Properties of concrete using high-lime PFA from a UK source.

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Abstract

Recent changes in the UK coal supply have resulted in the production of high-lime ash from a major UK power station. This paper offers results collected during a project **comparing** key performance characteristics of concretes using an ASTM class C (high lime) **and** an ASTM class F (low lime) ash as a partial replacement for Portland cement (PC). Mixes were produced using 40% replacement of PC by weight, with pulverised fuel ash (PFA), and a water/cement ratio of 0.4. Characteristics examined included workability, compressive strength, water permeability, water absorption, chloride permeability using the **Rapid Chloride Permeability test (RCPT),** resistance to sulphate attack, and freeze/thaw resistance. The results showed that the concrete containing the ASTM class C ash was superior in all of these areas except for sulphate resistance. Workability and compressive strength tests were also performed on mixes containing 60, 70, 80, and 90% replacement levels with the class C ash, all with 0.4 water/cement ratio. Results showed a steady increase in the workability and a decrease in the compressive strength. Samples made at 90% replacement level showed extreme unsoundness and could not be tested for strength.

1. Introduction

The use of pulverised fuel ash (PFA) as a partial replacement for Portland cement (PC) in concrete is well known. **This reduces the requirement for PC**, which is a significant contributor to greenhouse gas emissions, and uses an otherwise waste material which would require disposal in locations such as landfills or surface impoundments.

PFA has been used in the UK for many years but changes in the coal supply are causing significant changes in the ash. As a result of closures of UK coal mines substantial quantities of coal are being imported. **Continuously changing emission control regulations also** have a major influence on the choice of supply. **The class C ash used in this project came from one of the main base-load power stations at Rugeley in Staffordshire. The station was designed to burn bitumous UK coals with minimal lime content, but this ash came from a high lime Indonesian coal**. The remainder of the high-lime ash that was not used for this research was sent to land restoration.

Many factors contribute to the performance of concrete containing PFA, one of the most significant of these being the chemical composition of the ash. One method of classification of ashes based on chemical composition is offered by ASTM C618-92a. Ashes are classified as either class C or class F depending on lime content. Due to the pozzolanas present in PFA, **a** high lime content gives the ash cementitious properties. The result of this is that class C ashes can often be used in greater proportions than class F ashes (1).

The aim of this work was to study the properties of a high-lime ash from a UK source and to confirm that it conforms with known properties of similar ashes produced in other countries and to propose beneficial uses for it.

Jiang and Malhotra (2) tested several fly ashes of different compositions at 55% replacement. They showed a strong positive correlation between lime content and compressive strength at all ages, though more notably at later ages. Naik *et al* (1) noted more rapid development of strength with the use of class C PFA.

Dunstan (3) noted the effects of lime content of fly ash on sulphate resistance of concretes and stated the sulphate resistance factor as $\%CaO-5/\%Fe_2O_3$, a value below 0.5 showing the ash would improve sulphate resistance (4) (5). This is credited in many text books to the fact calcium hydroxide is one of the key reactive components when sulphates are present in concrete (4)(5)(6)(7).

2. Experimental Programme

An experimental programme was developed in order to compare the performance of concretes mixed with 40% replacement of PC with class C and class F PFA. Tests were then also performed on concrete utilising the class C ash at varying percentage replacement levels in order to **determine** the effect on performance.

Ash compositions

Chemical compositions of the ashes used are given in table 1.

Component	**Class C Ash % Content**	**Class F Ash % Content**
SiO2	33.30	46.38
TiO2	0.82	1.05
Al2O3	14.60	25.25
Fe2O3	16.89	8.33
MnO	0.16	0.18
MgO	8.32	2.42
CaO	19.62	5.27
Na2O	0.29	0.88
K2O	1.01	2.08
P2O5	0.27	0.64
SO3	1.32	0.70
LOI	3.56	6.33
Total	**100.18**	**99.53**

Table 1- Chemical composition of ashes

Mix Design

In order to keep the results easily comparable the same mix design was used for all samples, varying only the type of ash used and the replacement level of PC with PFA. Details of the mix used for samples of 40% replacement level are shown in table 2.

Mix Design per m^3	
Content	**Weight (kg/m^3)**
PC	258
PFA	172
Fine Aggregate	790
Coarse Aggregate	900
Water	180
Total	**2300**

Table 2- Mix design (40% replacement level of PC with PFA)

The cement which is designated PC in this paper was CEM1 to EN197-1

Mixing, casting and curing

Samples were cast according to BS 12390-2 and compact on a vibrating table. They were left under a plastic sheet for 24 hours before being de-moulded and left to cure in 21ºC lime water until the test date.

3. Test Information and Results

Tests were carried out to measure workability, strength, water permeability, water absorption, chloride migration, sulphate resistance and freeze-thaw resistance.

3.1 Workability

The workability of the mixes was measured using the slump test (BS 1881 part 102). Results for both types of ashes at 40% replacement level and the class C ash at 60, 70, 80, and 90% replacement levels are shown in figure 1.

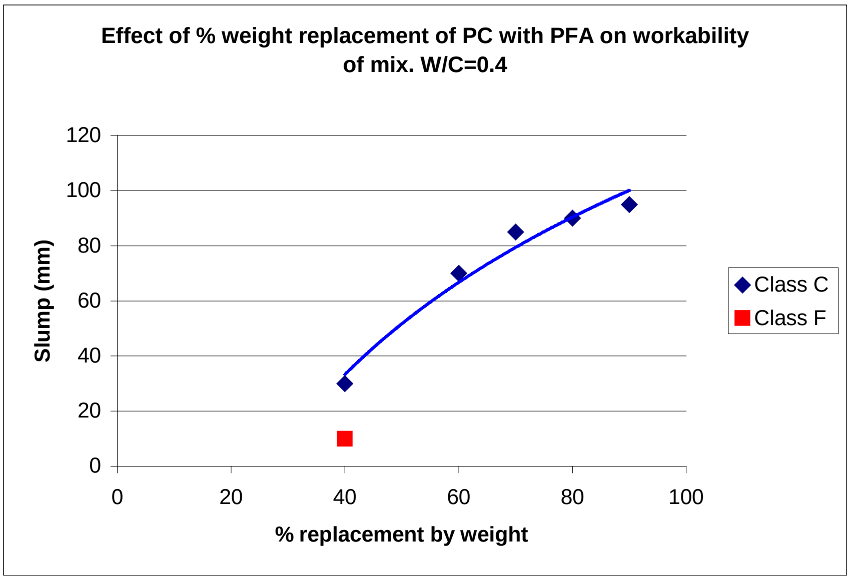

Figure 1

As is shown in figure 1 the mixes containing class C ash show significantly greater slump than the mix containing class F ash. This may be influenced by carbon content of the ashes (3)(6). The class F ash showed greater LOI. Alternatively increased workability may be due to the size/shape of the particles which was not examined. Increasing the replacement level of the class C ash can be seen to increase the workability. This is a well documented effect of PFA in concrete and is usually attributed to the fineness and spherical nature of the ash particles. (4) (3).

3.2 Compressive strength

Compressive strength tests were conducted according to BS 12390-3. 6 cubes were tested for each 40% replacement mix and 3 for each additional mix using the class C ash. Tests were conducted after 7, 14 and 28 days in order to trace comparative developments of strength. **Prior to testing the compressive strength, the cubes were measured with a ruler. This offered an approximate check for gross expansion which may have caused unsoundness in the cubes. None was apparent on any of the mixes.**

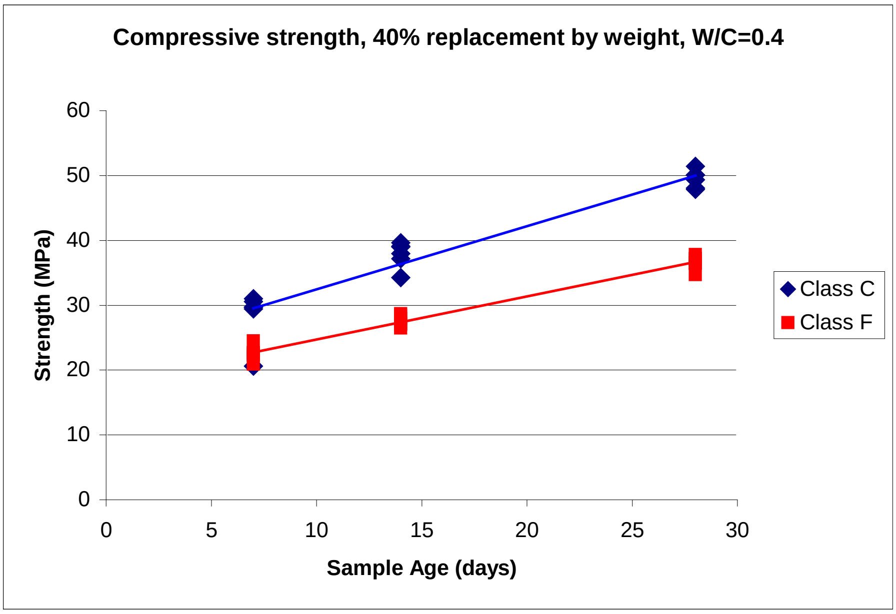

Figure 2

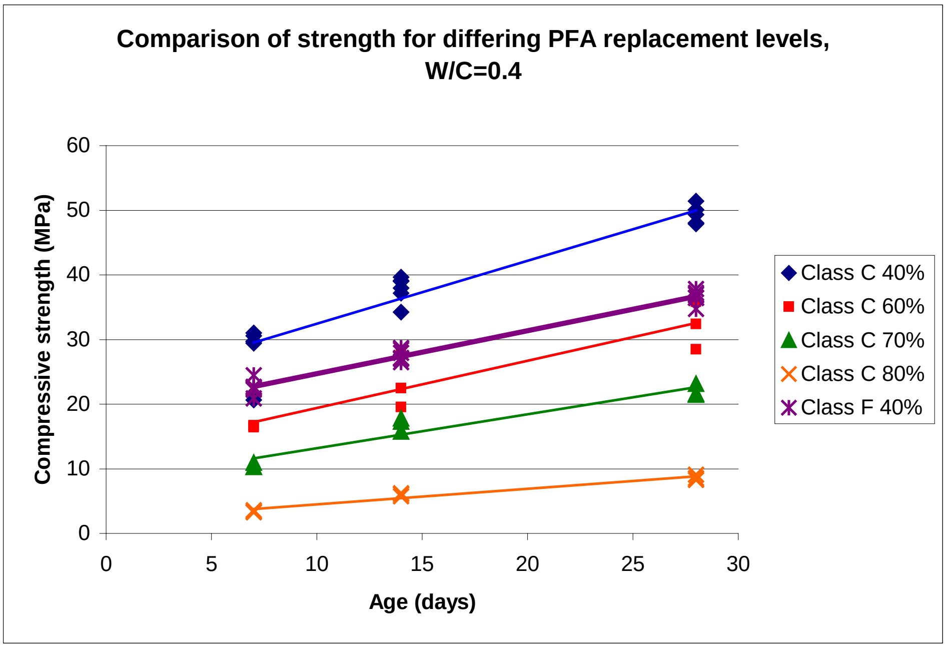

Figure 3

Figure 2 shows the strength development of the mixes containing 40% replacement of PC with PFA. Clearly the class C mix shows higher strengths from **a** very early age. The lines can also be seen to diverge slightly. The strength development of the mix containing class C ash is more rapid than that containing class F ash. This development possibly indicates pozzolanic reactions being more abundant and beginning earlier in the presence of a higher lime content available to react with the ash (4). Alternatively the increased reactivity may be attributed to finer particles (4)(2). The higher strength for greater lime contents noted here was also observed by Jiang and Malhotra (6).

Figure 3 shows the effects of increasing the PFA content on the compressive strength. As can be seen the strength abates fairly rapidly.

This may be attributed to excess lime leaving insufficient reactive phase for reactions to occur. It is notable that adequate strengths were obtained at a 60% replacement level.

3.3 Behaviour of Cubes at 90% Replacement Level

Figure 4 shows remnants of a cube with 90% replacement of PC with PFA in the curing tank. These cubes suffered from significant unsoundness, some collapsing within 60 seconds of exposure to water. Unsoundness is a known problem with class C ashes (4). The large molecular volume of the hydrated lime causes high internal pressures which can cause cracking. No unsoundness was noted in the experiments below the 90% replacement level however.

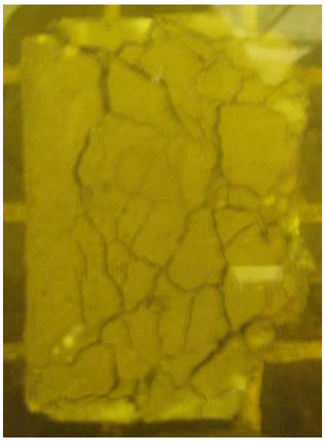

Figure 4 Unsoundness of 90% replacement cube.

A white build up occurred on the surface of the 90% replacement cubes. After exposure to phenopthalein this was shown to be alkaline. It **was concluded that this was** unreacted hydrated lime (calcium hydroxide), which shows a clear lime excess.

3.4 Permeability

Permeability was measured by pumping water through cylindrical specimen at high pressures whilst applying a confining oil pressure to prevent leakage around the sides (9).

Tests were performed on cylindrical samples with a 55mm diameter and 30mm length. Water was pumped through the circuit at a pressure of 500psi **(3.4 MPa)** whilst confining oil pressure was set at 750psi **(5.2 MPa)**.

The time was recorded for 25ml of water to permeate and be collected in a measuring cylinder. This test was conducted on 40% replacement samples after 7, 14 and 28 days in order to show the development of the permeability/pore structure of the concretes. The intrinsic permeability was calculated using the results and equation 1.

Equation 1:

$$K = V.e.x/(p_1 - p_2)$$

in which

V	is the Darcy Velocity
e	is the liquids viscocity, (0.001 for water)
x	is the sample thickness= 30mm
p_1, p_2	are the water pressure before and after the sample (750 psi and 0 psi) in Pascals

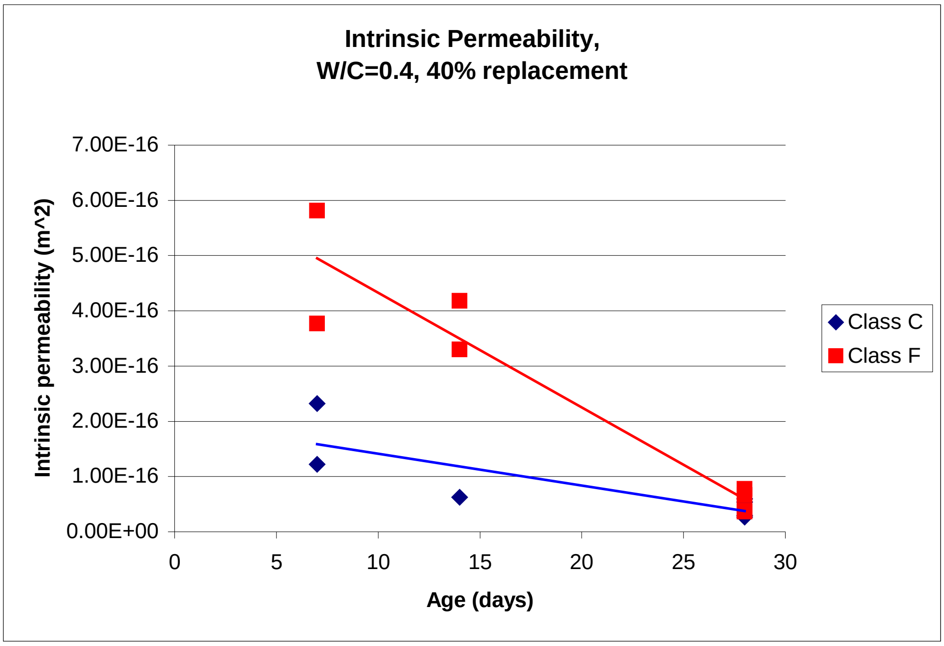

Figure 5

Figure 5 shows the results obtained for the permeability test. The class C ash is less permeable from an early age, again indicating early hydration and reactions filling in the capillary voids and pores. **By 28 days the permeability of the two mixes was similar.**

3.5 Water absorption

Water absorption tests were conducted to BS 1881-122 however 100mm cubes were used for convenience.

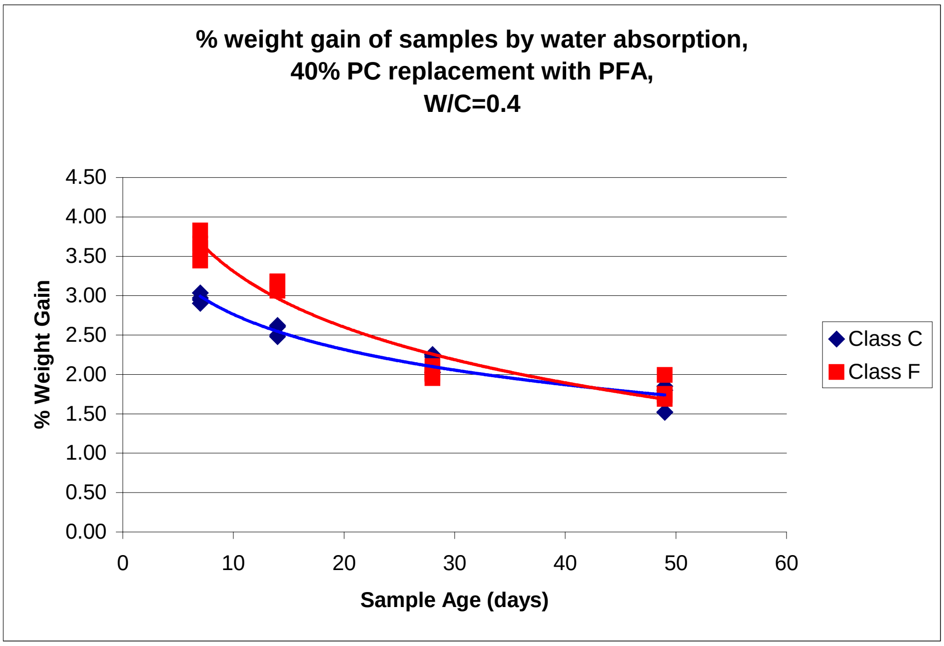

Figure 6

Figure 6 shows the results obtained for absorption. As can be seen, the results follow a similar pattern to those for permeability. At early ages the class C ash shows a denser pore structure, with less porosity or smaller pore radius, **but** by 28 days the results for the two mixes have converged. The slowing of the development of resistance to absorption shown by the curve of the graph was noted by Khatib (10).

3.6 Chloride Permeability

Chloride permeability was measured using the rapid chloride permeability test (RCPT) as described in ASTM C 1202-05 **except** that the voltage was reduced to 40V rather than the 60V suggested by the standard to prevent overheating. The resistivity of the samples was also measured by applying an AC current. After completion of the RCPT the samples were split through the middle to reveal the cross section and sprayed with silver nitrate solution to measure the distance migrated by the chloride ions. Samples were tested at 14 and 28 days.

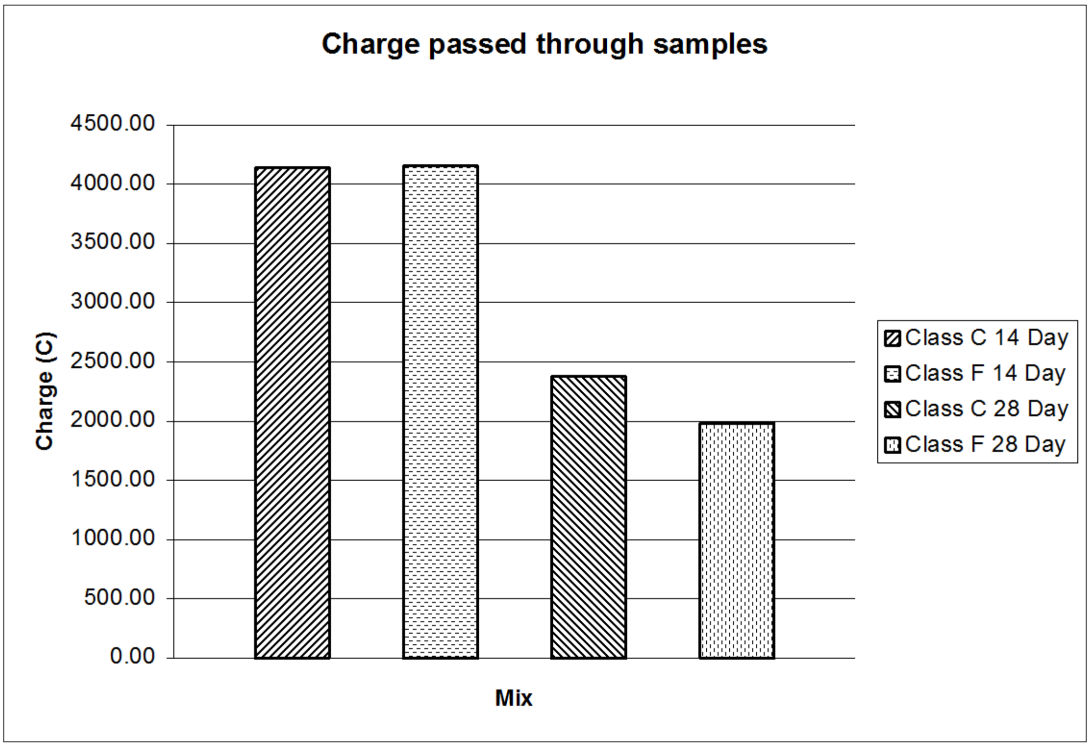

Figure 7

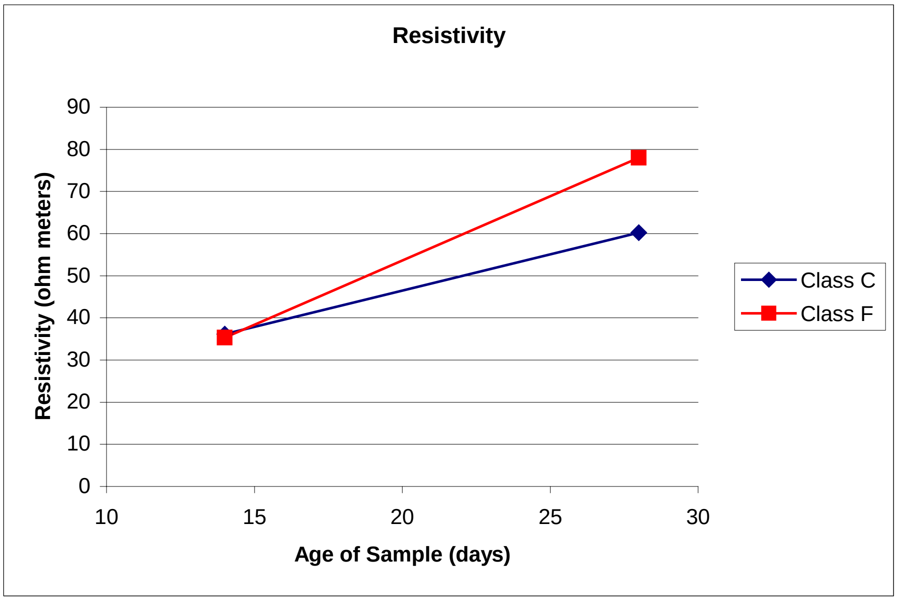

Figure 8

Figure 7 and 8 show the charge passed and resistivity of the concrete samples. A similar resistance to migration was shown at 14 days **but after that the results diverged**. The samples containing class F ash show greater resistivity and less charge passed after 28 days. When the results for the silver nitrate test (table 3) were examined however, it could be seen that chlorides had migrated a shorter distance in the class C ash samples at 14 days, and similar distances after 28 days. This **difference in** distances migrated by chlorides for equal charge passed **for** the two mixes is shown in figure 9.

	Class C Samples	Class F samples
14 day age	31.6	35.2
28 day age	21	19.5

Table 3 Distance migrated by chlorides as indicated by silver nitrate solution (mm).

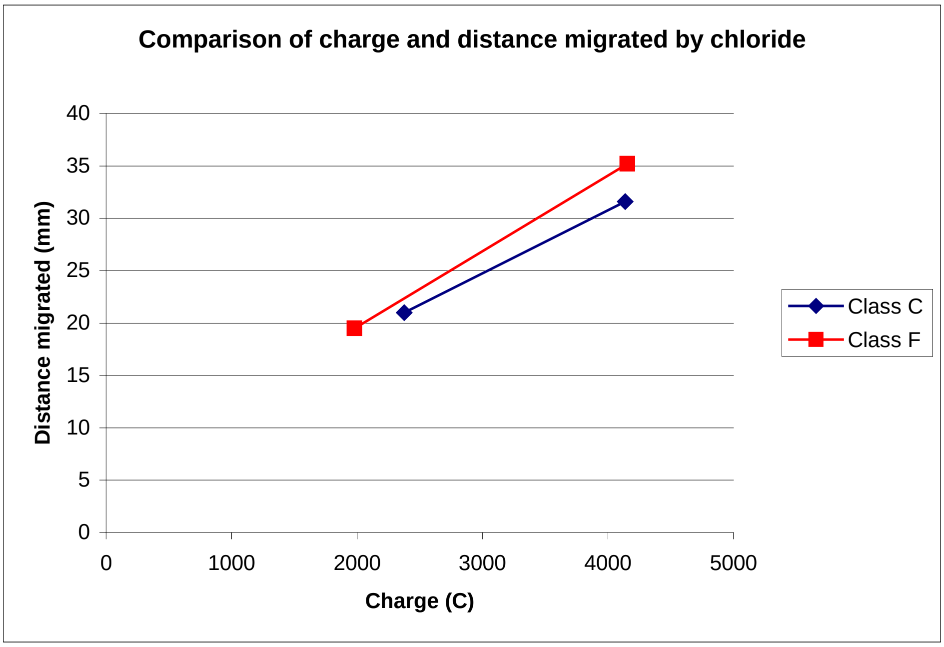

Figure 9

It may be seen that where an equal charge passes through the samples **the** chloride migration in the class C samples is less. This can be attributed to the increased presence of hydroxyl ions due to increased calcium hydroxide. These ions carry current through the sample and therefore increase the charge, but move easier than chloride ions and therefore distort the results of the RCPT test (9). When this is taken into consideration it can be said that after 14 days the class C samples are less permeable to chloride migration, and at 28 days both mixes are similar. This is shown by the silver nitrate experiment which are the only results obtained to rely solely on chloride migration.

These results again follow the pattern shown by permeability and absorption tests, of more rapid development in the samples containing class C ash but convergence around 28 day age.

Wang et al (11) also conducted the RCPT on class F and class C samples and also noted higher charge passed for class C samples.

3.7 Sulphate resistance

Sulphate resistance was tested by measuring the length change of mortar bars according to ASTM C1012-04. **A** deviation from the standard occurred in that whilst the standard dictates beginning exposure to the solution once cubes cast of the same mortar reach a compressive strength of 20 +/- 1 MPa, bars were exposed at ages of 14 days and 28 days regardless of strength. Section 7.1 of the ASTM standard, which dictates the mix design of the mortar, was also **not used**. The same mix was used for the mortar as for the concrete with only the coarse aggregate removed. Finally the expansion of the bars was only measured for 4 weeks due to time restraints.

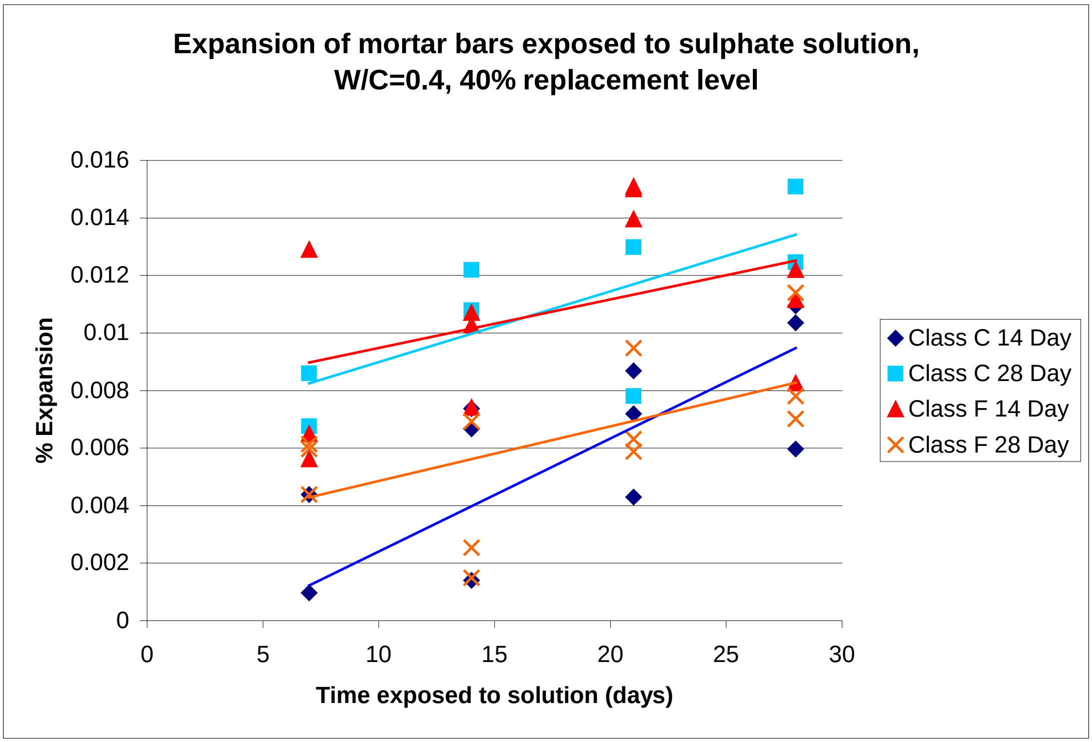

Figure 10.

After 14 days curing the class C samples showed less expansion than the class F samples. By 28 day age the class F samples showed less expansion however. The class C samples showed greater expansion and therefore less resistance to sulphate attack at 28 day age than 14 day. Calcium hydroxide is known to be one of the key element of the reactive phase in sulphate reactions (6), the behaviour of the class C mortar bars can be attributed to increased quantities of calcium hydroxide due to continued hydration, offsetting the effects of reduced permeability. The length change throughout the test can also be seen to be greater for the class C samples (steeper gradient), this is possibly a result of continued calcium hydroxide production due to continued hydration. This behaviour clearly renders class C ashes unsuitable for use in high sulphate environments.

3.8 Freeze/Thaw resistance

In order to test the freeze thaw resistance 100mm cubes were placed in a tray of water 3-5mm deep and subjected to the freeze thaw cycle described in ASTM C666-97. The ultrasonic pulse transit time was measured through the samples at intervals, according to ASTM 597-02. The results collected were used to calculate the dynamic modulus of elasticity for the samples. Visual inspection of samples was also conducted.

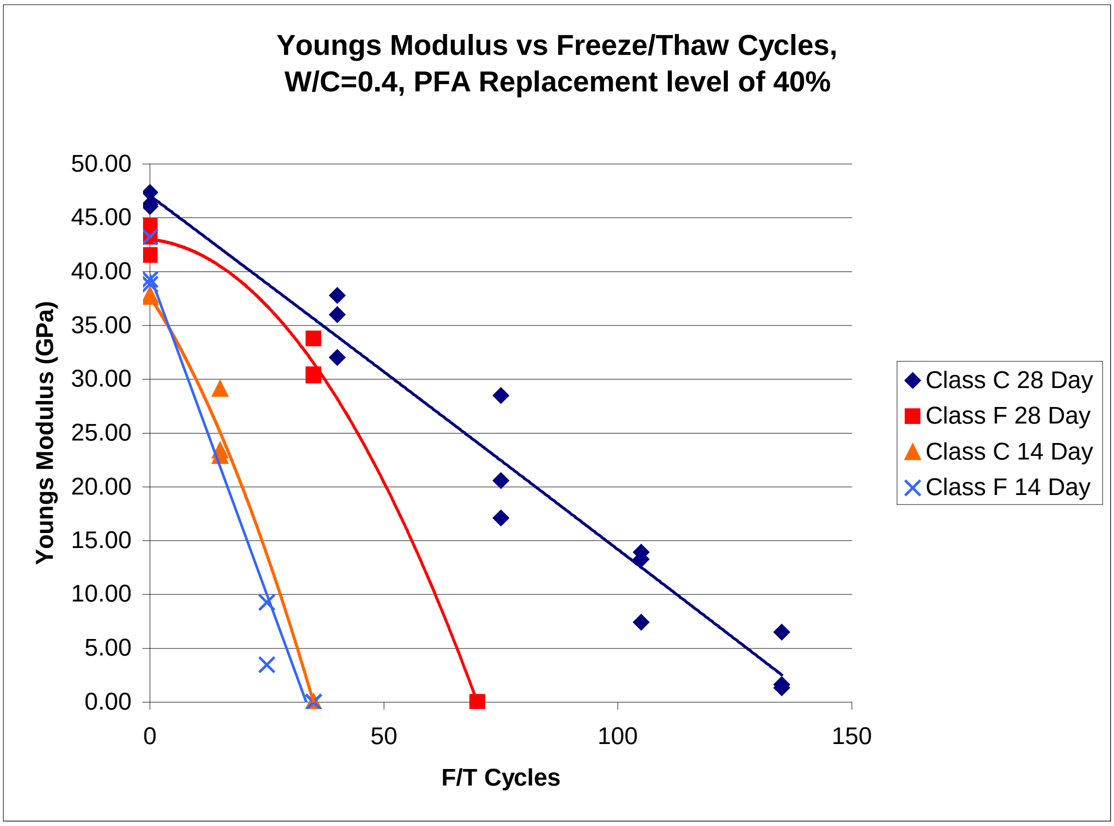

Figure 11

Figure 11 shows the results collected for freeze/thaw resistance. After 14 days the two mixes were fairly similar however after 28 days curing the samples containing class C ash showed a great advantage lasting for around twice as many cycles as the class F samples. Neither mix used any additives such as air entraining admixtures therefore results can be attributed to the basic concrete properties. These results then show the samples containing class C ash to again have superior strength.

Discussion.

The results confirm that the class C ash produced in the UK behaves as expected from overseas experience. This material is more reactive and has a greater latent energy than the class F ash and it would therefore be highly desirable to use it rather than waste it. There is also the problem that it is latently hydraulic so it will tend to set when placed in landfill which may cause operational problems and inhibit land re-use. It is of note, however, that shortly after this sample was taken the station started blending the Indonesian coal with Siberian coal as part of a complex strategy to comply with limits set for sulphate emissions. This reduced the lime content of the ash. Flue-gas desuphurisation is being installed but even with this the very regular quality of ash produced by UK stations in the past is unlikely to happen in future. In one UK station the desulphurisation process itself is actually producing a high-lime ash.

In order to meet our environmental targets it would therefore be desirable for markets to be developed to suit a range of different ashes which may be produced. The results in this paper show that the ash has good properties except for its sulphate resistance. It is therefore suggested that it could be used for precasting operations for items such as blocks and beams for which are going to remain well clear of sources of sulphate and significant advantage could be gained from the high early strengths.

4. Conclusions

a) High lime PFA as a partial replacement for PC offers earlier development of strength and pore structure than low lime PFA. This Improves properties such as strength, permeability and absorption at early ages.

b) Whilst the strength of concrete containing high lime PFA remains superior to that containing low lime at 28 day age, **other properties such as permeability, permeability to chlorides, and absorption may be similar regardless of lime content.**

c) High lime ash is unsuitable for environments with significant presence of sulphates.

d) High lime PFAs can be used to replace a greater proportion of PC than low lime PFAs, **up to 60% replacement by weight appears feasible for applications with lower strength requirements.**

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