x]	88	88	88	78	77	77	87	86	86

[#] Percent by mass, except for particle size distribution (by volume)
*Retained on 45µm sieve
[x] Not including LOI

Table A2. Effect of temperature, moistening water and stockpile storage on fly ash properties

PROPERTY[#]	FLY ASH 3[+]				FLY ASH 6[++]	FLY ASH 7[++]
	Dry	20ºC	5ºC	Sea	6 months External	6 year External
Physical and LOI						
Fineness*	29.6	40.1	36.3	43.0	44.6	22.7
LOI	3.7	3.9	3.7	3.9	4.2	2.4
Moisture Content	-	8.6	9.4	8.7	14.1	5.3
<6	24.7	25.1	30.9	29.5	24.1	31.7
6-13	14.3	15.8	15.7	16.5	14.4	16.1
13-26	14.2	15.5	14.0	14.7	13.7	14.2
26-45	14.5	14.2	12.4	13.3	13.3	12.7
45-75	16.3	15.3	12.6	13.3	15.6	12.5
75-125	13.3	12.1	10.5	10.0	14.1	9.6
>125	2.7	2.0	4.0	2.7	4.8	3.1
Oxide Composition						
SiO_2	52.0	50.4	43.6	44.1	51.0	53.0
Al_2O_3	27.2	28.1	25.5	25.7	28.1	27.9
Fe_2O_3	6.7	6.5	5.3	4.7	5.9	6.2
CaO	2.1	1.8	1.7	1.6	2.7	2.1
MgO	0.6	0.4	0.3	0.3	0.6	0.8
P_2O_5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TiO_2	1.5	1.4	1.3	1.3	1.4	1.5
SO_3	0.3	0.6	0.4	0.3	0.6	0.2
K_2O	3.5	3.9	3.4	3.5	3.8	3.8
Na_2O	2.1	3.0	3.1	4.5	1.6	2.1
Mineral Composition						
Quartz	2.4	2.6	1.8	1.6	2.1	1.6
Mullite	2.5	2.5	2.2	1.5	2.0	1.4
Magnetite	0.6	0.5	0.3	0.3	0.3	0.5
Hematite	3.1	2.6	2.2	1.9	2.2	1.8
Glass/others[x]	88	88	90	91	89	92

[+] Dry or moistened with tap water at 10% and laboratory stored at 20ºC, 5ºC, or with seawater (20ºC) for 6 months
[++] Moistened with tap water at 10 to 30% and stored externally in stockpiles for the periods indicated
[#] Percent by mass, except for particle size distribution (by volume)
*Retained on 45µm sieve
[x] Not including LOI