Changes in Coal Fired Power Station Fly Ash: Recent Experiences and Use in Concrete

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Abstract

The coal fired power generation industry has changed significantly over a relatively short time. Many of the changes that have taken place relate to protection of the environment, e.g. increasing EU regulation with corresponding UK implementation on reduced NOx and SOx emissions, co-combustion, dangerous substances, waste, IPPC, etc. In turn, these have affected fly ash characteristics and, at the same time, the number and content of both EU and UK product standards have changed significantly, particularly with respect to its use in concrete. This paper will describe and review these changes and the effects they have had on the ash products going on the market.

In parallel to this, the paper summarises research carried out by the Concrete Technology Unit at the University of Dundee that has examined the impact of the specification changes for fly ash for use in concrete. The effect of fineness and loss-on-ignition (LOI) of a range of ashes on concrete strength development is demonstrated. It is shown that while LOI has largely no effect on strength development (up to 8% wt), the well-established relationship with fineness remains with modern ‘low NOx’ ashes. A method for taking account of strength reductions is described, which involves simple adjustment to the w/c ratio, either via the free water content, cement content or a combination of both. Studies of concrete durability, covering, chloride diffusion, carbonation rates, sulfate attack and freeze/thaw resistance indicate that, providing there is adjustment for the effect of fly ash fineness on strength, then similar durability performance between concretes containing fly ash of different fineness is achievable.

The paper also discusses the influence of co-combustion on fly ash (FA) for use as a cement component in concrete. The results indicate that there were minor effects of co-combustion on the properties of ash and the performance of concrete containing these materials was generally indistinguishable from all coal-fired fly ash concrete.

Introduction

The burning of pulverised coal to make steam, to produce electricity and using the fly ash arising from the process has been established in the UK since the 1950's [1], although in the USA the history of use goes back further [2]. Coal hasn't changed substantially in the last 50 years and, as the power stations are at least 25 years old, one would have expected fly ash produced to have more or less remained the same. However, there have been changes reflecting developments in environmental regulations, the UK Government's energy policy, various economic operators such as the price of gas, etc. Coupled with these, new research and the publication of many British and European standards over the years have had a significant effect on how ash is used and on the properties of the ash itself.

The history of using fly ash in concrete

There is now a substantial history to the use of fly ash dating back to the early 20th century. Along the timeline, there have been many significant technical and application highlights, as shown in Figure 1.

In the USA, dam construction in the 1930's provided the drive to publish the first in-depth technical appraisal of the use of fly ash in concrete by Davis et al [3]. It must be acknowledged, that their work laid down the framework by which the 'quality' of ash is judged to this day, i.e. 45um fineness and loss-on-ignition (LOI). In the UK, the work of Watt and Thorne [4] stands out as the first fundamental investigation of coal and coal ash and paved the way for the first version of BS 3892 in 1965 [5], although the UK was slower to recognise that fly ash could be advantageously used as a cement component.

Notwithstanding this, major civil engineering projects were undertaken using fly ash concrete, including both dams and power stations [6, 7]. Eventually, BS 3892 was revised in 1982 [8] and paved the way for the modern use of fly ash as a cement in concrete. At around this time, significant independent research into the wider performance of fly ash in concrete was carried out by centres including the University of Dundee [9, 10, 11 and 12]. Since then, work at Dundee has covered diverse areas of research such as concrete durability [13, 14], high fly ash content concrete [15] and use of conditioned and lagoon fly ash [16, 17].

It must be recognised that this type of fly ash was a by-product of, so-called, base-load coal combustion conditions, i.e. at temperatures averaging 1400 to 1650^{o}C and typically resulted in a fine ash residue with a low LOI. However, while burning at these high average temperatures ensured the boiler efficiency was high, it also resulted in high levels of nitrous and sulfurous oxides, NO_x and SO_x. This was due to some parts of the flame reaching temperatures maybe as high as 2000^{o}C.

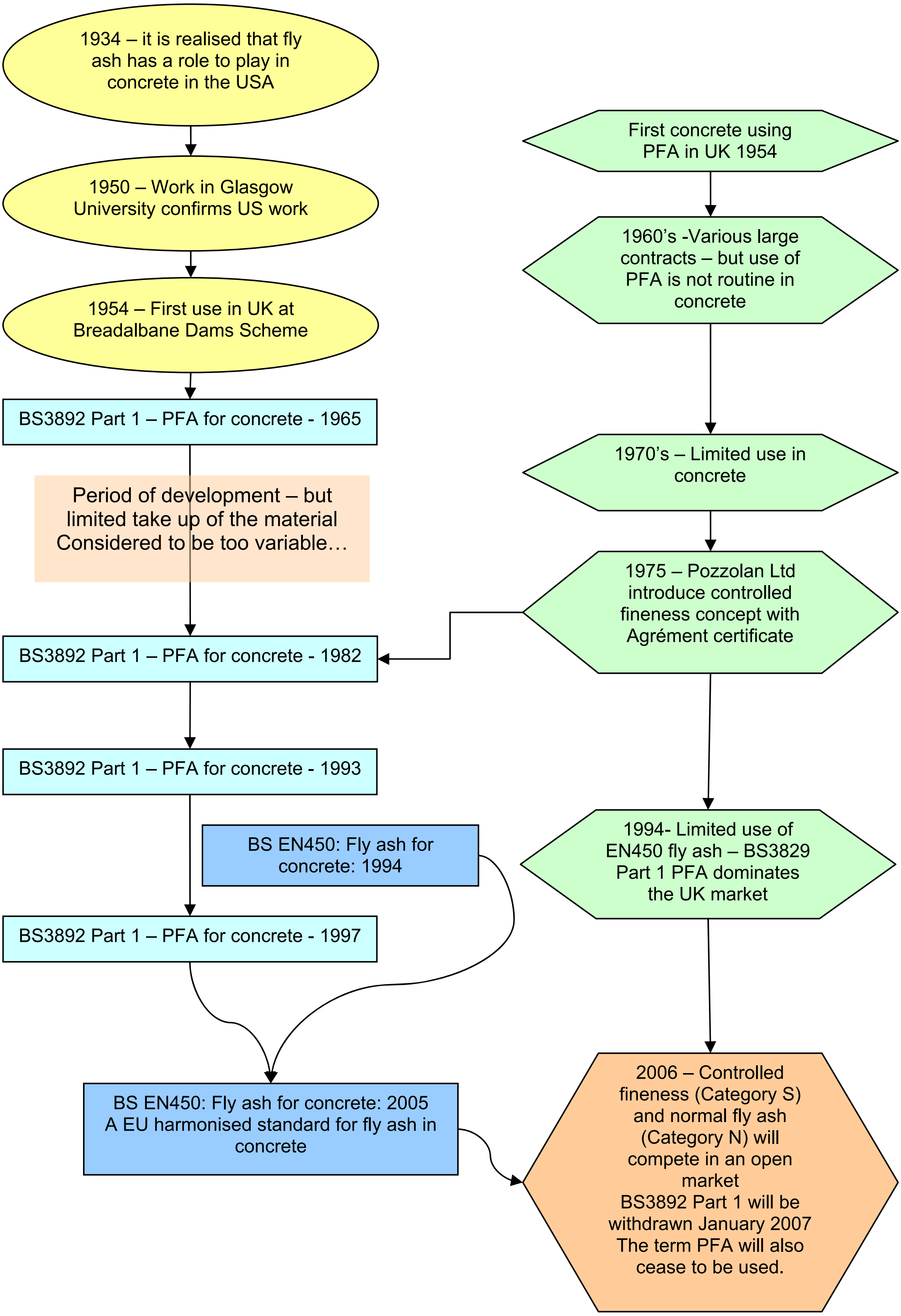


Figure 1. A timeline of standards for fly ash as an addition to concrete in the UK.

The present and future

The increasing pressure to reduce environmental impacts plus the issues of greenhouses gases and CO_2 emissions has had a significant impact on the power industry and ash quality over recent years. The main changes are as follows;

The Fuel Mix

Since the Kyoto Protocol [18] was signed in 1992, the UK has adopted a policy of reducing dependence on coal fired generation in order to reduce CO_2 emissions. This has been mainly achieved by using gas. Coal fired stations became increasingly used only for peak load conditions in the morning and evening, when the new more efficient gas fired stations couldn't keep up with demand, i.e. so-called 'double shifting'. The result was a reduction in investment and uncertainty for the future of coal fired generation.

However, in 2005/6 the higher price of gas and reduced availability, coupled with a cold winter and the reduction in UK nuclear power stations still producing, has resulted in coal fired stations operating as base load stations. The future is still uncertain, but it is clear that gas supplies and availability are more limited than originally thought, yet coal is readily available from the UK and many sources around the world.

NO_x and SO_x

From around the early 1990's restrictions in the UK on the amount of NO_x and SO_x that could be emitted, initiated a programme of fitting flue gas desulfurisation (FGD) units and the changing of burning regimes within the furnace to reduce NO_x emissions, the so-called Low NO_x burners. Although the methods vary at different power stations, generally the peak flame temperatures have reduced and fly ashes typically became coarser with a higher LOI. In 2007 more restrictions on NO_x and SO_x emissions will result in even lower NO_x burners and the introduction of more FGD plants, or the burning of low sulfur coals. As a result of these changes many producers have invested in plant to classify ash and reduce its carbon content.

Dust control

In order to maintain lower dust emission, fly ash needs to have some ability to retain charge for it to be attracted towards the electrostatic precipitators. Low sulfur coals are a particular problem, as the resulting ash tends not to hold charge. In order to reduce dust, sulfur and ammonium compounds can be injected in the furnace gas stream. This increases the precipitator efficiency significantly. A particular problem for concrete can be ammonium injection, partially because the quantities needed are very small and ammonium is easy to detect with the human nose. More serious is the effect of ammoniated fly ash coming into contact with alkali cement. This can release ammonium in sufficient quantities, to cause problems for people working with concrete due to the odour. It is important that ammonia levels are carefully monitored to ensure only just enough is used to increase precipitator efficiency without being carried over into the resulting ash.

Co-combustion

In order to reduce CO_2 emissions, many power stations in response to UK Government initiatives have, in recent years, begun combusting small proportions of secondary fuels, such as vegetable matter, green wood and biomass etc. In the UK the rates of additions are small and in the main have little effect on the resulting fly ash. However, there is the potential for problems if this aspect is not carefully monitored. EN450:2005 [19] does place restrictions on the types and quantities of co-combustion material in order to protect the performance of the resulting fly ash. This is discussed in more detail later.

Overall

In order that fly ash remains suitable for use in concrete, there is a trend to ever greater processing of the material to reduce LOI, remove ammonia, increase the fineness, etc. A number of systems have been developed in recent years to process ash, many of which you will here of during this conference. Another avenue is the considerable stockpiles of fly ash in the UK, some ~53,000,000 tonnes, which could be processed into viable material for use in concrete.

EU Directives and Regulation

Waste management directive and regulations

In 1991 UK regulations (revised in 1994 and 2005) enacting the Waste Framework Directive (WFD) [20] was introduced. The Environment Agency (EA) responsible for England and Wales decided in 2000 that Pulverised Fuel Ash (PFA)/fly ash was classified as waste. The result of this decision suggests that a series of exemptions or licenses are needed before the concrete producer or cement manufacturer could use ash. This has caused some problems and has the potential to reduce some markets, due to the ensuing costs and bureaucracy that has resulted.

The UK Electricity Supply Industry (ESI) has never accepted fly ash or other by-products from the generation of electricity from coal as being wastes [21], when sold for use in construction applications. Fly ash has been widely used since the 1950's in a variety of applications such as in cement manufacture, as a cementitious addition to concrete, for fill applications, for grouting caverns and mines, for ground stabilisation, for the manufacture of blocks and bricks, etc.

Fly ash is supplied to the various contractors and producers on the basis that the material is fit for the purpose intended and in many applications superior to naturally occurring materials, and has a beneficial use both commercially and environmentally. Many of these products are supplied to recognised and long established product standards and more recently to harmonised European standards.

There has been no known incident of coal fired power station ash products causing an environmental problem in the UK, to our knowledge. Fly ash is classed as 'non-hazardous' materials in the European Waste Catalogue [22], see code 10 01 01:

bottom ash, slag and boiler dust (excluding boiler dust mentioned in 10 01 04) and code: 10 01 02 coal fly ash.

Many of the trace metals contained in ash are bound into the glassy matrix, preventing them from leaching from the material. Less than 1% of ash is soluble in water, of which the water soluble material consists of sulfate from gypsum and limited amounts of alkalis. These will comply with the non-hazardous category as defined in the Waste Acceptance Criteria [23].

In the UK, some material is landfilled and the ESI accepts that this material, consisting of predominantly fly ash, is a waste. Landfill taxation is paid on this material and the requirements of the Environment Agency in respect of compliance with the Waste framework Directive and all UK regulations are wholly fulfilled.

The ESI has taken Senior Council's advice on the definition of waste and the situation regarding fly ash. Their advice has been that coal fired power station ash products sold for beneficial use are NOT wastes and the EA has no right to demand contractors or producers apply for exemptions or waste management licences under the UK regulations.

It is believed the EA's current position on the use of fly ash in concrete is as follows.

> **PFA/fly ash for the use in concrete as a Type II addition**
>
> All cement blending and manufacturing plants are required to be registered under IPPC Part B for control of emissions to air. Blending the cement in bulk or using cement in bulk other than at a construction site, including the bagging of cement and cement mixtures, the batching of ready mixed concrete and the manufacture of concrete blocks and other cement products are covered by Part B. Provided all the WFD requirements are met by the Part B recovery process, fly ash is likely to cease to be waste at the point that it is blended into a concrete mix or used as a raw feed material. The resulting concrete can be stored and sold as products with no waste management controls.

In practical terms the WFD and the UK regulations have had little effect on the fly ash market with respect to its use as cement or as an addition in concrete. However, the issue is still one of major concern to the many others applications for fly ash.

Dangerous Substances

One of the substantial problems with the European Community has been removing all barriers to free trade. One area that has always been a major issue is the varying environmental laws that range from virtually no controls in some countries to levels of government intervention that are draconian. As a result, environment regulations have never been harmonised across the EU. It is believed by many that some EU countries use the environmental regulations as a method of creating a trade barrier.

However, some attempt has been made to tackle these issues and the first steps have been to create harmonised testing standards for assessing environmental impacts of construction products, including concrete through CEN TC351. Though this committee has only recently formed and progress is slow, it is an important committee as it is the beginning of removing trade barriers.

In a similar vain, the environmental impact assessment of construction materials has again been subject to numerous differing techniques and approaches across the EU. Another CEN committee, TC350, is attempting to harmonise the various approaches into a single method acceptable to all.

The above represents only a small proportion of the various EU directives and regulations that impact on fly ash.

Summary of UK Standards for Fly Ash for use in concrete

There are numerous ways of incorporating fly ash within concrete in the UK. This may be as a so-called Type I addition, effectively as an inert aggregate or as a Type II addition counting towards the cement content. There are the manufactured equivalent cements.

The UK National Application document BS8500 [24], the complementary standard to BS EN260-1 [25] has a series of mix specifications permitting the use of the majority of the above additions and cement types. These make the best use of the properties of fly ash in respect of the durability circumstances that will be encountered by the concrete, e.g. for resistance to chloride ingress, sulfate attack, etc.

EN450 - 1 & 2:2005 – An overview

There have been major changes to the specification of fly ash for use in concrete due to the revision of EN450 [26] during 2005/6 see Table 1. This section reviews those changes for producers of fly ash/PFA and specifiers of concrete.

In May 2005 BS EN450 Parts 1 and 2:2005 were published

- BS EN450-1:2005, “Fly ash for concrete – Part 1, Definitions, specifications and conformity criteria
- BS EN450-2:2005, “Fly ash for concrete – Part 2, Conformity Evaluation

These standards replace BS EN450:1994 and eventually (by January 2007), BS3892 Part 1:1997 “Specification for PFA for use with Portland Cement” will be withdrawn. There are some significant changes from the previous standards as follows:

1. BS EN450-1:2005 is a European harmonised standard – this means that all conflicting standards, such as BS3892 Part 1, will HAVE to be withdrawn in January 2007.
2. BS3892 Part 1 PFA has been incorporated into the new standard.

Use as a filler aggregate in concrete to BS EN12620 as a Type I addition		
The fly ash in considered an 'inert addition' to the concrete.		
Grading	BS EN 933-10	Uses jet sieving.
Particle Density	BS EN 1097-6	
Bulk Density	BS EN 1097-3	
Use in concrete as fly ash for concrete to BS EN450-1&2:2005 as a Type II addition. **NB: EN450:2005 replaces BS3892 Part 1 from January 2007**		
The fly ash is considered part of the cementitious content.		
Fineness	BS EN 451-2	Category N ≤40% retained 45µm Category S ≤ 12% retained 45µm.
Water requirement	BS EN 450-1	Applies to Category S only
Activity Index	BS EN 196-1	
Soundness	BS EN 196-3	
Particle density	BS EN 196-6	
Sulfuric anhydride	BS EN 196-2	
Loss on ignition – modified	BS EN 196-2	Ignition time of 1 hour. Category A – 0 to 5.0% LOI Category B – 2.0 to 7.0% LOI Category C – 4.0 to 9.0% LOI* * Not used in the UK.
Chloride	BS EN 196-21	
Free Calcium oxide	BS EN 451-1	
Reactive Calcium Oxide	BS EN 196-21	
Co-combustion fly ash	Additional requirements including reactive silica content, total oxides, alkali content, magnesium oxide, soluble phosphate and initial setting time required.	
Use in concrete under BS3892 Part 2 as a Type I addition		
The fly ash in considered an 'inert addition' to the concrete.		
Moisture content	BS 3892 Part 1 Annex C	
Fineness	BS 3892 Part 1 Annex D	
Sulfuric anhydride	BS EN 196-2	
Loss on ignition – modified	BS EN 196-2	Ignition time of 1 hour
For use in cements		
Use in Portland fly ash, Portland composite cement or Pozzolanic cement manufacture to BS EN197-1 or for use in Very Low Heat Special Cements to BS EN BS EN14216.		
These all count fully towards the cementitious content of the concrete.		
Loss on ignition – modified	BS EN 196-2	Ignition time of 1 hour
Calcium oxide	BS EN 451-1	

Table 1. Summary of the various UK standards and requirements for fly ash use in concrete

3. This standard gives specific rules for co-combustion fly ashes. No such rules existed in any other standard for fly ash. There are requirements for additional testing for such ashes, which are more demanding to ensure the quality of the resulting concrete is maintained.
4. BS EN450-1:2005 has a level of attestation of 1+, the same as cement. In EU standards 'Attestation' defines the level of control required to produce a product, with 1+ being the highest level and 4 being the lowest. This means production and supply of fly ash for use in concrete has to be fully accredited by a third party accreditation body such as BSI.
5. CE marking is permitted for fly ash for concrete with the adoption of the new standard.

The major differences for the supplier…

BS EN450:1994 is a very short document in comparison to BS EN450-1&2:2005. However, while BS EN450-1 is a more comprehensive document, there are few technical changes that apply to coal only fly ashes. However, co-combustion ashes require considerably more testing, as detailed in the separate section below.

This is to ensure the concrete producer; specifier and client still receive a quality product. The main compliance criteria are as follows:

Clauses specific to all EN450:2005 fly ashes in comparison with BS3892 Part 1:1997

Loss on ignition: There are now 3 categories of fly ash permitted;

- Category A: LOI ≤5.0%,
- Category B: LOI ≥2.0 to ≤7.0% and
- Category C LOI ≥4.0 to ≤9.0%.

However – Category C ash is not permitted in UK concrete as BS8500 has a limit of 7.0%.

Chloride: No change - ≤0.10%.

Sulfuric anhydride: No change - ≤3.0%.

Free Calcium Oxide: The wording is slightly different, but the requirement is effectively the same, if ≤1.0% then no further testing needed, otherwise a maximum of ≤2.5% is allowed and soundness testing must be carried out.

Reactive Calcium Oxide: This is a new requirement. However, if the total CaO value is less than 10% then the reactive CaO is deemed to be complied with – this should be the case with all UKQAA members' ashes.

Fineness: There are two categories of fineness for fly ash;

Category N – ≤ 40% retained on the 45μm sieve and a limit of ±10% on suppliers declared mean value permitted.

Category S - ≤12% retained on the 45μm sieve.

Water Requirement: This is applicable to Category S fly ash only in order to demonstrate water reducing properties. The test method is described in Annex B and is similar to the method required in BS3892 Part 1 excepting a different flow table is now required.

Category S material is effectively the same material as BS3892 Part 1 PFA, i.e. it is a reduced fineness PFA with guaranteed water reduction.

Activity Index: There are no changes to the requirements – 75% at 28 days and 85% at 90 days.

NB: The Strength Factor as used in BS3892 Part 1 is not in the new standard – both Category S & N ashes must comply with Activity Index.

Soundness: No changes – a maximum of 10mm expansion is permitted.

Particle Density: The density shall now not deviate more than ±200kg/m^3 from the declared value.

Co-combustion fly ashes – additional requirements

Co-combustion fly ashes are produced when materials other than coal are fired with the coal in the power station. There are restrictions as to the quantity of co-combustion material that may be used with a maximum of 10% wt of the resulting ash and 20% by weight of fuel. These strict limits are designed to ensure the resulting fly ash will not have any significantly differing properties to coal only ashes. The standard requires the supplier to demonstrate that co-combustion ash behaves similarly to coal only fly ash using the following additional test methods:

Reactive Silica: >25% reactive silica. This has to be tested 1/month for routine testing.

Total Oxides: SiO_2, Al_2O_3 and Fe_2O_3 have to be tested regularly, again 1/month for routine testing. Must be >70% total oxides.

Alkali Content: Must be ≤5.0% and again 1/month for routine testing.

Magnesium Oxide: Must be ≤4.0% and again 1/month for routine testing.

Soluble Phosphate: Must be ≤100mg/kg and again 1/month for routine testing; see Annex C for details of test method.

Initial Setting Time: This has a requirement for a maximum increase in initial setting time of 120 minutes and again 1/month for routine testing.

Labelling

The fly ash shall be labelled with the CE mark, as required with all 'harmonised standards'. The supplier is also obliged to supply certain information on request. These are:

- Characteristics of the test Portland cement.
- Whether the fly ash is obtained from co-combustion.
- Typical chemical oxide composition of the fly ash and total alkali content.
- Declared fineness value (category N only).
- Declared value of particle density.
- Water content for standard consistence of a co-combustion fly ash/test Portland cement paste.
- Water requirement for category S fly ash.

Summary Points

EN450:2005 represents one of the most comprehensive standards for the use of fly ash in concrete. It reflects the recent trends on the power industry and provides sufficient requirements to give the concrete producer confidence in fly ash.

However, UK practice was very different to that adopted within the rest of Europe. For this reason the fly ash industry sponsored research in the performance of EN450 fly ash, which is described in the following section.

Research into fly ash conforming to BS EN450

The pan-European standard for fly ash EN 450, allows the use of ash that would not be permitted under BS 3892 Part 1, by specifying fineness up to 40% retained on a 45μm sieve and loss-on-ignition (LOI) up to 5%, increased to 7% on a national basis, (cf 12% and 7% respectively in BS3892 Part 1). Given EN 450 permits a wide range of fineness, there is an additional requirement in BS EN 450 that this should be within 10% of the suppliers declared mean. This is in order to minimise the need for users to vary mix proportions due to different ash characteristics.

PROPERTY	BS 3892, Part 1	BS EN 450
Fineness, max. % ret 45μm	12.0	40.0
Fineness variation, % ret 45um	-	ave. value ±10.0
LOI, max % mass	7.0	5.0 (7.0 on national basis)
Relative density, kg/m^3	2000	±150 on nominal value
Composition, max % mass		
SO_3	2.0	3.0
CaO - Free		1.0 or 2.5*
CaO –Total	10	10 (sub-bituminous ash)
Moisture content, max. % mass	0.5	**
Water requirement, max. % mass	95	
Strength factor/activity index, min. %	80 @ 28 days***	75 @ 28 days 85 @ 90 days***

* Soundness test required only if free CaO exceeds 1%.

** Fly ash to be stored and transported dry.

*** BS EN 450 uses 25% fly ash content, test carried out on equal water content basis, whereas BS 3892 uses 30% fly ash content, test carried out on equal flow basis.

Table 2. Differences in the requirements in BS 3892: Part 1 and BS EN 450

The work described in this section summarises a comprehensive study carried out at the Concrete Technology Unit of the University of Dundee to examine the impact of fly ash conforming to BS EN 450 on concrete construction practice.

Experimental Programme and Test Materials

Two Portland cements (class 42.5N) conforming to BS EN 197-1 were used (denoted PC1 and PC2) to produce the PC/fly ash concretes mixes. The main characteristics of these materials are given in Table 3

A total of 7 fly ash samples, collected from different sources from within the UK and Eire were used to provide a range of material properties essentially conforming to BS EN 450. The main properties of these materials, as specified in BS 3892: Part 1 and BS EN 450, are given in Table 4.

PROPERTY	CEMENT CODE	
	PC1	PC2
CaO	62.9	62.5
SiO_2	20.8	20.8
Al_2O_3	5.6	5.0
Fe_2O_3	3.2	2.9
MgO	2.1	2.8
SO_3	2.9	3.1
K_2O	0.56	0.7
Na_2O	0.07	0.3
C_3S	55.0	55.0
C_2S	18.0	19.0
C_3A	8.0	8.3
C_4AF	10.0	8.9
Specific surface, m^2/kg	355	350

Table 3. Main properties of the test Portland cements.

Property	FA 1	FA 2	FA 3	FA 4	FA 5	FA 6	FA 7
Fineness, % mass retained on 45µm	3.0	7.5	13.5[1]	18.0[1]	27.0[1]	41.5[1,2]	27.0[1]
LOI, % mass	3.5	3.8	5.5	5.0	3.5	5.2	8.0[1,2]
Water requirement, % of ref	87.0	89.0	93.0	96.0[1]	98.0[1]	98.0[1]	98.5[1]
Activity Index, 28 days % of ref	78.0	77.0	80.0	75.0	74.0[2]	73.0[2]	72.0[2]
Strength Factor, 28 days % of ref	102.0	96.0	93.0	88.0	86.0	85.0	86.0

1. Does not conform to BS 3892: Part 1. 2. Does not conform to BS EN 450

Table 4. Properties of fly ash specified in BS 3892: Part 1 and BSEN 450

The main work studied the effect of fly ash fineness using fly ashes 1 to 4 and 6 and the tests on the effect of variation in loss-on-ignition (LOI) used fly ashes 5 and 7. In considering the influence of each of these parameters, the other was held constant within a fixed range. It should be noted that for fly ash with fineness > 18.0% water requirement to BS 3892 Part 1 was not met, while for those with fineness >27% (fly ashes 5 to 7) the requirements for activity index specified in BS EN 450 were not achieved.

Design of Concrete Mixes with BS EN 450 Fly Ash

The mix proportions used in the initial part of the study were designed for a range of cement contents from 250 to 550 kg/m^3, see Table 5. The fly ash was used at 30% by mass of cement. The free water and coarse aggregate contents of these mixes were fixed (175 and 1210 kg/m^3 respectively) and the sand content reduced with increasing cement content to maintain concrete yield. The target slump for these mixes was 75 mm. For the 500 and 550 kg/m^3 cement content mixes a plasticizing chemical admixture was used.

Cement			Aggregate				W/C RATIO
PC	FA	Total	Sand	10mm	20mm	Total	
175	75	250	745	405	805	1955	0.70
245	105	350	650	405	805	1860	0.50
315	135	450	555	405	805	1765	0.39
385	165	550	460	405	805	1670	0.32

Free water content = 175 l/m^3.

Slump of 75±25mm (plasticized where necessary)

Table 5. Mix proportions for equal cement content mixes

Compressive Strength

The 28 day cube strength results for concrete using PC 2 combined with fly ash 1 to 4, and 6, with respect to ash fineness are given in Figure 2.

The results show that there was a general relationship between 28 day concrete cube strength and fly ash fineness, with concrete containing finer fly ash (low sieve retention) generally exhibiting higher strength at 28 days. However, it was noted that, in some cases, higher strength was obtained with coarser material.

It is also apparent that the effect of fly ash fineness on strength variation tended to become more significant with increasing cement content. The differences in cube strength between fly ash 1 and fly ash 6 concrete made with a cement content of 250 kg/m^3 was 4.0 N/mm^2 and 550 kg/m^3 was 11.5 N/mm^2.

The 28 day cube strength results for PC1 and PC2 concretes, containing fly ash with low LOI (fly ash 5) and high LOI (fly ash 7), over the range of cement contents 250 to 450 kg/m^3, are given in Table 6.

The results indicate that there was, in general, a slight reduction in strength at 28 days through the use of fly ash of higher LOI and this was observed in both PC1 and PC2 concretes. However, for both of these and the range of cement contents, differences generally amounted to no more than 1.5 N/mm^2. As noted with the fineness series, the differences in strength may equally reflect variations in chemistry between the fly ashes from separate sources.

Given these data, the permitted increase in LOI in BS EN 450 to 7.0 % on a national basis would appear to be of little practical significance.

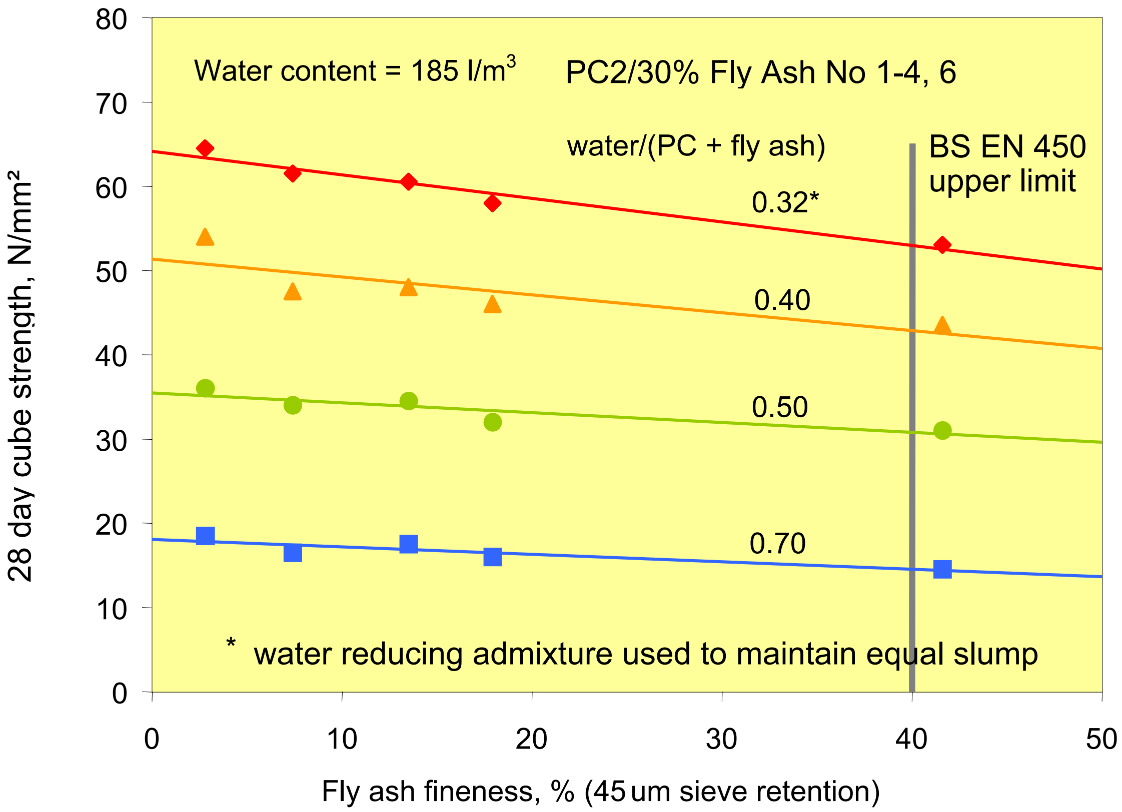


Figure 2. Effect of varying fly ash fineness on concrete strength.

Cement		28 Day Cube Strength, N/mm^2		
		Cement content, kg/m^3		
Portland cement	Fly Ash	250	350	450
PC 1	FA5 (LOI =3.5%)$^+$	21.5	34.0	42.0
	FA7 (LOI = 8.0%)$^+$	20.0	34.0	41.0
	Mean, N/mm^2	21.0	34.0	41.5
PC 2	FA5 (LOI = 3.5%)$^+$	21.0	36.5	45.0
	FA7 (LOI = 8.0%)$^+$	20.5	34.0	43.5
	Mean, N/mm^2	21.0	35.0	44.0

$^+$ Fineness = 27.0% mass retained 45um

Table 6. Effect of varying fly ash LOI on 28 day standard cube strength.

Durability

For this study the test concrete mixes were designed to have equal standard cube strengths with minor adjustments made to the w/c ratio between concretes to take account of the effects of fly ash noted in the earlier strength tests. The mix constituent proportions for these concretes are given Table 7.

DESIGN STRENGTH N/mm²	W/C	CONCRETE MIX PROPORTIONS, kg/m³					
		Free Water	Cement		Aggregate		
			PC	FA+	Fine	10mm	20mm
FA1 45µm = 3.0%, LOI = 3.5%							
25	0.60	165	190	85	760	395	795
35	0.51	165	230	95	715	395	800
50	0.39	165	295	125	620	400	800
60	0.34	165	350	150	545	400	800
FA3 45µm = 13.5%, LOI = 5.5%							
25	0.58	160	190	85	760	405	805
35	0.49	160	230	95	715	405	805
50	0.38	160	295	125	620	405	805
60	0.32	160	350	150	545	405	805
FA5 45µm = 27.0%, LOI = 3.5%							
25	0.58	160	190	85	760	405	805
35	0.49	160	230	95	715	405	805
50	0.38	160	295	125	620	405	805
60	0.32	160	350	150	545	405	805
FA7 45µm = 27.0%, LOI = 8.0%							
25	0.58	160	190	85	760	405	805
35	0.49	160	230	95	715	405	805
50	0.38	160	295	125	620	405	805
60	0.32	160	350	150	545	405	805
FA6 45µm = 41.5%, LOI = 5.2%							
25	0.56	155	190	85	760	410	810
35	0.47	155	230	95	715	410	810
50	0.36	155	295	125	620	410	810
60	0.31	155	350	150	545	410	810

+ F/F+C = 0.30 (nominal).

Table 7. Mix proportions for equal 28 day design strength concrete

These were then tested for durability to:

- chloride diffusion,
- depth of carbonation,
- sulfate expansion and
- freeze/thaw resistance.

Selective results fom the durability tests are shown in Figure 3.

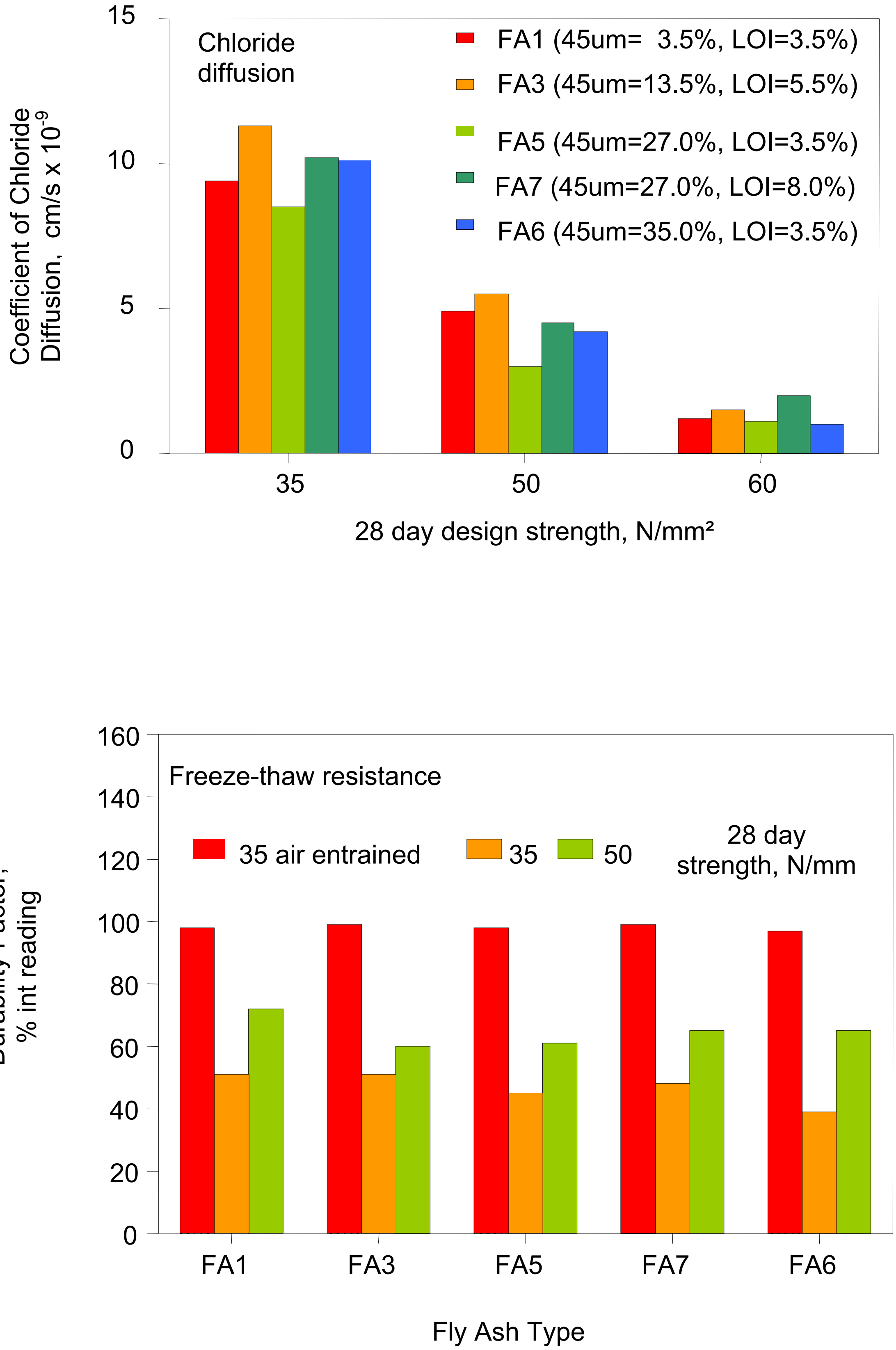


Figure 3. Comparison of durability of concrete made with different fly ash qualities.

The results from a two compartment chloride diffusion test [27], shown in Figure 3, indicate there were no direct effects of FA fineness on the D-values for concretes of equivalent strength. The results also suggest LOI does have an effect, possibly due a reduction in the quantity of chloride binding phases with increasing LOI.

Carbonation rates were measured on concrete cubes exposed to an enriched atmosphere of 4% CO_2. [28], periodically tested by splitting and spraying with phenolphthalein indicator solution. The results indicate that there was a slight variation in carbonation rates between concretes containing FA of different fineness. However, no consistent trend was apparent and the maximum difference at a given exposure period was 2.5 mm.

Considering the effect of LOI, the results suggest only minor variations in carbonation of concrete after 30 weeks exposure, with the high LOI concrete exhibiting slightly lower resistance. The maximum differences observed between concretes at a given exposure period for the 25 N/mm^2 concrete was 2.5 mm. However, for the 35 N/mm^2 concrete no clear differences were obtained. Overall, differences in carbonation for both fineness and LOI are very small and likely to fall well within the accuracy of the test method.

Sulfate resistance of concrete was assessed by measuring the linear expansion of concrete prisms (75 x 75 x 300 mm) exposed to Sulfate Class DS-5m (magnesium sulfate) to BRE Special Digest 1 [29]. Concretes of design strength 25, 35 and 50 N/mm^2 were tested.

The 25 N/mm^2 concrete mixes containing the finest ash exhibited least expansion and the coarsest the largest. However, these differences reduced with time and by 184 days, differences of approximately 15% were obtained. At 35 N/mm^2 there was little difference in expansion between the different FA concretes, while only minor expansions were observed at design strength 50 N/mm^2 for all fly ash concretes throughout the test period.

The effect of LOI indicates slightly reduced expansion in fly ash concrete with low LOI at both 25 and 35 N/mm^2 design strength, but these differences tended to reduce towards the end of the test period. Again in the 50 N/mm^2 concrete, very little expansion was obtained.

Freeze-thaw resistance was measured using the ASTM C666 Procedure A method [30]. The 35 N/mm^2 concretes containing 5.5% AEA generally all had maximum durability factors of 100%, see Figure 3, suggesting no direct effect of varying ash fineness and LOI. However, the dosage of air entraining admixture to achieve an air content of 5.5% was approximately 25% greater for concrete using fly ash 7 (LOI = 8.0%) than that for the other fly ash concretes.

Summary Points

The results show that fly ash with finenesses covering the BS EN 450 range influences concrete strength in the expected manner and that this varies with cement content and hence quantity of ash in the mix. As a general rule of thumb over a range of cement contents from 250 to 550 kg/m^3 for each 5% increase in 45µm sieve retention, the standard cube strength of a concrete can be expected to reduce by between 0.5 and 1.5 N/mm^2. Assuming a maximum variability of ±10% of a suppliers declared mean value for fly ash to BS EN 450, standard cube strength could vary by between 1.5 and 6.0 N/mm^2 (compared to 1.0 to 4.0 N/mm^2 for ash conforming to BS 3892: Part 1).

Changes in the LOI, up to the maximum allowable, ie 7% by mass, did not have a significant effect on strength development. However, for air-entrained concrete, variable LOI may lead to significant changes in entrained air content and, as a result, standard cube strength. While it is possible to vary the dosage of air entraining admixture to compensate for this, particular care will have to be taken to ensure concrete with the correct specification is placed. Where air entrainment is required, it is recommended that a 'tighter' specification limit for LOI is negotiated with the supplier.

The concrete durability results, for chloride ingress, carbonation rates, sulfate resistance and freeze/thaw resistance, indicate that similar performance irrespective of ash fineness or LOI is achievable, providing the concrete mixes are of equal strength.

Research into the Use of Co-combustion Fly Ash in Concrete

Another contemporary development that will become increasingly widespread is the use of co-fuels from non-fossil fuel sources. There are many advantages to co-combustion but particularly the reduced amount of fossil CO_2 emitted per unit of electricity, associated with the reduced hydrocarbon level of the fuel.

However, co-combustion is likely to change the resulting fly ash both physically and compositionally [31, 32] and of particular interest here, whether the effects on ash characteristics are sufficient to affect their use in concrete.

Test Materials

A total of eight co-combustion fly ash samples and where available, their coal-fired references, were obtained from the UK, Europe and USA. These were all from full-scale electricity generation operations, see Table 8. The reference ashes were produced under similar combustion conditions to the co-combustion fly ash materials.

Co-combustion fly ash characteristics

Composition

The key compositional characteristics of the co-combustion and reference ashes are given in Table 9. The effect of co-combustion at the levels used was generally negligible, although the wood chip co-combustion ash did stand out as having a particularly high silica to alumina ratio. As a reference ash could not be sourced, it is not clear whether this was due to co-combustion or was a characteristic of the particular coal source. Between co-combustion and their reference ashes, the CaO content was found to increase slightly for the former. In addition, sawdust and paper sludge ashes gave the highest CaO contents measured. In terms of alkali contents and sulfates, most co-combustion ashes gave similar values compared to their references, except for cocoa shells, where the co-combustion material gave minor increases.

Ash Code	Co-Fuel Material	Co-fuel/Coal Ratio, % by Mass
CS+	Cocoa shells	9.0
CW	Cereal waste	3.0
MB+	Meat & bone meal	4.7
PL+	Poultry litter	3.0
PS	Paper sludge	4.0
SD	Saw dust	10.0
SS+	Sewage sludge	5.0
W	Wood chips	5.0

\+ Materials with reference coal-fired fly ash test samples, denoted by R, e.g. CSR is reference for CS

Table 8. Co-combustion fuels.

Oxide, % mass	Fly Ash Type									
	CS	*CSR*	MB	*MBR*	PL	*PLR*	PS	SS	*SSR*	W
SiO_2	44.05	*44.75*	46.08	*46.64*	46.50	*47.85*	43.30	47.98	*47.69*	67.33
Al_2O_3	22.56	*23.23*	25.38	*25.84*	23.22	*24.00*	23.02	29.29	*29.92*	12.30
Fe_2O_3	6.16	*6.12*	4.85	*4.61*	6.89	*6.89*	6.16	5.24	*5.07*	4.51
CaO	3.93	*3.49*	3.46	*3.16*	3.33	*2.88*	4.92	3.91	*3.09*	2.04
Na_2O	2.27	*1.83*	0.51	*0.50*	0.63	*0.72*	0.96	0.40	*0.31*	0.43
K_2O	1.96	*1.75*	0.60	*0.58*	0.86	*0.85*	1.63	1.11	*1.28*	0.55
SO_3	1.21	*0.84*	0.36	*0.27*	0.66	*0.44*	0.38	0.93	*1.61*	0.72

Note: Characteristics in italics are for the reference (R) coal-only ashes.

Table 9. Key characteristics of the co-combustion and reference ashes.

Fineness and Loss-on-Ignition

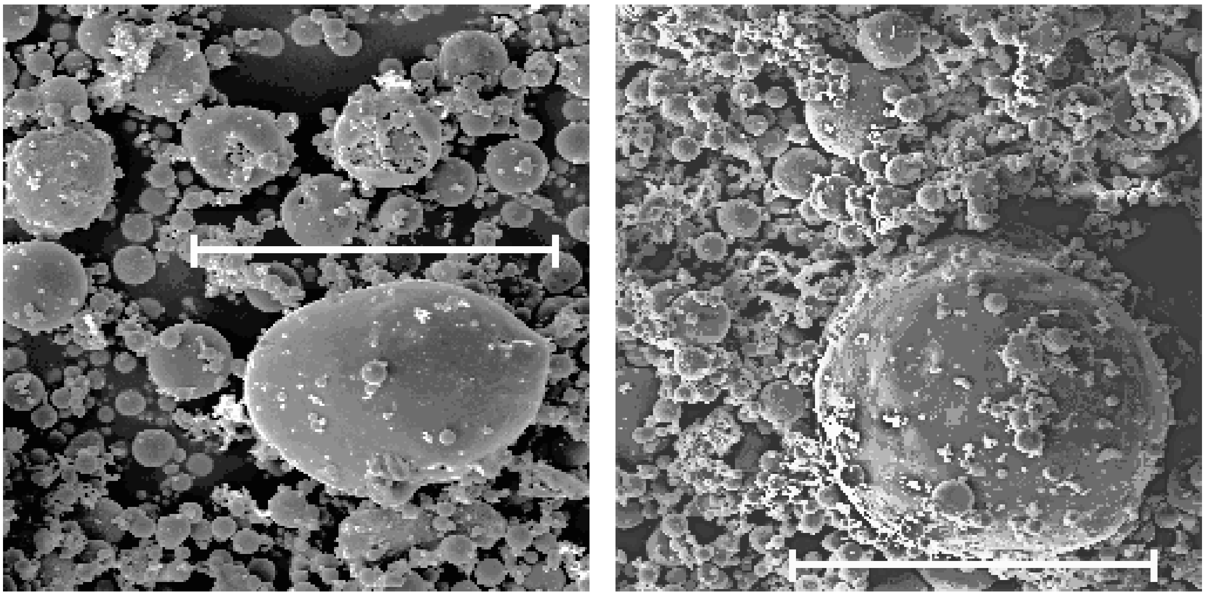
The effects of co-combustion on ash fineness and LOI are given in Table 10. All of the ashes were in the range of 20 to 35% retained on a 45 μm sieve, ie conforming to BS EN 450, except for cereal wheat fly ash, which was at the limit of BS 3892: Part 1 fineness (there were no special circumstances regarding the production of this ash). Co-combustion in all cases produced ash of similar fineness (the cocoa shell ash was marginally finer) although LOI tended to increase.

Fly Ash	Fineness, % ret 45um	Loss-on-Ignition, % mass
SD	34.3	7.6
WC	31.1	6.6
CS	21.1	4.2
CSR	*23.0*	*4.0*
SS	27.0	7.0
SSR	*26.6*	*6.8*
PS	22.8	8.2
MB	26.2	7.1
MBR	*25.8*	*6.4*
CW	12.2	6.7
PL	29.2	5.9
PLR	*25.3*	*4.9*

Note: Characteristics in italics are for the reference ashes

Table 10. Effects of co-fuelling on fineness and loss-on-ignition

The typical effect, by consideration of fuel particle size distributions, was an increase in the number of coarse (larger) particles above 10μm. It is suggested [32] that this is due to the lower temperature at which these particles will agglomerate when co-fuels are used, although this was not particularly evident from electron-microscopy, as for example shown in Figure 4.



(a) Reference ash   scale bar = 100 μm   (b) Co-combustion with cocoa shell

Figure 4. Morphologies of reference and co-combustion fly ash.

Water Demand/Strength Factor

Strength factor tests were carried out on mortar prisms using the material from water demand tests, which was cast in prism moulds (i.e. that with water contents giving equivalent flow to the reference PC) and subsequently tested in compression. The results from both tests are given in Figure 5.

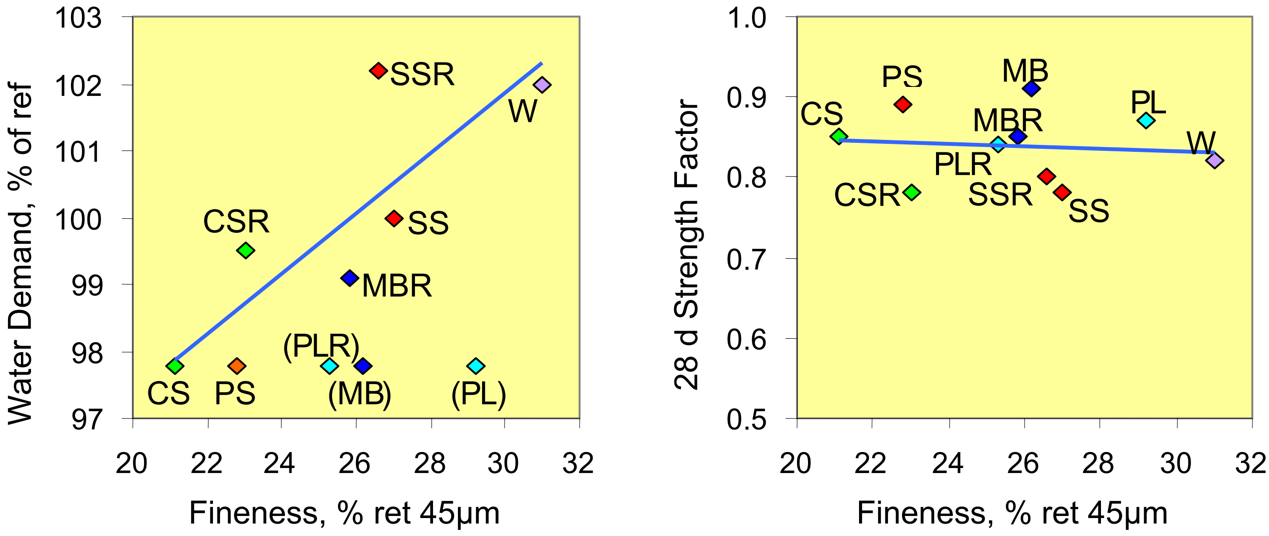


Figure 5. Water demand and strength factors for the reference and co-combustion ashes.

The dependence of water demand on fineness was no different to that for coal-fired fly ash and the values obtained of between 98 and 102% with respect to the PC reference, are typical for the fineness range tested.

The strength factor results reduced slightly with decreased ash fineness and increased water content (due to the increased water demand of the ashes) to achieve equivalent spread. All ashes followed expected behaviour and co-combustion did not have any significant impact.

Performance of Co-combustion Fly Ash in Concrete

Two series of tests were carried out to examine the impact of co-combustion fly ash as a cement component on the properties of concrete. In the first series, mixes containing fly ash at the 30% level in cement and a fixed w/c ratio (0.50) were tested. These were used to examine the effects on consistence, strength and engineering properties and absorption. In the second series, the concrete mixes were designed to achieve specific standard cube strengths, ie 35 and 50 N/mm^2 and were tested for aspects of durability. Details of the test mix proportions are given in Table 11.

The consistence (slump to BS EN 12350, Part 2) and standard cube strength (to BS EN 12390, Part 3) data for the fixed water/cement ratio test series are given in Figure 6.

Test Mix	W/C Ratio	Concrete Mix Proportions, kg/m^3					
		Free water	Cement		Aggregate		
			PC	FA	20 mm	10 mm	Sand
Fixed W/C Ratio	0.50	175	245	105	805	405	650
Fixed Standard Cube Strength+							
35 N/mm^2	0.52	165	220	95	820	410	635
50 N/mm^2	0.38	165	310	130	820	410	520

+ Inclusive of superplasticizing admixture to achieve target 75 mm nominal slump.

Table 11. Test concrete mix constituent proportions for the co-combustion and reference ashes.

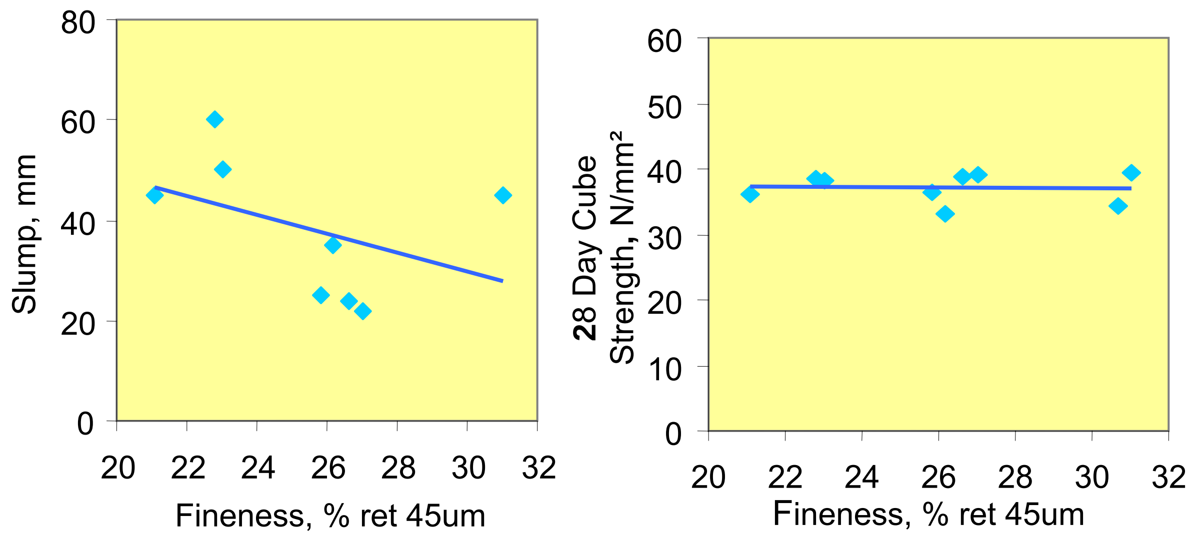


Figure 6. Effect of co-combustion ash on consistence and standard cube strength for the fixed water/cement ratio concrete test series.

Fly ash concretes gave slumps ranging from 25 to 60 mm and these approximately reduced with increasing coarsening of the fly ash. Between a co-combustion fly ash and its reference, for the range of ashes, differences in slump of no more than 10 mm were obtained, which indicate little or no influence of co-combustion fly ash on the property. In general, there was agreement between the water demand test mortar, reported above, and slump measured on concrete.

There was little or no difference in cube strength of all ashes at 28 days and the behaviour of the co-combustion ash was essentially indistinguishable from the reference ash concretes. Again, the trend obtained was broadly similar to that of strength factor reported above.

Durability

Durability behaviour was studied using another set of mixes in this case with concrete designed to give a standard cube strength of 35 and 50 N/mm^2, (see Table 11). Accelerated tests were used for both carbonation, ie 4% CO_2, 60% RH and 20^{o}C [see reference 28], and chloride ingress, ie 2-cell, 5M NaCl at 12v DC [see reference 27], typical results for which are given in Table 12.

Fly Ash	Accelerated[1] Carbonation Depth, mm		Accelerated[2] Chloride Diffusion Coefficient, cm²/s × 10^{-9}	
	35N/mm^2	50N/mm^2	35N/mm^2	50N/mm^2
CS	31.0	11.0	12.0	3.6
CSR	*30.5*	*11.0*	*8.4*	*3.1*
PS	28.0	12.5	6.8	4.3
SS	30.5	12.5	13.1	4.0

All specimens were standard cured to 28 days.

[1] After 30 weeks exposure.

[2] Exposure period sufficient to achieve steady state.

Table 12. Results of the accelerated carbonation and chloride-ingress tests

The carbonation results again showed no behavioural differences between the co-combustion and reference fly ash concretes. There were small differences with the chloride diffusion tests, with the reference ashes performing slightly better. The differences are, however, small and within the accuracy of the test method.

Summary Points

Overall, the use of non-fossil based co-fuels result in fly ashes that are of essentially equal performance to coal fly ash, at the coal/co-fuel ratios tested. Morphological observations revealed that co-combustion gave minor changes in composition. The oxide composition gave similar values or slight increases in potassium, sodium and calcium contents in co-combustion fly ashes. However, there were greater differences noted between oxide composition of ashes from different sources than between companion co-combustion and coal-fired ashes. In terms of loss-on-ignition, again, there were only minor differences between materials. The water demand and strength factor, using the BS 3892-1 mortar test, did not show any difference between performance of co-combustion and reference fly ashes of similar fineness.

The fresh properties of similar fineness hard coal and co-combustion fly ash concrete were found to be almost identical. Likewise, there were only minor differences in engineering and permeation properties of concrete to, or at 28 days. The only differences in durability were with chloride diffusion but these were small.

Given this the use of co-fuels, not only reduce fossil fuel consumption but using the resulting fly ash in concrete will further enhance sustainability.

Summary Points and Future Directions for Fly Ash Research

The use of fly ash as a cement has over the last 25 years made an important contribution to the technical, economic and environmental performance of concrete. Yet for all of these benefits the UK along with many other countries only uses around 50% of the fly ash produced. However, the ever present effects of environmental regulations and need to reduce emissions have led to changes in ash characteristics. The work reported here shows that these changes can be accommodated through concrete mix design.

There can be other non-structural issues such as the increased LOI content that can give rise to surface discoloration and variable mix colour. Again the producers have responded to this and carbon removal is gradually becoming routine. There is much to be gained by further processing raw ash other than for classification purposes. Processes to obtain the ultra-fine component of ash and even carbon recovery as fuel are being developed to full-scale.

The use of co-combustion with non-fossil fuels is also likely to increase and again the extensive study summarised here shows that, up to 10% by mass of co-fuel does not significantly change the performance of ash in concrete. Although LOI is normally increased and that could impact on colour, as noted above.

The future is somewhat difficult to predict, as for example until recently it was believed that coal fired power generation in the UK would reduce with increased gas fired electricity production. However, the recent increases in gas prices, the dependence on fuel from foreign countries, plus the uncertainty of whether more nuclear power stations will be or can be built quickly enough, suggests the future for coal fired generation is not one of decline.

Carbon dioxide capture systems, more efficient methods of burning coal, gasification systems, differing ways of extracting the energy from coal, etc are all on the horizon. Co-combustion will no doubt become more common place with greater proportions and types of secondary fuels being used. Pulverised coal combustion systems may be replaced by fluidised bed combustors or more exotic methods, which are likely to have a significant effect on the ash type and quality.

Much of this is uncertain as the government prevaricates on the future of power generation. However, the industry recognises that coal fired generation is economical and there are ways that the emissions issues can be overcome. This may have impacts on the ash and no doubt appropriate research on the properties of these new ashes will be paramount. However, it is prudent that research is carried out in good time to ensure that the best use of the ash, whatever its form, given the volumes of material involved is made.

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