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S252

STUDIES ON THE RATE AND EXTENT OF REACTION BETWEEN CALCIUM HYDROXIDE AND PULVERISED FUEL ASH AT 38 °C

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SYNOPSIS

The ASTM test Method C311 has been extended to cover the use of calcium hydroxide and pulverised fuel ash (pfa) in three different ratios in order to determine the rate and extent of alkali ion extraction, the pfa reaction rate and the quantity of silicon and aluminium oxides in the reaction products. An explanation is given why pozzolans such as pfa are effective in reducing expansion.

SAMEVATTING

Die ASTM-toetsmetode, C311, is uitgebrei om die gebruik van kalsiumhidroksied en poeierkoolas in drie verskillende verhoudings te dek ten einde die tempo en omvang van die alkali-ioonekstraksie, die poeierkoolasreaksietempo en die hoeveelheid silikon- en aluminiumoksiede in die reaksieprodukte te bepaal. Die doeltreffendheid van possolane, soos poeierkoolas, om uitsetting te verminder, word verduidelik.

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1. INTRODUCTION

There is international acceptance of the ASTM test method, C311, for determining available alkalis in fly ashes and natural pozzolans for use as mineral admixtures in Portland cement concrete. Particular conditions are specified in the test method, and the results obtained are useful when comparing one pulverised fuel ash (pfa) with another. In this study the test has been extended, using three different mass ratios of calcium hydroxide: pfa, to determine, for several different pfa samples,

(a) the rate and extent of extraction of alkali metal ions
(b) the rate of reaction of the pfa particles
(c) the amounts of silicon and aluminium oxides in the reaction products.

2. EXPERIMENTAL

Mixtures of pfa: calcium hydroxide: water were made and stored at 38 °C in sealed containers for varying lengths of time. In each case the combined mass of pfa and calcium hydroxide was 7 g and 10 cm³ of water was used. The mass ratios of pfa: calcium hydroxide were 5g:2g (ASTM, C311 method), 3,5g:3,5g and 2g:5g. Most of the experiments were stopped after 28 days (ASTM, C311 method) but other times of extraction were also used.

Each sample was analysed for available alkalis by the method specified in ASTM C311 which involves extracting the products of reaction with water and the removal of the insoluble material by filtration. The available alkalis were then determined using the aqueous extracts.

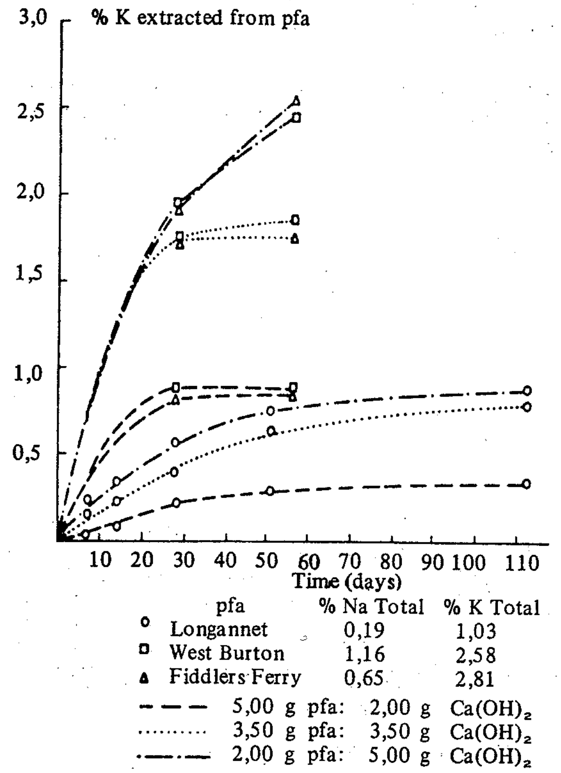

FIGURE 1: Relationship between % K extracted from pfa and time of exposure to $Ca(OH)_2$.

To obtain additional information the insoluble residues were then suspended in 2 M hydrochloric acid in order to dissolve the solid products of reaction between the pfa and the calcium hydroxide, and the suspensions were then centrifuged. The precipitates were washed with water and the washings added to the hydrochloric acid extracts. The mass of the precipitates were determined after drying at 120 °C.

The sodium and potassium ion concentrations of the aqueous and hydrochloric acid extracts were determined by flame photometry, and the silicon and aluminium contents, expressed as oxides, were found for both sets of extracts by atomic absorption. The total sodium and potassium content of each pfa was determined by flame photometry on solutions obtained by complete dissolution of the samples in mixtures of nitric, perchloric and hydrofluoric acids as described in BS 1902.

3. RESULTS

The results showing the amount of sodium and potassium ions present in the aqueous extracts of those samples which have been studied for more than one period of time are given in Figures 1 and 2. As expected the silicon and aluminium content of the aqueous extracts were found to be extremely low because of the low solubility of hydrated calcium silicates and aluminates in lime solution. In Figures 1 and 2 the quantities of alkali metal ions extracted are expressed as percentages of the amounts of pfa used. On this basis it is clear that:

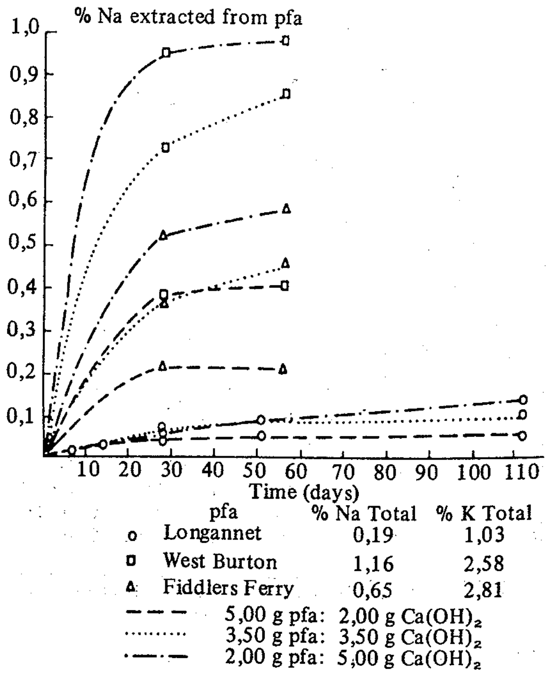

FIGURE 2: Relationship between % Na extracted from pfa and time of exposure to $Ca(OH)_2$.

(a) the rate and amount of extraction of sodium and potassium ions increases as the mass ratio pfa: $Ca(OH)_2$ decreases

(b) provided the mass ratio pfa:$Ca(OH)_2$ is low all of the sodium and potassium ions present in the pfa samples would ultimately be extracted

(c) for the ASTM C311 ratio of 5 g pfa:2g $Ca(OH)_2$ there is little change in the amount of sodium and potassium ions extracted if the pastes are stored at 38 °C for periods longer than 28 days.

Figure 3 shows the percentage loss in mass of the pfa samples determined by the method described above. It should be noted that these results are subject to small errors due to the low solubility of the pfa in the dilute hydrochloric acid used, and no corrections have been made for these errors. Despite this it is apparent that the curves shown in Figure 3 closely parallel those shown in Figures 1 and 2. For all of the pfa samples used in this study 90 per cent of the particles were < 45 μm in diameter, and the glass spheres contained > 50 per cent SiO_2 and > 25 per cent Al_2O_3. It therefore follows from the results shown in Figure 3 that considerable amounts of silica and alumina from the pfa have reacted to form hydrated calcium silicates and aluminates. This has been confirmed by monitoring the quantities of silicon and aluminium, expressed as SiO_2 and Al_2O_3 respectively, present in the acid soluble products of reaction from some of the samples. These results are shown in Figures 4 and 5 where they are expressed as percentages of the pfa used. It is clear that the conclusions drawn earlier regarding the rate and amount of extraction of sodium and potassium ions are also valid with respect to the silica and alumina from the pfa which have reacted to give acid soluble products.

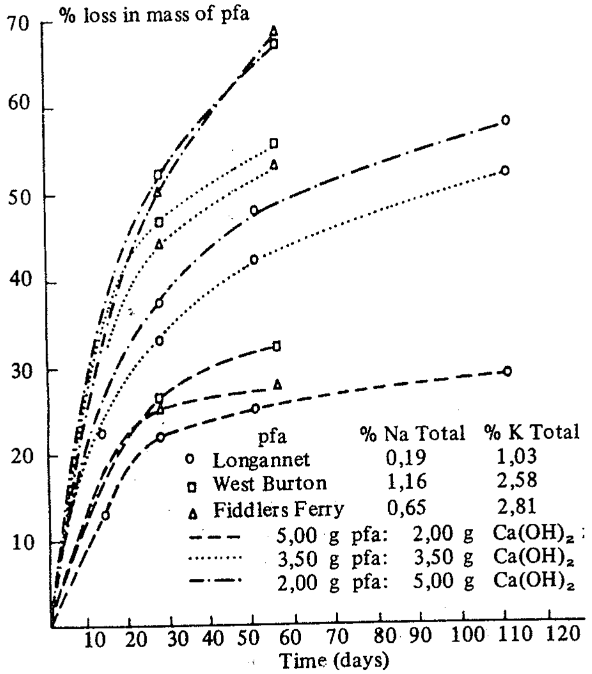

FIGURE 3: Relationship between loss in mass of pfa and time of exposure to $Ca(OH)_2$.

In Figure 6 the percentage alkali metal ions extracted from a considerable number of pfa samples are compared with their total alkali content. These results are from experiments lasting 28 days or longer. For any particular experiment the agreement between

$$\frac{\%\ \text{Na extracted}}{\%\ \text{Na total}} \quad \text{and} \quad \frac{\%\ \text{K extracted}}{\%\ \text{K total}}$$

was surprisingly good, indicating that sodium and potassium ions have similar abilities to leave the pfa particles. In all cases the amount of sodium and potassium ions retained in the products of reaction, ie the hydrochloric acid extract, was very small.

4. DISCUSSION

The ASTM specification (C618) for pfa required for the production of concrete where the pfa is required to counteract alkali-aggregate reaction, gives a limit of 1,50 per cent Na_2O equivalent for the available alkalis. It should be noted that this limit was not reached with any of the samples examined using the ASTM test conditions, but was exceeded in a number of cases when the mass ratio pfa: $Ca(OH)_2$ was decreased. One of the reasons for carrying out tests with lower mass ratios was that with many modern Portland cements the mass of $Ca(OH)_2$ produced approximates to 30 per cent of the anhydrous mass of the cement used. If 25 per cent of the cement is replaced by pfa the mass ratio pfa:$Ca(OH)_2$ in the mixture is much closer to 1:1 than the 2,5:1 specified in ASTM C311.

The alkali-silica reaction is caused by hydroxyl ions present in the pore fluids of the concrete reacting with certain poorly crystalline forms of silica which may be present in the aggregates used. A gel is formed which can absorb water and swell, and in so doing the expansive forces can disrupt the concrete. Damage to concrete in the USA due to alkali-silica reaction was recognised by Stanton[1] in 1940, and subsequently a limit of 0,6 per cent Na_2O equivalent was imposed by many countries on the alkali content of Portland cement when used with potentially reactive aggregates. Since then there have been numerous papers demonstrating the effectiveness of pulverised fuel ash in reducing expansion caused by alkali-silica reaction[2, 3], and recently this has also been shown with the pulverised fuel ashes used in this study[4].

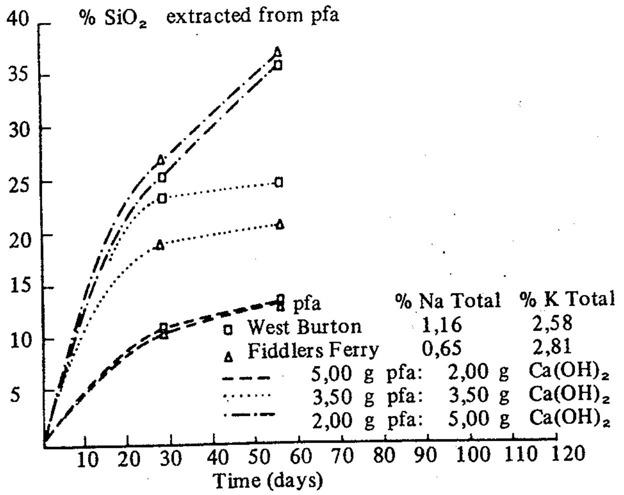

FIGURE 4: Relationship between % SiO_2 extracted from pfa and time of exposure to $Ca(OH)_2$.

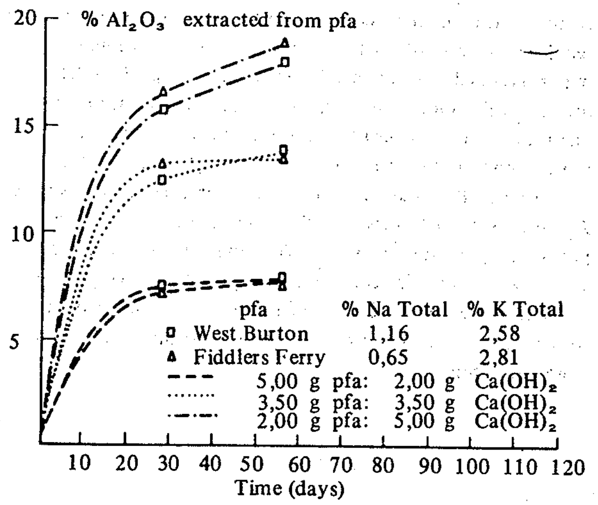

FIGURE 5: Relationship between % Al_2O_3 extracted from pfa and time of exposure to $Ca(OH)_2$.

At first sight it would appear strange that, using the mortar bar expansion test, ASTM C441, the inclusion of pulverised fuel ash could reduce expansion caused by the alkali-silica reaction. The present work shows that at 38 °C, ie the same temperature as that at which the mortar bar expansion tests are performed, considerable quantities of sodium and potassium ions are liberated, and the amount of 'available alkali' from the pfa can be greater than that arising from the Portland cement. It is therefore necessary to give an explanation of this apparent anomaly. In addition it should be noted that the amount of water soluble alkali metal ions extracted from these pfa samples was very small (between 0,02 and 0,12 per cent Na_2O equivalent), and can be accounted for as arising from thin coatings of sodium and potassium sulphates on the surface of the pfa particles. These thin coatings are readily water soluble and are dissolved during the initial mixing of the mortar bars (and concretes). It would therefore appear to be fallacious to relate any changes in the mortar bar expansions to the water soluble alkalis from the pfa, since such an approach ignores the alkalis extracted in the presence of calcium hydroxide solutions.

The apparent anomaly can be explained in terms of the reaction between the hydroxyl ions in the pore solution and the pfa particles. Silicate and aluminate ions are liberated which precipitate as a gel containing hydrated calcium silicates and aluminates around the pfa particles. The solubility of the compounds in this gel is very low because of the amount of calcium hydroxide present in the system. It therefore follows that the overall effect is to remove some of the calcium hydroxide which has been produced by the hydration of the Portland cement and to replace it by hydrated calcium silicates and aluminates. This reaction is most rapid during the early stages of hydration with large concrete structures because of the temperature rise within the system, and has been demonstrated using mortar cubes[5]. The same reaction has now been shown to occur at 20 °C, and although the rate of reaction is much slower the amount of reaction is very similar[6]. During this reaction, in which the pfa particles can be regarded as contracting spheres which eventually are completely removed, the alkali metal oxides present in the particles are liberated as ions. The present results show that the dissolution of the pfa, the production of hydrated calcium silicates and aluminates and the liberation of alkali metal ions occur simultaneously and their individual rates of reaction are related to the chemical composition of the pfa particles. The results also show that the molar ratio Na_2O equivalent:SiO_2 arising from the pfa is very low and well within the region of low risk as described by others[7]. It has also been found that the alkali-silica reaction can be effectively inhibited if a sufficient amount of pozzolanic material is used and this has been related to the reduction in the amount of $Ca(OH)_2$ present[8]. The average size of the pfa particles used as pozzolans is in the range 10 - 15 μm and the particles are therefore situated within the gelatinous material arising from the hydration of the cement. The overall effect of the pfa/$Ca(OH)_2$ reaction is to reduce the CaO:SiO_2 molar ratio of the reaction products as a whole[9], and the alkali metal ions are trapped within this gelatinous material.

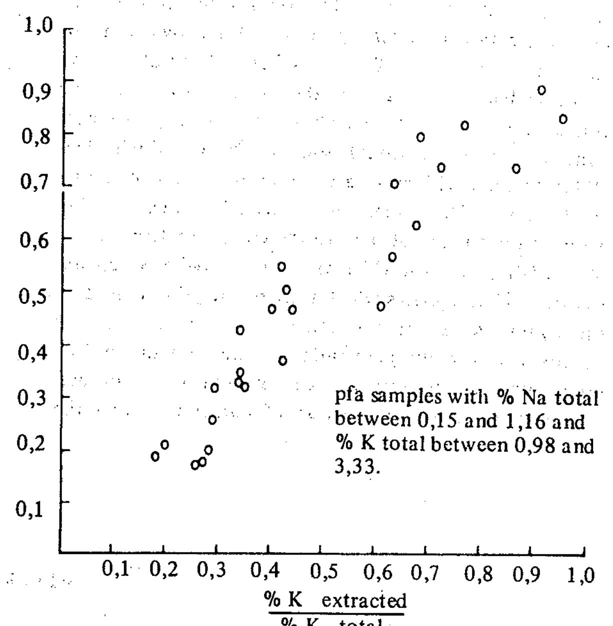

FIGURE 6: Relationship between % Na^+ and % K^+ extracted from pfa samples.

As already described the alkali-silica reaction is caused by the reaction of hydroxyl ions with reactive forms of silica in the aggregate. The rate of any chemical reaction is dependent not only on the concentrations of the reactants but also on their mobility, and for any particular concentration of hydroxyl ions in the pore fluids their ability to react with aggregate will decrease as their mobility decreases. The inhibition of the alkali-silica reaction arising from the use of pfa can therefore be related to the pfa/Ca(OH)$_2$ reaction which gives rise to hydrated calcium silicates and aluminates which thicken the gel produced by the hydration of Portland cement. The mobility of the hydroxyl ions in the pore fluid is therefore reduced. The use of pfa as a partial replacement for some of the Portland cement used in the production of concrete enables the water:solid ratio to be reduced, but the water: Portland cement ratio is increased. If, in concrete, a minimum replacement level of 25 per cent of the Portland cement by pfa is assumed, the gel produced during the pfa/Ca(OH)$_2$ reaction will more than compensate for the decrease in the quantity of gel as a result of the removal of 25 per cent of the cement in the concrete. The C$_3$ S:C$_2$S ratio in many modern UK Portland cements is much greater than it was 25 years ago, and therefore the amount of C - S - H gel produced per unit mass of Portland cement is lower. The use of pfa in concretes can therefore change the Ca(OH)$_2$:C - S - H molar ratio of the final reaction products to a value nearer that existing when alkali-silica reactions were less common.

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Corrigendum

Figure 6, page 3: vertical axis shows

$$\frac{\%\ \text{Na extracted}}{\%\ \text{Na total}}$$

Addendum

The following additional text and data were presented by the authors to the conference.

'The effect of the C$_3$ S:C$_2$S ratio on the amount of CSH gel produced and of the use of pfa in concretes on the Ca(OH)$_2$: CSH molar ratio of the final reaction products are illustrated by Figures 7 and 8.

'For the purpose of illustration it has been assumed that:

(a) the phase composition of Portland cement has changed from 35 per cent C$_3$ S and 35 per cent C$_2$S to 60 per cent C$_3$ S and 10 per cent C$_2$S
(b) the percentages of all other phases have remained the same
(c) the formula of the CSH gel can vary between the limits C$_2$SH$_8$ to C$_1$ SH$_5$
(d) the cement has completely hydrated
(e) there has been no alteration in the packing of the aggregate particles as a result of changes in the water: cement ratio.

'Obviously other values for the water content of the gel can be used, and the mass of CSH gel has been used since the molar volume of such a material is unknown.

'In Figure 7 the kg CSH gel produced/kg of mixing water is plotted against the water:cement ratio. It is clear that the quantity of gel produced between the aggregate particles increases as the water:cement ratio is decreased, and that for any particular water:cement ratio less gel is produced from 60 per cent C$_3$ S/10 per cent C$_2$S Portland cement than from one containing 35 per cent C$_3$ S/35 per cent C$_2$S. The permeability of a concrete made using a cement of high C$_3$ S:C$_2$S molar ratio should therefore be greater than that produced when the C$_3$ S: C$_2$S molar ratio is low. It is probable that the decrease in the permeability will be even more marked if the relative heats of hydration of C$_3$ S and C$_2$S are also taken into account.

'The effect of the replacement of some of the Portland cement by pfa is shown in Figure 8. In this figure the kg CSH gel produced/kg of mixing water is plotted against the percentage reaction of the pfa. In these calculations it has been assumed that the pfa contains 50 per cent SiO$_2$ and 0 per cent CaO. Other mixes than those illustrated could be used.

'It should be noted that:

(a) with some replacement levels the kg CSH gel produced/kg of mixing water is reduced in the first in-

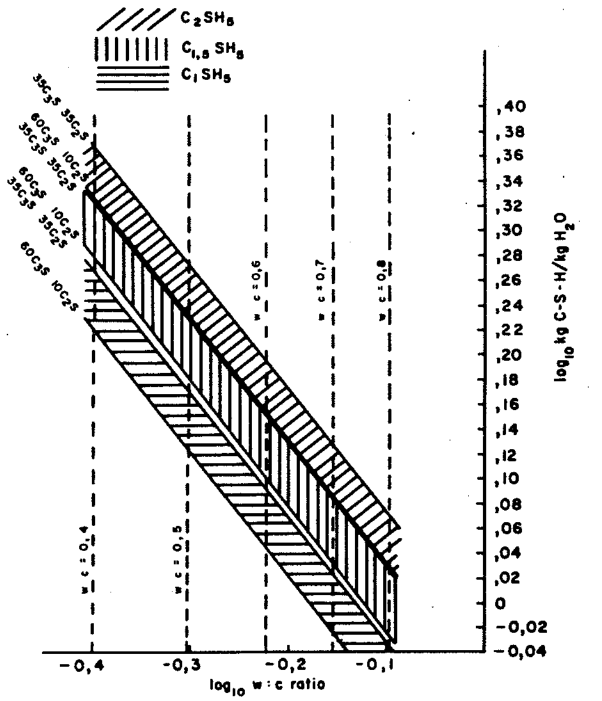

Figure 7: Relationship between quantity of gel produced and w/c ratio

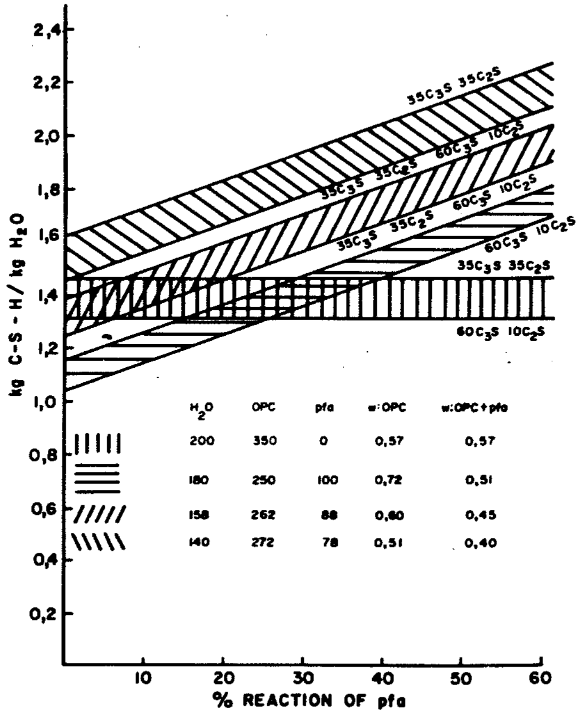

Figure 8: Relationship between quantity of gel produced and percentage reaction of pfa