

Ash utilisation – impact of recent changes in power generation practices

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Abstract

Whenever coal is burnt, ash is produced by the thermal transformation of the mineral matter present. Large-scale uses of coal, such as power generation, give rise to significant quantities of ash and a number of uses for this by-product have been developed over time.

During the last two decades a number of changes have occurred in the coal-fired power generation sector that have affected ash production, and trends for the future use of coal are likely to have a continuing impact on ash in respect of quality and quantity. These changes include: the increasingly common practice of cofiring coal with other non-coal fuels, especially biomass; modifications to coal-fired power generation plant to reduce emissions (in-boiler and post combustion); the development of more fuel-efficient and more operationally flexible boiler plant; and fundamental changes to the basic combustion process to prepare for carbon-capture technologies (for example oxyfuel combustion).

This report reviews the impact of these developments on ash production and ash properties, and the implications for the more important utilisation routes.

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Acronyms and abbreviations

ABB	Asea Brown Boveri
ACAA	American Coal Ash Association
ASTM	American Society for Testing and Materials
BS	British Standards
CAER	Center for Applied Energy Research
CCP	Coal Combustion Products
CCSEM	Computer Controlled Scanning Electron Microscopy
CFBC	circulating fluidised bed combustion
COM	combustion operations modifications
CSA	Canadian Standards Association
CTF	Combustion Test Facility
CUAP	Common Understanding of Assessment Procedures
DAM	dust assessment methodology
ECOBA	European Coal Combustion Products Association
EPRI	Electric Power Research Institute (USA)
ETA	European Technical Approval
EU	European Union
EUBION	European Bioenergy Networks
FA	fly ash
FBA	furnace bottom ash
FGD	flue gas desulphurisation
HTNR	High Temperature NO _x Reduction
IEA	International Energy Agency
IGCC	integrated gasification combined cycle
IHI	Ishikawajima-Harima
KEMA	Keuring van Electrotechnische Materialen
LNB	low NO _x burner
LOI	loss on ignition
mg/L	milligramme per litre
mL/kg	millilitre per kilogramme
NO _x	oxides of nitrogen (NO and N ₂ O)
OFA	overfire air
OPC	ordinary Portland cement
PC	Portland cement
PFA	pulverised fuel ash
RDF	refuse derived fuel
RFG	recirculated flue gas
RH	relative humidity
SCR	selective catalytic reduction
SEM	scanning electron microscopy
SNCR	selective non-catalytic reduction
SRF	solid recovered fuel
TLV	threshold limit value
UKQAA	United Kingdom Quality Ash Association
US EPA	US Environmental Protection Agency
XRD	X-Ray diffraction

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I Introduction

Whenever coal is burnt, ash is produced by the thermal transformation of the mineral matter present. Large-scale uses of coal, such as power generation, give rise to significant quantities of ash and a number of uses for this by-product have been developed over time. Coal ash production and utilisation have been reviewed in previous IEA Clean Coal Centre reports, and by others (Couch, 2006; Sloss, 2007; Smith, 2005; Adams, 2004; Cox and others, 2008; Barnes and Sear, 2004).

The markets for ash are important to the economics of power generation and to a number of industries that have been developed to promote ash use, particularly in the construction sector where large quantities of ash are used. Ash utilisation is a mature market and is covered by relevant product legislation, international standards and codes of practice, for example.

During the last two decades a number of changes have occurred in the coal-fired power generation sector that have affected ash production, and trends for the future use of coal are likely to have a continuing impact on ash in respect of quality and quantity. These changes include:

- the increasingly common practice of cofiring coal with other fuels, especially biomass;
- modifications to coal-fired power generation plant to reduce emissions (in-boiler and post combustion);
- the development of more fuel-efficient and more operationally flexible boiler plant;
- fundamental changes to the basic combustion process to prepare for carbon-capture technologies (for example oxyfuel combustion).

This report reviews the impact of these developments on ash production and ash properties, and the implications for the more important utilisation routes. Ash standards and possible future trends are also considered and discussed. During the background research for the study, discussions with important stakeholders in the ash utilisation sector revealed that the impact of the above changes on ash 'quality' is considered to be a timely and important issue for the continuing development of the ash utilisation sector (Adams, 2010; Feuerborn, 2010; Sear, 2010).

2 Ash production and utilisation

2.1 Ash production

It has been estimated that there are over 847 Gt of proven coal reserves worldwide; which is enough to last over 130 years at current rates of production (World Coal Institute, 2010). Coal reserves are available in almost every country worldwide, with recoverable reserves in around 70 countries. The largest reserves are in North America, Russia, China and India, as shown in Figure 1. Over 5845 Mt of hard coal is currently produced annually worldwide and 951 Mt of brown coal/lignite – Table 1 (IEA, 2009). The largest coal producing countries are: China, the USA, India, Australia and Russian Federation. Much of the global coal production is used in the country of origin, with approximately 16% of hard coal production traded on the international coal market.

The vast majority of this coal is used for power generation, largely by pulverised coal combustion, and it is the ash produced by this process that is the principal focus of this study.

ECOBA estimated that in 2007 the world production of coal ash was approximately 720 Mt, distributed as shown in Figure 2 (Feuerborn, 2010). Fully updated statistics on the production of coal ash and associated materials (for example FGD residues) were reported to be in hand by the WWCCPN (Worldwide Coal Combustion Products Network), a coalition of international ash organisations interested in information exchange concerning management and use of CCPs (Feuerborn and vom Berg, 2005), but no details have yet been published.

The ash produced during pulverised coal combustion is in a molten state and remains in suspension in the furnace gases. It is transported by the combustion gases (now the ‘flue gas’) through the convection sections of the boiler after which it is

captured, usually in an electrostatic precipitator at the boiler outlet. This is conventionally known as fly ash, sometimes referred to as PFA (pulverised fuel ash), especially in the UK. Approximately 80–85% of the ash exiting the furnace is extracted by an ash retention system (for example an electrostatic precipitator). The remaining 15–20% of the ash produced condenses on the boiler tubes and subsequently falls to the bottom of the furnace where it melts and sinters to form furnace bottom ash (FBA) which is removed and processed, prior to transportation (Figure 3).

Fly ash comprises three predominant elements: silicon, aluminium and iron, the oxides of which account for 75–85% of the material. It consists principally of glassy spheres together with some crystalline matter and unburnt carbon (Figure). The nature and properties of fly ash are dependent on a variety of factors that include the coal’s mineral composition, temperature, type and fineness of the coal, and the length of time the minerals are retained in the furnace. Some of the more important properties of fly ash are the carbon content and chemical and mineralogical properties, and the former, as assessed by measuring loss on ignition (LOI), can vary widely. LOI depends on the coal type (or mixed fuel composition in the case of co-combustion) and the configuration and operation of the plant in which the coal is burnt. Some typical compositions of fly ash produced by the main coal types are given in Table 2 (ACAA, 2009).

2.2 Ash utilisation

Coal ash utilisation can be dated from the advent of widespread pulverised coal combustion for electricity generation in the 1920s, when large amounts of fly ash began to become available. The first significant work on the use of coal-derived ashes in construction products is generally acknowledged to be that carried out by Davies and others in

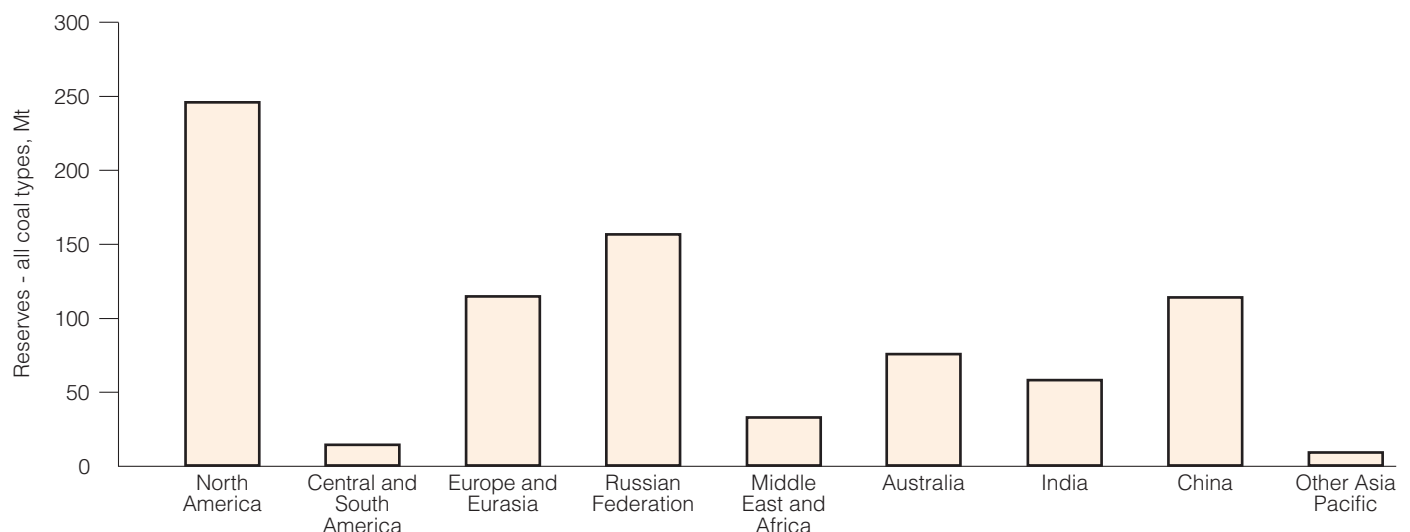
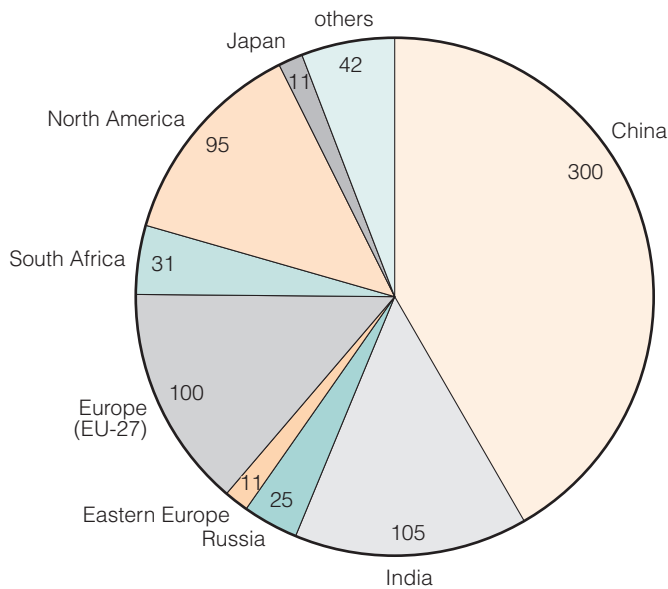
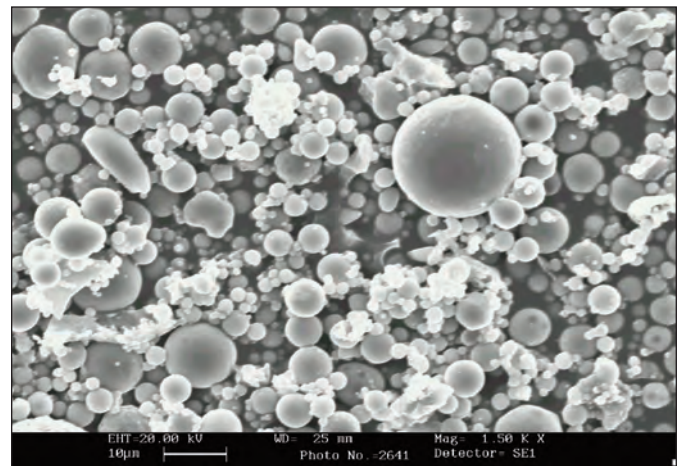


Figure 1 Principal coal reserves (World Coal Association, 2010)

Table 1 Top ten hard coal producers, Mt (estimate, 2008) (IEA, 2009)

PR China	2761	Indonesia	246
USA	1007	South Africa	236
India	490	Kazakhstan	104
Australia	325	Poland	84
Russia	247	Colombia	79

**Figure 3 FBA collection pits at a coal-fired power station** (photograph courtesy of UKQAA, 2009)**Figure 2 Estimated worldwide annual production of coal ashes in 2007** (Feuerborn, 2010)**Figure 4 Typical fly ash particles** (photograph courtesy of UKQAA, 2009)

the 1930s, and published in a series of papers that established the groundwork for many of the specifications and formulations still in use today (Davies and others, 1935, 1937, 1941).

Table 2 Typical range of chemical composition for fly ash produced from different coal types, wt% (ACAA, 2009)

Component	Bituminous	Subbituminous	Lignite
SiO ₂	20–60	40–60	15–45
Al ₂ O ₃	5–35	20–30	10–25
Fe ₂ O ₃	10–40	4–10	4–15
CaO	1–12	5–30	15–40
MgO	0–5	1–6	3–10
SO ₃	0–4	0–2	0–10
Na ₂ O	0–4	0–2	0–6
K ₂ O	0–3	0–4	0–4
Loss on ignition (free carbon)	0–15	0–3	0–5

Fly ash and furnace bottom ash can be used in a variety of applications. Many of these applications are bound: that is the fly ash is mixed with some form of binding agent such as cement, lime and bitumen. In such circumstances any potential for leachates is minimised by the nature of the binding agent, as the ash becomes part of a low permeability, high alkalinity system that is fully encapsulated.

Common applications for fly ash include (UKQAA, 2009):

- Aerated concrete blocks – Here, fly ash forms the primary material within the blocks, which are widely used in house and office buildings.
- Ready-mixed and precast concrete – Fly ash that has been classified or selected to appropriate standards is widely added to concrete partially replacing the Portland cement.
- Grouting of mines and caverns – Fly ash is widely used for stabilising large voids in the ground, allowing it to be returned to productive use and remediating problems of subsidence. It compares favourably in this application with naturally occurring aggregates.
- Gill and ground remediation – Fly ash has been extensively used for example for building embankments and restoring old quarries, for over fifty years.
- Blended cement and cement raw material – Fly ash is increasingly used by the cement manufacturers both as a source of silica, and as a blend material. This enables them to produce more environmentally friendly and cost effective cements, reducing overall CO₂ emissions, energy and use of natural aggregates.

Examples of dense and lightweight concrete blocks are given in Figure 5

Furnace bottom ash is used mainly in concrete blocks, cement, bricks, tiles, aggregates, road construction, embankments, structural fill and in surface mine reclamation. Additional applications include medium/low technology road construction, mainly substituted for sand and gravel, blasting



Figure 5 Examples of dense and lightweight concrete blocks (photograph courtesy of UKQAA, 2009)

grit, in concrete and grouting material, aggregates, snow and ice control. Generally, furnace bottom ash is fully utilised.

The major chemical properties of fly ash which affect its use in applications such as cement and concrete include pozzolanicity and reactivity. A pozzolan is a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in divided form, combine with lime in the presence of water to form cementitious compounds. Most fine fly ashes (particle size <5 µm) react with CaO in water to act as a pozzolan. Fly ash with low calcium content is pozzolanic whereas fly ash with high calcium content is hydraulic, that is, it becomes solid when mixed with water. Fly ash reacts with lime to form water-insoluble calcium silicate and calcium aluminate, which are highly cementitious. The presence of Ca-aluminosilicates in fly ash is thus one of the sources of self-binding properties. The most important parameters with respect to the pozzolanicity of fly ash appear to be the ratio of CaO/(SiO₂ + Al₂O₃), the fineness and particle surface area and the presence of crystalline minerals. Many attempts have been made to relate the basic chemical content of ash, determined by standard tests, to pozzolanic activity and the suitability of any individual ash to its use in concrete and cement. However, experts such as Manz (1998) suggest that no prediction system is perfect and that ash should be tested in practice in the chosen application for the most reliable results.

The advantages of using fly ash in concrete have been summarised by Barnes and Sear (2004) as follows:

- improves long term strength performance and durability;
- reduces permeability, which reduces shrinkage, creep and gives greater resistance to chloride ingress and sulphate attack;
- minimises the risk of alkali silica reaction;
- reduces the temperature rise in thick sections;
- makes more cohesive concrete that has a reduced rate of bleeding, is easier to compact, gives better pumping properties and improves the surface finish of the finished structure (for example when used in Self Compacting Concrete);
- reduced overall environmental impact, for replacing 1 t of Portland cement reduces overall CO₂ emissions by approximately 900 kg;
- produces an economic concrete.

The following chapters explore developments in coal-fired generation that affect ash properties.

3 Co-combustion of other fuels with coal

In the drive to mitigate the effects of climate change, renewable sources of energy have become increasingly important in the production of electricity and heat worldwide. Many governments operate policies that encourage co-combustion through financial incentive schemes. One of the fastest and easiest ways to replace large amounts of fossil fuel by sustainable energy sources is to replace the fossil fuel with biomass. Part replacement of the fossil fuel feedstock, principally coal, by an alternative fuel, for example biomass, has been adopted widely during the last fifteen years.

Worldwide, about 40% of electricity is produced using coal, and each percent of coal that is replaced with biomass in all coal fired power plants results in a biomass capacity of 8 GWe, and a yearly reduction of approximately 60 Mt of CO₂ emissions. Cremers (2009) has estimated that if only 5% of coal energy could be replaced by biomass in all coal-fired power plants, this would result in a fossil fuel CO₂ emission reduction of around 300 Mt of CO₂ each year.

Significant progress has been made in the utilisation of co-fuels in coal-fired power stations and, currently, over 234 units have either tested or demonstrated cofiring of biomass or are currently cofiring on a commercial basis (Cremers, 2009). Coal is often replaced in pulverised coal plants by up to 20% biomass, as in Belgium, Canada, Denmark, Finland, the Netherlands, Sweden, the UK and the USA. Currently, approximately 30% of cofiring is considered to be the maximum, but the aim of many new and existing coal-fired power stations will be to increase the cofiring percentage, in some cases up to 50% or higher. Technical issues such as fuel handling, combustion, corrosion, slagging and fouling, flue gas cleaning, ash properties, handling and health and safety issues will need to be addressed for plants utilising these higher percentages of co-fuel. A number of co-fuels have been employed for electricity generation and each of these affect the properties of the resulting ash in different ways. Three of the more important co-fuels and their impact on ash properties are discussed below. Other co-fuels that have been utilised include: animal meal (meat and bone meal), paper sludge and virtually ash free liquid and gaseous fuels.

3.1 Biomass

Biomass is a term that can embrace a wide range of materials. Four categories that are frequently used to classify the biomass materials used for energy generation are:

- forestry and timber processing waste;
- energy crops;
- agriculture;
- wastes and residues.

The physical and chemical properties of biomass can vary widely, as illustrated by the examples in Table 3.

The ash contents of different biomass fuels can also vary

significantly (Table 4). Straw and other herbaceous fuels like miscanthus or grass usually have higher ash contents than wood because they take up relatively more nutrients during plant growth. In the case of wood fuels, the bark content in the fuel has an influence on the ash content, as bark tends to have a higher ash content and can include a high level of mineral impurities such as sand and soil (Van Loo and Koppejan, 2004).

The composition of biomass ash can vary greatly from feedstock to feedstock and it is known that certain ash components (for example, alkali metals) can give rise to problems of deposition and corrosion within the boiler (Barnes, 2009). For this reason, it has been customary to limit the amount of biomass cofired to 20% or less of the total thermal input. Given the relatively low ash content of many biofuels, the contribution of the biomass elemental composition to the overall 'bulk ash' composition is relatively small. Consequently, the implications for the utilisation of mixed biomass/coal ash are similarly limited. However, where the biomass feedstock is particularly rich in trace elements that could impede the utilisation of the ash, special attention must be paid to ensure that the bulk ash properties do not exceed the formal specifications for use in, for example, cement. Examples of the trace element composition of some biomass feedstocks are given in Figure 6.

The ash species found in co-combustion ash are difficult to predict, even from a full characterisation of the contributory coal and co-fuel ashes, since complex interactions can occur between the 'parent ashes' in the solid and vapour phases (Figure 7).

An interesting example of these interactions is given by Saraber and van den Berg (2006) who described cases in which fuels containing phosphorus and calcium (meat and bone meal, poultry dung) are cofired. The glass-phase was found to be only slightly enriched in Ca and P. He concluded that there must be no significant interaction between the glass-forming matter in the coal and the solids in the secondary fuel otherwise there would be more influence on the bulk glass composition. The same was found for paper sludge where two glass phases were present, from mineral matter in the coal and mineral matter in the paper sludge. This implied that there are two ash formation systems, with limited exchange between them due to collision but more significantly via volatile components in the fuels.

Cross (2006) summarised the impact of several biomass co-fuels on the properties of the resulting fly ash (Table 5).

Wang and others (2003) carried out a set of experiments on combinations of cofired wood and biomass fly ashes in concrete mixtures to determine the effects on slump, air content, flexure, compression, rapid chloride permeability, freeze-thaw and setting time. The five types of fly ash used in this study are listed in Table 6. The wood fly ash was sieved to guarantee better mixing.

The compression tests indicated that the concrete with class C and biomass (cofired with 20% switchgrass, 80% galatia coal) fly ash showed higher strengths three months after mixing than concrete without the additive. The fresh concrete tests showed that concrete mixes with biomass fly ash require a large amount of air-entraining agent to obtain the desired air content. Concrete with the higher percentage of calcium oxide (such as wood, class C, biomass) exhibited higher

compression strength at 90 days. Both wood and class C fly ash had little effect on reducing the permeability of concrete. However, class F and biomass as admixtures in concrete decreased the chloride ion permeability. Almost without exception, the addition of fly ash derived from biomass-based fuel did not adversely influence the properties of concrete, and in some cases, improved the properties investigated in this study.

Table 3 Proximate analysis, ultimate analysis and heating values of selected solid fuels (Moghtaderi and Ness, 2007)

	Alfalfa stems	Wheat straw	Rice hulls	Rice straw	Switch-grass	Sugar cane bagasse	Willow wood	Hybrid poplar
Proximate analysis, %, dry fuel								
Fixed carbon	15.81	17.71	16.22	15.86	14.34	11.95	16.07	12.49
Volatile matter	78.92	75.27	63.52	65.47	76.69	85.61	82.22	84.81
Ash	5.27	7.02	20.26	18.67	8.97	2.44	1.71	2.70
Ultimate analysis, % dry fuel								
Carbon	47.17	44.92	38.83	38.24	46.68	48.64	49.90	50.18
Hydrogen	5.99	5.46	4.75	5.20	5.82	5.87	5.90	6.06
Oxygen, by difference	38.19	41.77	35.47	36.26	37.38	42.82	41.80	40.43
Nitrogen	2.68	0.44	0.52	0.87	0.77	0.16	0.61	0.60
Sulphur	0.20	0.16	0.05	0.18	0.19	0.04	0.07	0.02
Chlorine	0.50	0.23	0.12	0.58	0.19	0.03	<0.01	0.01
Ash	5.27	7.02	20.26	18.67	8.97	2.44	1.71	2.70
Elemental composition of ash, %								
SiO ₂	5.79	55.32	91.42	74.67	65.18	46.61	2.35	5.90
Al ₂ O ₃	0.07	1.88	0.78	1.04	4.51	17.69	1.41	0.84
TiO ₂	0.02	0.08	0.02	0.09	0.24	2.63	0.05	0.30
Fe ₂ O ₃	0.30	0.73	0.14	0.85	2.03	14.14	0.73	1.40
CaO	18.32	6.14	3.21	3.01	5.60	4.47	41.20	49.92
MgO	10.38	1.06	<0.01	1.75	3.00	3.33	2.47	18.40
Na ₂ O	1.10	1.71	0.21	0.96	0.58	0.79	0.94	0.13
K ₂ O	28.10	25.60	3.71	12.30	11.60	4.15	15.00	9.64
SO ₃	1.93	4.40	0.72	1.24	0.44	2.08	1.83	2.04
P ₂ O ₃	7.64	1.26	0.43	1.41	4.50	2.72	7.40	1.34
CO ₂ /other	14.80						18.24	8.18
Undetermined	11.55	1.82	-0.64	2.68	2.32	1.39	8.38	1.91
Higher heating value, constant volume								
MJ/kg	18.67	17.94	15.84	15.09	18.06	18.99	19.59	19.02
Btu/lb	8025	7714	6811	6486	7766	8166	8424	8178
Alkali index, as oxide								
kg alkali/GJ	0.82	1.07	0.50	1.64	0.60	0.06	0.14	0.14
lb alkali/million Btu	1.92	2.49	1.17	3.82	1.41	0.15	0.32	0.32

In later work, Wang and Baxter (2006) studied the effect of the co-combustion of coal and wood on ash properties with respect to utilisation applications. The fly ashes included coal fly ash (US Class C and Class F), wood fly ash from pure wood combustion, biomass (wood or switch grass), and coal cofired fly ash SW1 and SW2. Furthermore, wood fly ash was blended with Class C or Class F ash to produce Wood C and Wood E. The particle size of Class C, Class F, SW1, and SW2

ranged from 3 to 45 µm, but the wood fly ash had a much larger particle size, ranging from 10 to 150 µm. Concrete samples were prepared with fly ash replacing cement by 25% (mass). The ratio of water/(cement fly ash) was fixed at 0.5, slump was 3 to 5 inches (7.6 to 12.7 mm), and air content 4–6% for all fly ash mixes. All of the fly ash mixes except wood were found to have a lower water demand than the pure cement mix. The wood mixes were considered to have a

Almond shells	Almond hulls	Pistachio shells	Olive pits	Demolition wood	Yard waste	Fir mill waste	Mixed paper	RDF
20.71	20.07	16.95	16.28	12.32	13.59	17.48	7.42	0.47
76.00	73.80	81.64	82.00	74.56	66.04	82.11	84.25	73.40
3.29	6.13	1.41	1.72	13.12	20.37	0.41	8.33	26.13
49.30	47.53	50.20	52.80	46.30	41.54	51.23	47.99	39.70
5.97	5.97	6.32	6.69	5.39	4.79	5.98	6.63	5.78
40.63	39.16	41.15	38.25	34.45	31.91	42.10	36.84	27.24
0.76	1.13	0.69	0.45	0.57	0.85	0.06	0.14	0.80
0.04	0.06	0.22	0.05	0.12	0.24	0.03	0.07	0.35
<0.01	0.02	<0.01	0.04	0.05	0.30	0.19		
3.29	6.13	1.41	1.72	13.12	20.37	0.41	8.33	26.13
8.71	9.28	8.22	30.82	45.91	59.65	15.17	28.10	33.81
2.72	2.09	2.17	8.84	15.55	3.06	3.96	52.56	12.71
0.09	0.05	0.20	0.34	2.09	0.32	0.27	4.29	1.66
2.30	0.76	35.37	6.58	12.02	1.97	6.58	0.81	5.47
10.50	8.07	10.01	14.66	13.51	23.75	11.90	7.49	23.44
3.19	3.31	3.26	4.24	2.55	2.15	4.59	2.36	5.64
1.60	0.87	4.50	27.80	1.13	1.00	23.50	0.53	1.19
48.70	52.90	18.20	4.40	2.14	2.96	7.00	0.16	0.20
0.88	0.34	3.79	0.56	2.45	2.44	2.93	1.70	2.63
4.46	5.10	11.80	2.46	0.94	1.97	2.87	0.20	0.67
17.38	20.12					18.92		
-0.53	-2.89	2.48	-0.70	1.71	0.73	2.31	1.80	12.58
19.49	18.89	18.22	21.59	18.41	16.30	20.42	20.78	15.54
8378	8119	7831	9282	7916	7009	8779	8934	6679
0.85	1.75	0.18	0.26	0.23	0.49	0.06	0.03	0.23
1.98	4.06	0.41	0.60	0.54	1.15	0.14	0.06	0.54

higher water demand because of their high unburnt carbon content and irregular particle shape. The authors concluded that the spherical shapes of the remaining fly ash materials lowered water demand by increasing flowability and decreasing the apparent viscosity of the wet cement mix.

Matolepszy and Tkaczewska (2007) researched the use of fly ashes from co-burning bituminous coal and other fuels in the

cement production process. Fly ashes arising from cofiring bituminous coal and biomass and ashes from coal combustion were analysed. The physical and chemical properties of the fly ashes were examined by determining: fineness, chemical and phase composition, pozzolanic activity and the structure of the glassy phase. Cement samples with different fly ash contents were prepared. The following properties of the samples were tested: porosity, compressive strength as well as heat of hydration. The results showed that cement samples containing fly ashes from co-burning bituminous coal and biomass demonstrated adverse characteristics like higher porosity, lower compressive strength after specified times, than the samples containing fly ashes from bituminous coal combustion.

Table 4 Ash content of different biomass fuels compared to coal (van Loo and Koppejan, 2004; Kavalov and Peteves, 2004; EUBION, 2005; Foster and others, 2004)

Biomass fuel	Ash content, wt%, dry basis
Bark	5–8
Wood chips with bark (forest)	1–2.5
Wood chips without bark (industrial)	0.8–1.4
Sawdust	0.5–1.1
Waste wood	3–12
Straw and cereals	4–12
Miscanthus	2–8, 8–22
Coal	5–45 (8.5–10.5 typically)

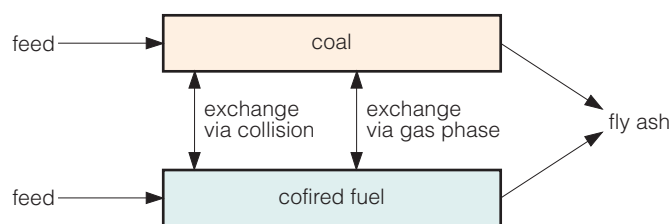


Figure 7 Interactions between coal and co-fuel during combustion (Saraber and van den Berg, 2006)

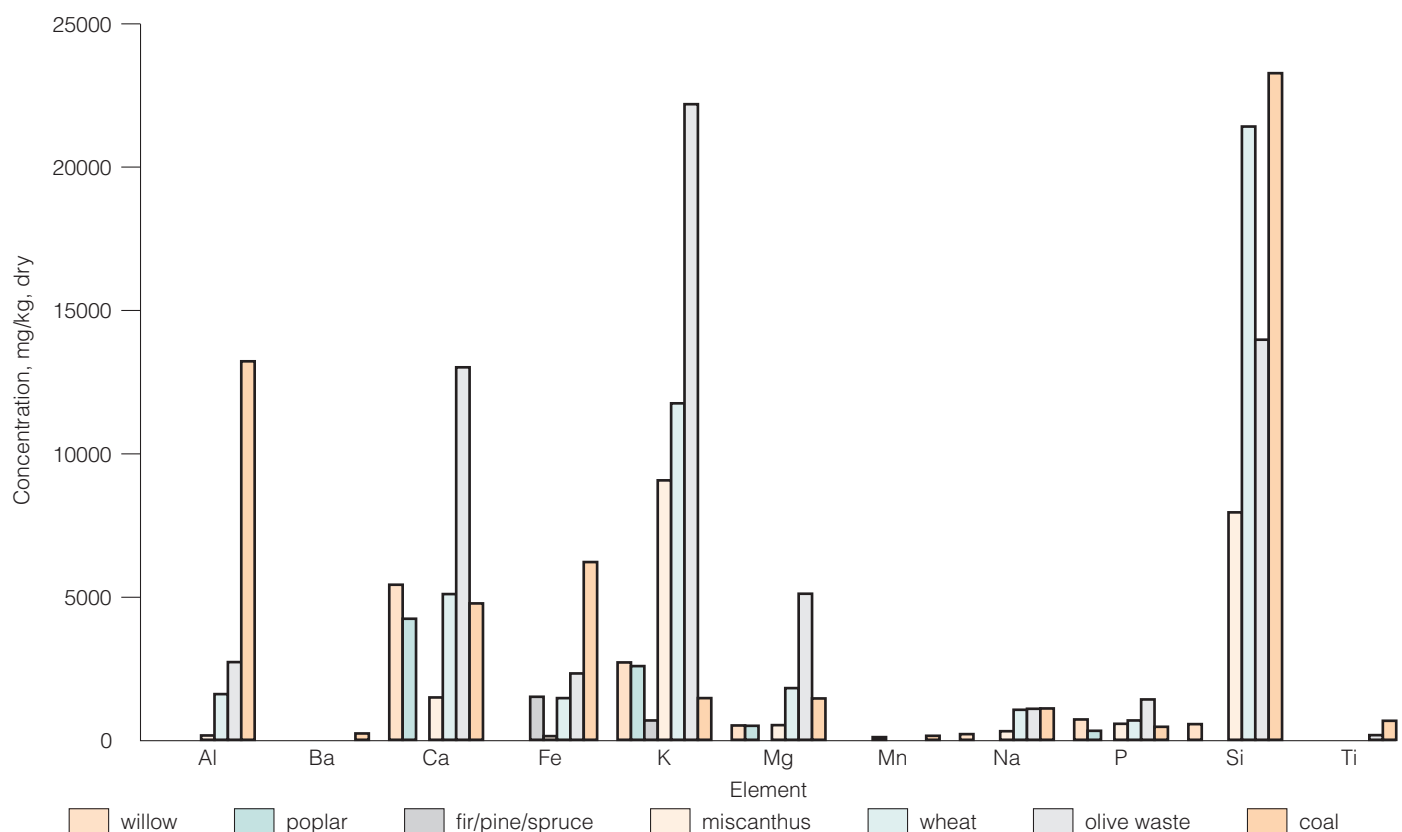


Figure 6 Example biomass trace element compositions (Kilgallon and others, 2008)

Table 5 The impact of different co-fuels on ash composition (Cross, 2006)

Biomass feedstock	Notable characteristics of cofiring fly ash
Cereal co-product product	<p>Trace elements</p> <ul style="list-style-type: none"> – Levels of phosphorous and barium are enriched <p>Major oxides</p> <ul style="list-style-type: none"> – Calcium oxide present at over twice normal levels – Potassium and sodium moderately increased but within normal range for coal only combustion <p>Physical properties</p> <ul style="list-style-type: none"> – No apparent impact
Palm kernel expedia	<p>Trace elements</p> <ul style="list-style-type: none"> – No discernable impact <p>Major oxides</p> <ul style="list-style-type: none"> – Expected increase in calcium and magnesium not found <p>Carbon contents show increased variability</p> <p>Physical properties</p> <ul style="list-style-type: none"> – Water requirement increased through increased carbon contents
Olive cake	<p>Trace elements</p> <ul style="list-style-type: none"> – No discernable impact <p>Major oxides</p> <ul style="list-style-type: none"> – Expected increase in calcium and magnesium not found <p>Carbon contents show increased variability</p> <p>Physical properties</p> <ul style="list-style-type: none"> – Water requirement increased through increased carbon contents – <i>Caution should be exercised as product properties may be compromised if elevated levels of magnesium oxide are found</i>
Petcoke	<p>Trace elements</p> <ul style="list-style-type: none"> – Increased levels of vanadium and nickel present as expected <p>Major oxides</p> <ul style="list-style-type: none"> – Increase in sulphuric anhydride due to high sulphur nature of petcoke <p>Carbon content elevated with increasing replacement of coal with petcoke</p> <p>Physical properties</p> <ul style="list-style-type: none"> – No obvious impact however caution should be exercised as elevated carbon levels may lead to increased water demand
Tall oil	<p>No sample available without use of other alternative fuels</p> <p>Tall oil + other co-fuels has been used to produce CEM II cement</p> <p>Tall oil co-combustion causes soft carbon within fly ash leading to marked darkening of concrete and an increase in carbon deposits on the surface of concrete pours</p> <p>Can cause extreme variability in the performance of air entraining admixtures</p>

Table 6 Fly ash type, LOI and commercial supplier (Wang and others, 2003)

Type	Specification	LOI, %	Commercial supplier
Class C	ASTM 618	1.58	Alabama Power Plant
Class F	ASTM 618	0.52	Georgia Power Co
Wood	–	5.44	Woodland Biomass Power Ltd
Biomass 1	Cofired with 20% switchgrass and 80% galatia coal	2.66	Southern Research Institute
Biomass 2	Cofired with 10% switchgrass and 90% galatia coal	2.60	Southern Research Institute

3.2 Sewage sludge

Sewage sludge, usually in a dried form, has been cofired with coal since the early 1990s. Luts and others (2000) carried out a series of trials at the Mol and Rodenhuize power plants in Belgium where sewage sludge was cofired with coal. During the three trial campaigns in Mol, coal of Polish origin was incinerated. During the first two (short-duration) campaigns, undigested sludge was incinerated while part of the sludge in

the third (long-duration) campaign was subjected to digestion before drying. The moisture content of the dried sewage sludge was found to be highly dependent on the operation of the drier. During the first two test campaigns the sludge was inadequately dried in a drum drier with direct heat transfer and the dried product had a relatively high moisture content of 20–25 wt%. During the third trial campaign a new multiple hearth drier was used for the sludge drying. In this case the moisture content of the dried product was lower than 10 wt% which was about the same as the average moisture content of

Table 7 Characteristics of coal and dried sewage sludge during the various campaigns in Mol (Luts and others, 2000)

	Polish coals	Dried sewage sludge	Digested and dried sewage sludge
Moisture content, wt%	9–10	21–26	5–8
Ash content, wt% dry basis	10–15	41–44	45–46
Volatile substances, wt% dry basis	25–30	51–53	47–49
High Heating Value, MJ/kg dry basis	28–31	13.7–14.4	13.2–13.6
Organic HH Value, MJ/kg dry basis	33.6–34.9	24.3–24.4	24.2–24.7
Elemental composition			
Carbon, wt% dry basis	70–76	30.5–31.6	30.1–31
Hydrogen, wt% dry basis	4–4.5	4.3–4.7	7.1–7.6
Oxygen, wt% dry basis	6–8	19.4–20.5	13–15
Nitrogen, wt% dry basis	1.2–1.5	0.4–0.6	0.48–0.6
Sulphur, ppm dry basis	7000–10,000	11000–12,000	13,100–15,000
Chloride, ppm dry basis	1100–1600	3100–4100	900–1300
Fluoride, ppm dry basis	70–200	750–950	200–300
Arsenic, ppm dry basis	3–4	9–14	11–14
Cadmium, ppm dry basis	<1	4–5	4.5–6.6
Chromium, ppm dry basis	26–33	190–530	104–156
Copper, ppm dry basis	21–32	330–400	585–743
Mercury, ppm dry basis	0.16–0.2	2.1–5.4	1.4–1.8
Lead, ppm dry basis	14–19	220–250	321–346
Nickel, ppm dry basis	12–19	40–45	46–62
Zinc, ppm dry basis	40–50	1700–4900	1620–1800
Sodium, wt% dry basis	0.05–0.14	0.3–0.4	0.3–0.7
Potassium, wt% dry basis	0.23–0.4	0.5–0.7	0.55–0.72
Calcium, wt% dry basis	0.35–0.45	6–8.5	3.8–4.7
Magnesium, wt% dry basis	0.1–0.3	0.35–0.45	0.36–0.45
Silicon, wt% dry basis	2.4–4.2	5.1–9.2	8.7–9.3
Aluminium, wt% dry basis	1.5–2.2	2.4–2.9	3.1–3.5
Iron, wt% dry basis	0.70–0.9	2.5–3.1	3–4
Titanium, wt% dry basis	0.09–0.11	0.08–0.16	0.3–0.34

the coal being burnt at the power plant. The properties of the coal and the sewage sludges are given in Table 7.

The co-incineration of the sewage sludge was found to increase the total concentration of heavy metals in the bottom and fly ashes, but the leachability of the heavy metals in bottom and fly ashes was found to be far below the limit values for applications as aggregates. This was thought to be due to the high flame temperatures (>1400–1600°C) in the boiler leading to vitrified structures in which the heavy metals were immobilised, and thus not released on contact with water.

Cenni and others (2001) undertook an experimental study on the suitability of fly ash from the combustion of mixtures of bituminous coal and municipal sewage sludge as an additive to cement and concrete, and for use in open-air construction works, based on the ash chemical composition and the results of leaching tests on the ash. At the time of the study, European standards forbade the use of ash from cofiring as an

additive to cement or concrete. The study demonstrated that the ash derived from coal and sewage sludge cofiring contained generally less unburnt carbon, alkali, magnesium oxide, chlorine, and sulphate than 'pure' coal ash. Only the concentration of free lime in the mixed ash was higher than in coal, although, at firing levels up to 25% of the thermal input, it was still below the requirements of the European standards. The ash was also found to meet the requirements for the use of fly ash in open-air construction.

The leaching of Cd, Cr, Cu, Ni, Pb and Zn was investigated with three leaching tests when the concentration of these metals in the extracts was found to be below the detection limit in most cases. The concentration of Cu and Zn in the extract from fly ash was found to increase with an increasing share of sewage sludge in the fuel mixture. However, the concentration of these two metals in the extract was not regulated at the time of the work. One noteworthy observation relating to the cofiring of sewage sludge, is the relatively high phosphorus content of the sludge which can report in the ash

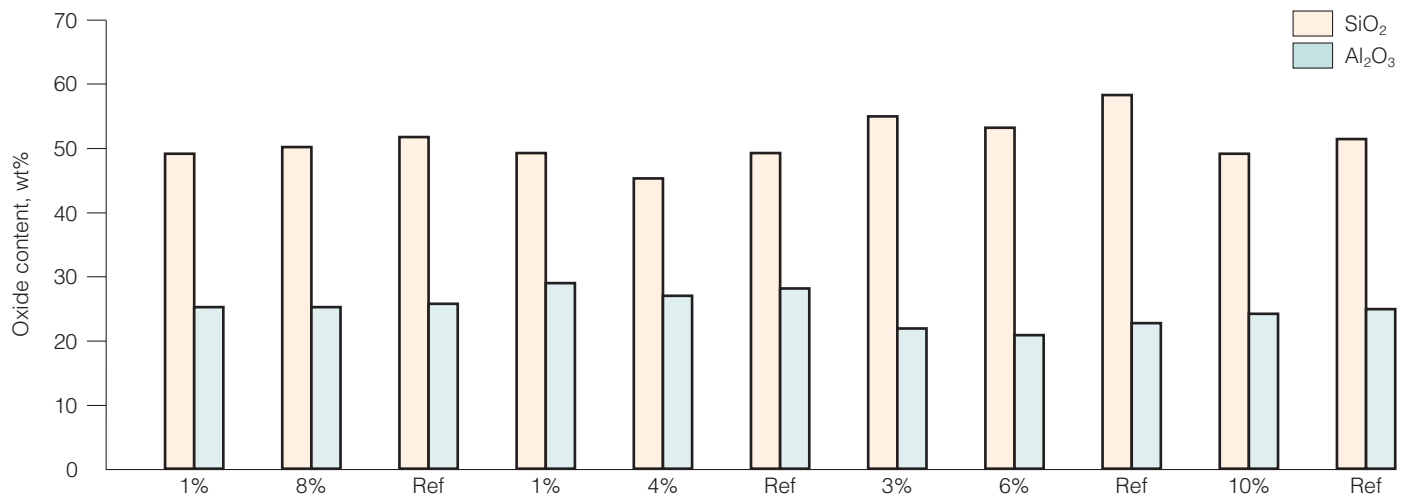


Figure 8 SiO₂ and Al₂O₃ contents of fly ash obtained from co-combustion of sewage sludge (Cenni and others, 2001)

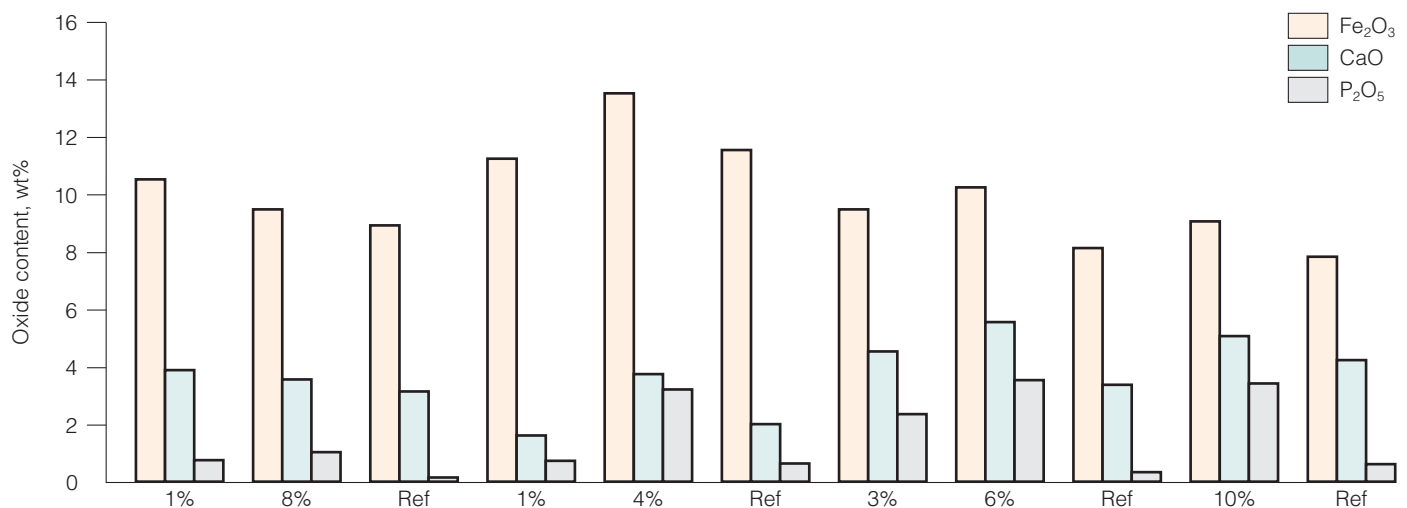


Figure 9 Fe₂O₃, CaO and P₂O₅ contents of fly ash obtained from co-combustion of sewage sludge (Cenni and others, 2001)

as phosphorus pentoxide and give rise to problems during subsequent ash utilisation.

The SiO₂ content of fly ash obtained from sewage sludge co-combustion decreases with increasing content of sewage sludge since the ash content of sewage sludge is lower in silica compared with a pure coal ash. Conversely, the concentrations of Fe₂O₃, CaO and P₂O₅ increase, as a consequence of the use of iron oxide as a sludge flocculation agent and the high phosphate content of the sewage sludge. With the exception of P₂O₅ (0.8–3.6 wt% in the fly ash obtained from co-combustion) the concentrations of all major elements in the fly ash obtained from co-combustion are within the normal range of the contents of fly ash obtained from combustion of pure coal (Figures 8 and 9).

The concentration of alkali-soluble vitreous constituents in the fly ash, which are potentially responsible for the pozzolanic reaction, increased slightly with the amount of sewage sludge employed. This was thought to be due to a higher content of CaO and P₂O₅. CaO is present not as free lime, but in connection with phosphate in the form of calcium phosphates, which are found preferentially near the surface of the glassy ash matrix. The solubility of calcium phosphate is however very small, so the possibility of an adverse impact on the fresh concrete characteristics is reduced. In conclusion, the workers opined that the crystalline phases of the fly ash were not considered to be significantly influenced by the co-combustion of sewage sludge and that the trace element concentrations in the co-combustion ash lay within the normal scatter range for the coal ashes studied.

Table 8 Analyses of fuels used in Drax petroleum coke trials (AES Drax Power Ltd, 2002)

Determinand	Petcoke A	Petcoke B	Gascoigne Wood	Rossington	Maltby	Station average
Sulphur, %	4.43	6.51	1.15	1.19	1.24	1.37
Chlorine, %	0.05	<0.01	0.45	0.51	0.2	0.37
Carbon, %	79.6	79.6	60.7	59.7	62.6	60.8
Vanadium, mg/kg	984	335	47.5	32.7	39.4	53.3
Nickel, mg/kg	239	101	24.2	19.8	23	28.8
Mercury, mg/kg	0.03	0.03	0.009	0.03	0.07	0.03
Arsenic, mg/kg	0.6	1	3.8	5	12	6.3
Antimony, mg/kg	0.1	0.1	1.3	1.9	1.5	1.5
Boron, mg/kg	5	5	26.9	21.5	23	26.7
Cadmium, mg/kg	0.03	0.01	0.03	0.03	0.04	0.045
Cobalt, mg/kg	5	5	10.8	8.6	11	11.4
Chromium, mg/kg	8	9	30.5	19.8	28.3	28.7
Copper, mg/kg	7	8	26.9	18.9	19.2	29.6
Iron, mg/kg	562	965	6979	7753	8834	8899
Lead, mg/kg	3.6	1.6	7.3	5.7	6.5	8.7
Manganese, mg/kg	9	14	122.8	96	134	116
Molybdenum, mg/kg	12	8	11.6	6.9	8.2	11.1
Tin, mg/kg	0.1	0.1	1	0.7	0.5	0.9
Selenium, mg/kg	0.1	0.1	0.75	0.8	0.98	1.01
Thallium, mg/kg	0.1	0.09	0.27	0.17	0.27	0.29
Zinc, mg/kg	8	11	21.5	15.5	23.8	21.6
Aluminium, mg/kg	1213	2048	24,977	18,777	22,391	23,716
Silver, mg/kg	0.2	0.1	0.1	0.1	0.1	0.2
Fluoride, mg/kg	13	12	70	53	55	61.5
Ash, %	1.2	1.4	15.8	12.5	17.3	15.4
Net CV, kJ/kg	30,961	30,940	23,456	24,263	25,277	23,791

3.3 Petroleum coke

Petroleum coke, or petcoke, is the solid residue remaining following the extraction of all valuable liquid and gaseous components from crude oil (IEA CCC, 2010). It constitutes a major and increasing by-product of the petroleum refining industry. Its relatively low price and high energy content make it attractive as a fuel, and petcoke has been used by a number of utility companies worldwide as a co-fuel with coal in pulverised coal fired plant (IEA CCC, 2010). Compared with coal, petcoke can be higher in levels of sulphur and vanadium and nickel, the latter being particularly relevant from the perspective of ash utilisation. However, burning petcoke results in a significantly lower quantity of ash, typically less than 0.5% compared with the 5–20% normally associated with the burning of coal, and this limits the impact of the petcoke mineralogy on the ultimate fly ash composition. Table 8 illustrates the properties of two commercially

available petcokes and three British deep-mined coals used in co-combustion trials at Drax power station (AES Drax Power Ltd, 2002).

In January 2002, AES Drax Power Ltd submitted an application for a variation to its Authorisation under the auspices of the IPC (Integrated Pollution Control) regime, requesting permission to carry out an extended trial of up to eighteen months on a single unit to investigate the co-combustion of a blend of up to 20% petroleum coke mixed with 80% coal. As a prelude to the trial, the company was required to undertake an assessment of the possible impact of the practice on a number of topics, including ash quality and utilisation potential.

Fly ash from the power station was routinely used for cement addition, aerated concrete blocks, grout and fill operations, and road base construction. The compositions of the fly ash that would result from firing different levels of petcoke were

Table 9 Comparison of fly ash produced with the UKQAA published data, mg/kg (AES Drax Power Ltd, 2002)

Substance	Option 1 coal	Option 2 10% petcoke A'	Option 3 10% petcoke B	Option 4 15% petcoke A'	Option 5 15% petcoke B	UKQAA, maximum concentration
Vanadium	318	961	534	1334	659	1339
Nickel	183	350	252	446	292	583
Mercury	0.076	0.083	0.083	0.088	0.088	0.61
Arsenic	33.3	31.7	32.0	33.4	33.7	109
Antimony	6.27	5.93	5.93	6.25	6.24	325
Boron	80.0	77.4	77.3	81.5	81.3	310
Cadmium	0.28	0.29	0.27	0.31	0.28	4.0
Thallium	1.13	1.13	1.12	1.19	1.18	–
Cobalt	46.0	46.4	46.3	48.9	48.8	115
Chromium	174.4	171.4	172.1	180.5	181.2	192
Copper	171.0	166.8	167.5	175.8	176.4	474
Iron	36,016	34,099	34,320	35,924	36,127	150,000
Lead	38.8	39.0	37.4	41.1	39.4	976
Manganese	443	421	423	443	445	1550
Molybdenum	49.1	54.8	51.8	57.7	54.5	81
Tin	4.34	4.15	4.14	4.37	4.36	1847
Selenium	6.25	5.95	5.94	6.27	6.26	162
Zinc	110	110	112	116	118	918
Aluminium	95,980	90,683	91,111	95,536	95,908	320,000
Silver	0.86	0.94	0.87	0.99	0.92	–
Fluoride	*	*	*	*	*	200

* below the limit of detection

calculated, and compared against the maximum limits set by the UK Environment Agency and reported by the UKQAA, the UK industry association on ash utilisation, and the European Standard EN450 Fly Ash for Concrete, then under review (Table 9).

The projected quality of fly ash to be produced burning the designated coal/petroleum coke blends was not expected to be outside the specifications, and this was confirmed during the subsequent trials which reported, 'there had been no noticeable effect on the quality of water discharged after use in the generation process or on the quality of by-products such as ash and gypsum which have all remained within specification' (Drax Power, 2007).

In another cofiring exercise Weatherley (2006) described the results of a trial cofiring petcoke from the Motiva refinery in Norco, Louisiana, with coal at E.ON's Ratcliffe-on-Soar power station. Motiva petcoke was blended with Daw Mill coal at blends of 5%, 10%, 15% and 20% and firing trials were undertaken over several months. The ultimate and elemental analyses of the coal (Daw Mill deep-mined) and petcoke are given in Tables 10 and 11.

A sampling and testing programme was established to collect by-products from the co-combusted fuels and test them to demonstrate their performance, compared with by-products from coal-only generation. The tests were planned to evaluate the chemical composition, bulk oxide analysis and leaching

	Daw Mill coal	Motiva petcoke
Total moisture, % ar	10.1	6.5
Volatile matter, % ar	32.3	10.8
Fixed carbon, % ar	48.5	81.6
Ash, % ar	9.1	1.0
Gross CV, % ar	26.958	32.412
Sulphur, % ar	1.71	6.58
Chlorine, % ar	0.27	0.02
Hydrogen, % ar	4.27	3.48
Net CV, kJ/kg	25.778	
Ash, % dry	10.1	
CV, dry kJ/kg	29.981	
Volatile matter, % daf	40.0	
CV, daf, kJ/kg	33.364	
Hydrogen % daf	5.29	
VM Volatile matter, FC fixed carbon, CV calorific value, are as received, daf dry ash free. Figures are averages of results of actual deliveries		

characteristic of the by-products. The results of the bulk oxide and trace element analysis of PFA are given in Tables 12 and 13, and for FBA are given in Tables 14 and 15. The results of the leaching tests carried out on PFA are given in Table 16.

The average level of nickel in the cofired PFA matrix was 230 mg/kg for Motiva petcoke, Table 13. This compares with a level of 178 mg/kg in the coal-ash samples from the trial. However the level of nickel in the leachate was consistently below the level of detection thus the slightly elevated levels in the solid phase of the cofired ash are not reflected in the leachate, Table 16. For comparison, the average level of nickel in the Daw Mill coal was 23.1 mg/kg and in the petcoke was 133 mg/kg.

The average level of vanadium in the cofired PFA matrix was 445 mg/kg, Table 13. This compares with a level of 267 mg/kg in the Daw Mill coal-ash samples from the trial. The average level of vanadium in the leachate was 0.10 mg/L against <0.02 mg/L for PFA from Daw Mill. This is consistent with earlier findings that <1% of the total vanadium in PFA is

Table 11 Elemental analysis of coal and petcoke
(Weatherley, 2006)

Trace element	Daw Mill coal	Motiva petcoke
Ag	<1	<1
Al	11069.4	1143
As	11.7	0.6
B	40.9	<10
Ba	388.8	20.7
Be	7.80	<3
Cd	<0.2	<0.2
Co	6.03	1.1
Cr	22.7	2.6
Cu	17.0	2.2
F	46.1	5.9
Fe	7011.4	600
Hg	0.19	0.0
Mn	205.1	8.7
Mo	2.89	4.8
Ni	23.4	133
Pb	10.1	1.40
Sb	0.61	0.19
Se	2.50	<0.5
V	22.7	405
Zn	13.8	3.88
Units mg/kg on a dry basis		

Table 12 Bulk oxide analysis of PFA from coal and coal co-combusted with petcoke, wt% ar
(Weatherley, 2006)

blend, %	Daw Mill coal		Motiva petcoke			
	0	0	5	10	15	20
Al ₂ O ₃	24.09	22	27.1	27.2	20.8	26.5
BaO	0.22	0.11	0.31	0.36	0.16	0.3
CaO	4.84	3.9	7.62	7.73	6.42	7.14
Fe ₂ O ₃	11.78	16.2	10.1	10.7	13.5	10.2
K ₂ O	2.41	1.33	1.91	2.01	1.19	1.67
MgO	2.17	1.72	3.06	3.07	2.36	2.77
Mn ₃ O ₄	0.16	0.2	0.24	0.21	0.21	0.2
Na ₂ O	0.57	0.31	1.11	1.36	0.48	0.98
P ₂ O ₅	0.43	0.24	0.76	0.84	0.41	0.75
SO ₃	0.73	0.43	1.9	2.42	0.78	2.57
SiO ₂	46.95	52.3	44.7	44.4	52.8	46
TiO ₂	0.86	0.88	1.07	1.09	0.82	1.11

Table 13 Trace element analysis of PFA from coal and coal co-combusted with petcoke, mg/kg
(Weatherley, 2006)

blend, %	Daw Mill coal		Motiva petcoke				Daw Mill coal	Motiva petcoke
	0	0	5	10	15	20	0	15
Ag	n/a	<5	<5	<5	<5	<5		
As	142	13	110	124	13	97.2	135	133
B	250	73.2	238	315	95.2	264	303	363
Ba	2025	752	2663	3071	1228	2506	2412	2882
Cd	0.9	≤0.5	1.51	1.12	≤0.5	1.21	0.94	1.3
Co	64.7	49.5	61.3	52.4	43.7	60	69.5	65
Cr	134	132	156	139	92.1	149	175	159
Cu	180	131	166	158	88.3	153	190	170
F	39.9	72	126	6.12	74.9	5.96	14.9	20.0
Hg	0.72	≤0.01	0.676	0.558	0.072	0.169	0.521	0.510
Mn	1168	1317	1572	1342	1307	1265	1320	1352
Mo	24.6	3.47	34.1	24.5	7.68	32.9	25.8	29.3
Ni	175	157	200	236	157	305	201	254
Pb	159	29.8	130	134	22.6	142	161	154
Sb	9.7	1.32	5.4	5.43	≤1	4.84	7.14	6.68
Se	9.3	≤1	9.19	8.52	≤1	8.61	10.1	10.6
V	283	185	361	493	202	652	332	518
Zn	244	69.8	147	174	20.2	170	175	224

Table 14 Bulk oxide analysis of FBA from coal and coal co-combusted with petcoke, wt% ar
(Weatherley, 2006)

blend, %	Daw Mill coal		Motiva petcoke			
	0	0	5	10	15	20
Al ₂ O ₃	24.88	23.6	23.6	23.3	26.1	22
BaO	0.12	0.24	0.28	0.27	0.25	0.24
CaO	5.94	6.84	7.68	7.17	6.72	6.85
Fe ₂ O ₃	18.21	12.7	12.9	13.7	12.4	12.9
K ₂ O	1.89	1.44	1.59	1.48	1.42	1.35
MgO	2.55	2.53	2.92	2.65	2.52	2.5
Mn ₃ O ₄	0.21	0.21	0.27	0.22	0.21	0.21
Na ₂ O	0.34	0.72	0.87	0.85	0.71	0.69
P ₂ O ₅	0.23	0.46	0.55	0.52	0.49	0.47
SO ₃	0.12	0.16	0.11	0.48	0.28	1.39
SiO ₂	46.79	52.2	51.1	48.1	51.6	48.3
TiO ₂	0.84	0.96	0.94	0.93	1.05	0.93

Table 15 Trace element analysis of FBA from coal and coal co-combusted with petcoke, mg/kg
(Weatherley, 2006)

blend, %	Daw Mill coal		Motiva petcoke				Daw Mill coal	Motiva petcoke
	0	0	5	10	15	20	0	15
Ag	n/a	<5	<5	<5	<5	<5		
As	15.4	11	14.5	13.8	12.2	21	22.5	29.5
B	64.1	113	116	128	120	118	135	145
Ba	1258	2137	2483	2469	2199	2114	2141	1828
Cd	0.2	≤0.5	≤0.5	≤0.5	≤0.5	≤0.5	0.14	0.16
Co	72.9	51.8	39.7	53.2	63.8	52.4	50.5	53
Cr	131	130	109	119	148	121	120	130
Cu	188	110	92.3	105	120	113	127	106
F	≤5	68.5	46	32.7	39.9	36.9	5.0	145
Hg	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01	≤0.004	≤0.004
Mn	1640	1458	1825	1470	1426	1373	1488	1796
Mo	5.5	6.78	11.8	5.91	6.43	12.7	22.8	19.3
Ni	225	149	175	209	258	234	148	215
Pb	44.4	31.7	35.9	42.3	46.7	51.8	33.8	44.8
Sb	3.3	≤1	≤1	≤1	≤1	≤1	1.83	1.96
Se	≤0.5	≤1	≤1	≤1	≤1	≤1	<1	<1
V	350	187	243	357	408	389	193	370
Zn	141	63.5	51.5	79.3	70.2	105	71.3	84.2

Table 16 Leaching data on PFA from Ratcliffe petcoke trials, mg/L (Weatherley, 2006)

blend, %	Daw Mill coal		Motiva petcoke			
	0	0	5	10	15	20
Al	0.15	0.29	0.05	0.06	0.16	0.08
As	0.0187	<0.002	0.006	0.004	<0.002	<0.002
B	2.4	0.06	0.17	0.3	0.06	0.8
Ba	1.64	0.94	0.74	0.66	1.35	0.8
Ca	410	440	730	160	220	180
Cd	≤0.001	<0.001	≤0.001	<0.001	<0.001	<0.001
Cl	8.8	2.26	5.76	4.23	2.88	16
Co	≤0.01	<0.05	≤0.05	<0.05	<0.05	<0.05
Cr	0.08	0.02	0.13	0.12	0.02	0.13
Cu	≤0.01	<0.01	≤0.01	<0.01	<0.01	<0.01
F	1.15	0.15	0.9	0.32	0.43	0.46
Fe	≤0.01	0.11	<0.01	<0.01	0.08	<0.01
Hg	≤0.00002	<0.00002	<0.00002	<0.00002	<0.00002	<0.00002
K	14.3	10.7	15.4	21.6	8.8	20.6
Mg	≤0.01	<0.05	≤0.05	≤0.05	≤0.05	≤0.05
Mn	≤0.01	<0.01	≤0.01	≤0.01	≤0.01	≤0.01
Mo	0.88	0.09	0.88	1.5	0.11	1.42
Na	12.3	11	21	18	88	65
Ni	≤0.01	<0.05	≤0.05	≤0.05	≤0.05	≤0.05
P (PO ₄)	≤0.05	<0.1	0.22	<0.1	0.32	<0.1
Pb	≤0.001	<0.001	<0.001	<0.001	0.002	<0.001
S (SO ₄)	303	200	598	662	254	1045
Sb	≤0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Se	0.007	<0.002	0.013	0.028	<0.002	0.06
Si (SiO ₂)	3.1	1.63	1.06	1.85	0.64	2.92
Ti	≤0.01	<0.02	≤0.02	≤0.02	≤0.02	≤0.02
V	≤0.01	0.02	0.03	0.08	0.03	0.27
Zn	≤0.01	<0.05	≤0.05	≤0.05	≤0.05	≤0.05

leachable and that it is mostly fixed in the solid phase of the particles. For comparison, the average level of vanadium in the Daw Mill coal was 22.7 mg/kg and in the petcoke was 405 mg/kg.

Other species showing elevated levels in the leachate of the cofired ash, compared with coal only ash are boron, potassium, sodium, selenium and sulphate. With the exception of sulphate these species exist in lower levels in petcoke than in coal, hence the elevated results are most likely influenced by the variability of the coal rather than by cofiring with petcoke.

The results shown in Table 17 indicate that the co-combustion of petcoke results in an increase in the sulphate in the PFA compared with PFA from coal-only firing. The concentration of sulphate in the PFA remained within the 3% limit for fly ash for use in concrete to EN450.

A comparison of the leaching values against the UKQAA leaching data (Sear, 2001) indicates that the results of tests on material cofired at Ratcliffe falls within the range of results for ash from coal-only firing from UK power stations and would be suitable for the normal ash utilisation routes.

Table 17 Sulphur in fuel, flue gas and solid by-products (Weatherley, 2006)

Blend, %	Sulphur		SO ₂ in FGD inlet flue gas		SO ₃ in PFA	SO ₂ in FBA
	in blend	increase, %	mean	increase, %		
0	1.71		3062		0.73	0.12
5	1.95	14	3065	0.1	1.9	0.11
10	2.20	28	3393	11	2.42	0.48
15	2.44	43	3726	22	0.78	0.28
20	2.68	57	3776	23	2.57	1.39

In another detailed review and study on ash from petcoke-coal co-combustion, Scott (2007) investigated the impact of including mineral components derived from the petcoke on overall ash properties. The results from the study of petcoke fly ash showed that the material behaved in a manner very similar to that of coal-only fly ash. Once again, these similarities are to be expected given the low ash content associated with the burning of petcoke. Assuming an ash content of 0.5% for petcoke and 10% for coal (typical for bituminous coal used at the Canadian power station, N B Power, that was the focus of the work) and a maximum replacement level of 25% petcoke, the direct contribution of ash (that is, inorganic residue) from the burning of petcoke is approximately 1.6% of the total. This represents a very small fraction of the material that could contribute to any deviations in performance and reflects the findings from the complimentary investigations discussed above.

The carbon content of raw petcoke fly ash was recognised as being likely to be greater than the maximum stated in the Canadian standards (8% for Type F FA and 6% for Types CI and CH) and beneficiation would normally be necessary for the material to meet the standard specifications. However, there appeared to be no problem entraining air in the beneficiated fly ash from petcoke, although an increase in air-entraining admixture dosage above that required in concrete without fly ash should be expected. The extent of the increase was no greater than that for concrete with coal-only fly ash of the same LOI, and in some examples slightly lower.

The only significant differences between petcoke fly ash and coal-only fly ash were with respect to the higher level of vanadium. The available test results indicate that the vanadium present is largely unavailable due to its low solubility and was not thought likely to be an impediment with respect to the use of petcoke co-combustion fly ash in concrete.

As a consequence of this study, the definition for fly ash in the Canadian standard CSA A3001-03 was revised in July 2004 to include ash resulting from the combustion of pulverised coal blended with up to 30 wt% of petcoke (Canadian Standards Association, 2008). Fly ash produced from blends of coal and coke must meet the same chemical and physical requirements as fly ash produced from coal only.

3.4 Summary

The cofiring of coal with a wide range of different co-fuels has been demonstrated successfully. Through interactions in the solid and gaseous phase, species derived from the mineralogy of the coal and co-fuel respectively coalesce to give rise to a hybrid fly ash. The composition of the cofiring fly ash tends to be dominated by the composition of the coal, as most co-fuels have a relatively low ash content. However, in some cases, a co-fuel may be rich in a specific component, for example vanadium and nickel in petcoke, and care must be taken to ensure that these do not impact adversely on the use of the ash, or on its environmental impact. In most cases reported in the literature, adverse effects are rare and the cofiring ash may be used without penalty.

4 NO_x reduction techniques

4.1 Combustion modifications

Utility companies operating coal-fired power plant worldwide have been progressively investigating and incorporating technologies to reduce the emissions of oxides of nitrogen (NO_x) from those plants. Primary measures or combustion modifications are the first methods generally used to control NO_x emissions, and have been employed since the early 1970s. Combustion modifications usually achieve 30–70% reduction in NO_x emissions. Techniques include process optimisation, low NO_x burners (LNB), air staging (overfire air (OFA)) and fuel staging (reburning). These technologies have been reviewed previously by Wu (2002) and Nalbandian (2009).

Combustion-based techniques aim to achieve NO_x reduction through a longer, cooler flame and a much more reduced atmosphere compared to that found in traditional burners. Figure 10 illustrates a generic low NO_x burner flame. Differences in low NO_x fly ash compared to fly ash from conventional boilers have been predicted, however, relatively little is known about how fly ash characteristics are affected by the different types of NO_x reduction technology (Golden, 2001a). The important characteristics of fly ash for concrete quality that may change with low NO_x burners include unburnt carbon content, particle size distribution, ash morphology, ash reactivity and composition. The introduction of ammonium salts, the latter through the post-combustion emissions control technologies discussed later (Hemmings and others, 1997; Bijen and Selst, 1992; Golden, 2001b).

4.1.1 Effects on unburnt carbon

The reduction of NO_x by combustion modifications is usually accompanied by an increase in the carbon content of the fly ash. This carbon is primarily unburnt coal and is greatest in the coarser fractions of fly ash, with higher LOI values in the

larger size fractions of the ash. For example, Dutch fly ashes from low NO_x retrofits have higher unburnt carbon levels (LOI of 4–15%) compared with pre-conversion ashes (LOI of 2–3%). Studies at the Center for Applied Energy Research, University of Kentucky (CAER) demonstrated that, in general, fly ash carbon increases following the conversion of a pulverised coal fired boiler for low NO_x combustion (Hower and others, 1999). These studies have included the investigations of a wall-fired unit burning low sulphur western US bituminous and subbituminous coal, wall-fired and tangentially-fired units burning medium sulphur Central Appalachian high volatile bituminous blends, and wall- and tangentially-fired units burning high sulphur Illinois Basin high volatile bituminous blends. Of these units, only the tangentially-fired unit burning Central Appalachian coal showed a decrease in fly ash carbon following conversion to low NO_x combustion.

A major study undertaken by EPRI (1996) to determine the effect of low NO_x control technologies on coal fly ash, involved extensive literature searches and interviews with industry workers, including trade associations, US utilities, their own in-house knowledge bases, ash marketers, and selected European groups. In the study they correlated fly ash quality with factors such as coal characteristics, additive concentrations, residence time, and pulveriser efficiency. The key findings of this study were as follows:

- Combustion control technologies (COM, LNB, OFA) can increase the unburnt carbon content and relative coarseness of fly ash. Post-combustion controls (SCR, SNCR) can cause ammonia contamination of the fly ash.
- High unburnt carbon levels can adversely affect the following current fly ash uses:
 - concrete and concrete products;
 - blended cement;
 - polymer fillers;
 - grouts;
 - metal-matrix fillers.

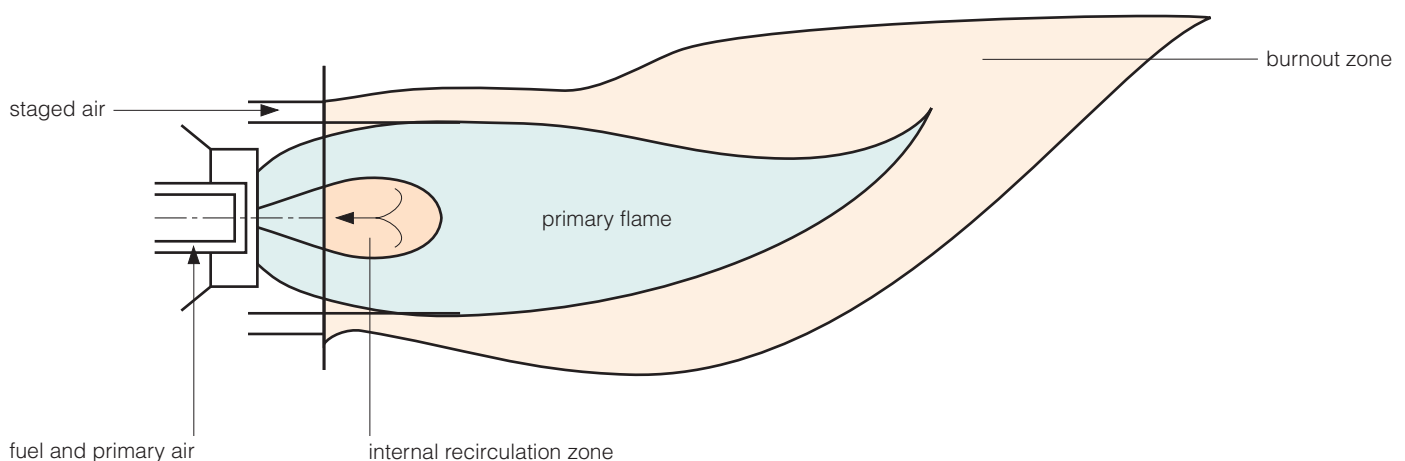


Figure 10 Generic low NO_x burner flame (Nalbandian, 2009)

- Ash with high unburnt carbon levels can continue to be used successfully in the following uses:
 - cement feedstock;
 - highway construction (roadbase, subbase, asphalt filler);
 - structural fills;
 - physical and chemical waste stabilisation;
 - controlled density fills;
 - mine backfill;
 - agricultural amendments (fertilisers, soil amendments, synthetic soils);
 - resource recovery (carbon, cenospheres, metals).
- Ash with high ammonia levels may not be acceptable as a cement feedstock.
- Concrete applications are not suitable due to the release of ammonia at high pH.
- Construction and other bulk applications are not impacted unless personnel exposure in enclosed spaces is possible.
- With suitable mitigation measures, low NO_x ashes can still be used in existing pozzolan and concrete markets—albeit at a cost.
- Disposal costs for low NO_x ash can increase due to lower bulk density. The lower density requires more water for compaction and greater volumes; landfills do not last as long.
- Methods are available for beneficiating high unburnt carbon and ammonia contaminated fly ash.
 - In the tangentially-fired units that were retrofitted, first generation low NO_x burners from ABB-Combustion Engineering were used, whereas the most recent tangentially-fired unit surveyed was fitted with PM burners from Mitsubishi;
 - In the two opposed wall fired units studied HTNR-burners from Babcock-Hitachi were fitted. In an older unit that was retrofitted with these burners there was not enough space in the boiler to incorporate overfire air (OFA). However, in the newly-built unit in Amsterdam the HTNR-burners together with two layers of OFA-ports gave excellent results for NO_x and unburnt carbon;
 - Characterisation of low NO_x fly ashes showed:
 - a lower fraction (<10 μm) than the conventional fly ashes;
 - the specific surface of the low NO_x ashes from the Maasvlakte and Borssele units was larger, because of the higher porosity of the particles;
 - the particles were more-or-less agglomerated;
 - there is a positive linear relationship between the melting point of the low NO_x ashes and the bitumen value;
 - no differences were found between the low NO_x ashes and the conventional ashes with regard to leaching behaviour.
 - For carbon reduction, sieving proved to be the most appropriate technology. Precipitator field separation was considered economic only for newly constructed units.

The EPRI researchers concluded that at the time of the study the literature contained little information relating fly ash characteristics to specific NO_x reduction technologies, although many reports of higher carbon contents, higher coarseness, and ammonia contamination in low NO_x fly ashes were cited. There did not seem to be a good understanding of exactly which characteristics of the fly ash are affected by the different low NO_x technologies. In a follow-up study, EPRI engaged KEMA to undertake a parallel survey of European utilities with special attention to Dutch plant, for their experiences (EPRI, 1997). A large variety of coal types was included in the project, as Dutch plant routinely burns coal from all over the world.

The main findings of the KEMA survey were:

- Combustion control technologies can increase the unburnt carbon content and relative coarseness of fly ash. Post-combustion controls (SCR, SNCR) can cause ammonia contamination of the fly ash.
- The view that the introduction of low NO_x technologies will be accompanied by an increase in unburnt carbon is only substantiated in the case of a boiler retrofit. Completely new units designed for low NO_x combustion can be designed for low unburnt carbon levels. This is achieved by installing modern milling equipment in order to improve the fineness of the pulverised coal and by increasing the boiler dimensions in order to increase the burn-out time.
- In the Netherlands low NO_x combustion systems have been installed in tangentially-fired boilers as well as in opposed wall fired boilers, both as retrofits and in newly built boilers. With one exception, all low NO_x boilers use a system of air-staging.

KEMA considered that it was possible to take measures in order to continue the use of low NO_x fly ash in:

- concrete and cement;
- fired-clay bricks and sand-lime bricks;
- cellular concrete;
- light-weight aggregates (Aardelite and Lytag);
- hydrophobic soils;
- alkali-slag cements;
- foundations of road constructions.

Unburnt carbon from low NO_x burners is coarser, more coke-like, extremely porous, of high surface area, and very active chemically as compared with 'conventional' fly ash carbons (Fox and Constantiner, 2007). These properties impede the use of this type of fly ash in concrete as the more highly active form of carbon that reduces the effectiveness of admixtures, especially air-entraining admixtures. The increased water demand that arises from the highly porous unburnt carbon particles can impede the workability of the concrete. Higher carbon ashes are usually darker in colour, and this may be unacceptable aesthetically for some uses. These impediments can be reduced through fly ash beneficiation, where a reduction in unburnt carbon is accompanied by a corresponding reduction in water demand. New pulverised coal fired plant designs optimised for NO_x control tend to be larger than existing units, and have fewer mills and burners. Flames have 'more room', and these larger furnaces tend towards lower furnace exit temperatures and longer residence times (1.5–2 s) allowing more complete carbon burnout (Hough, 2008). Improved coal milling and modifications to the air/ fuel mixture accompany new build and modern low NO_x retrofits, and these changes help to keep unburnt carbon contents down.

4.1.2 Effect on particle size

The particle size of fly ash has been found to increase when plants are retrofitted with low NO_x burners (Fox and Constantiner, 2007). It is thought that the lower combustion temperature and the more reducing environment inherent in low NO_x retrofits lead to a coarser fly ash with a rougher texture due to increased particle agglomeration. The presence of increased amounts of partially fused coal particles in post-conversion fly ashes has also been attributed to lower combustion temperatures (Fox and Constantiner, 2007). Fly ashes have been shown to be coarser after low NO_x conversion even when the retrofit also included optimisation of the pulverisers to reduce the particle size of coal feed. Compared with the pre-retrofit fly ash, the 'low NO_x' fly ashes also have greater porosity and higher specific surfaces. However, new low NO_x installations with modified boiler dimensions can produce fly ashes with agglomeration and porosity characteristics comparable to that of conventional boilers before conversion, as described in the EPRI reviews above. Low NO_x fly ash can display reduced pozzolanic activity and this has been attributed to an increase in the proportion of coarse particles. Although the lower peak flame temperature in low NO_x burners results in a fly ash with fewer particles less than 10 µm, the percentage of particles less than 45 or 32 µm is not necessarily changed. It is the decrease in particles less than 10 µm that is thought to reduce the pozzolanic activity of the low NO_x fly ash. The decrease in the fraction finer than 10 µm also results in poorer workability of concrete containing low NO_x fly ash as compared with conventional fly ash. A reduction of -10 µm particles leads to poorer particle packing and an increase in water demand in concrete.

4.1.3 Effect on mineralogy

The mineralogical changes in fly ash after conversion to low

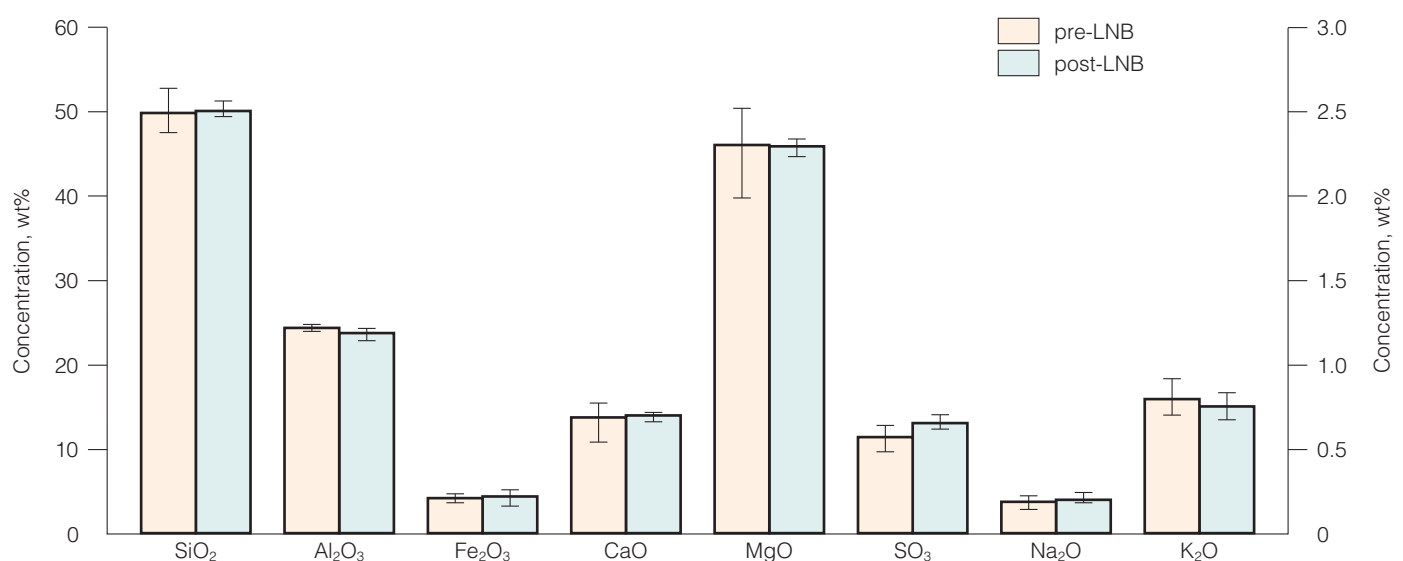


Figure 11 Elemental composition expressed as oxides of pre and post low NO_x conversion ashes (Hower and others, 1997)

NO_x burners are not well documented. Hower and others (1997) studied X-ray diffraction (XRD) patterns of fly ash from a Tennessee plant burning Appalachian bituminous coal before and after conversion to low NO_x burners. The ashes appeared to be qualitatively similar; however, petrography showed the post-conversion ash had a higher concentration by volume of quartz content which was attributed primarily to the lower combustion temperature of the low NO_x environment. In a further study on a plant burning bituminous coal from the eastern USA, little variation was found for the main fly ash components pre- and post-NO_x conversion (Figure 11).

Similarly, the mineral components determined by X-ray diffraction were broadly in line with the natural variation in parent coal composition, although some enrichment of quartz may be evident (Table 18).

4.1.4 Effect on glass phase components

Changes in the glass content of fly ash after low NO_x conversion have been predicted but rarely documented. The glass content of a bituminous coal fly ash from the Tennessee plant described above was found to increase after a low NO_x burner retrofit coupled with increased coal fineness and modification of the air/fuel ratio. Petrographic glass determinations on fly ashes sampled before and after conversion showed increases in all size categories and much higher glass contents in the coarser fractions. Longer residence times as ash particles pass through the boiler flame and into the dust collection systems in low NO_x systems were thought to permit more glass devitrification than with conventional systems.

Table 18 Fly ash mineralogy based on XRD, wt% (Hower and others, 1997)

Ash	Glass	Mullite	Quartz	Calcite	Anhydrite	Magnetite	Anorthite	Lime	Hematite	Portlandite
Pre-1	81.4	8.6	6.0	0.0	0.7	1.5	0.6	0.4	0.3	0.5
Pre-2	80.6	8.8	7.5	0.1	0.1	1.0	0.7	0.3	0.6	0.3
Pre-3	84.7	7.1	5.3	0.0	0.1	0.8	0.6	0.3	0.4	0.7
Pre-4	75.8	13.2	8.6	0.0	0.1	0.7	0.4	0.3	0.7	0.2
Pre-5	80.8	9.5	5.9	0.0	0.2	0.8	0.8	0.4	0.8	0.8
Average pre-ash	80.7	9.4	6.7	0.0	0.2	1.0	0.6	0.3	0.6	0.5
Post-1	79.5	10.2	7.9	0.1	0.2	0.3	0.5	0.3	0.7	0.4
Post-2	76.8	10.1	8.9	0.1	0.2	0.6	1.7	0.4	1.1	0.1
Post-3	77.1	10.1	8.2	0.1	0.2	0.9	1.7	0.3	1.0	0.4
Post-4	80.8	8.4	7.3	0.0	0.2	0.6	1.4	0.2	0.6	0.5
Post-5	77.8	8.8	8.8	0.0	0.2	0.8	2.3	0.3	0.7	0.3
Average post-ash	78.4	9.5	8.2	0.1	0.2	0.6	1.5	0.3	0.8	0.3

4.2 Post-combustion modifications

4.2.1 Selective catalytic reduction and ammonium injection

Flue gas treatment technologies, first installed in the early 1980s, are used to meet more stringent NOx emission limits, usually in combination with combustion measures. Those include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) as well as multi-pollutant control systems (Nalbandian, 2009). Post-combustion controls use chemical reagents (usually ammonia or urea, which decomposes to ammonia in the furnace) to react with NOx and form nitrogen and water. Traces of the reagents are adsorbed on the fly ash and can affect ash marketability. A common problem is the odour of ammonia when the ash is wetted.

Problems associated with ammoniated fly ash have become a major concern for coal-fired facilities in recent years. A project funded by the Department of Energy (DE-FC26-00NT40908) and conducted by the University of Kentucky Center for Applied Energy Research (Rathbone and Tyra, 2003) investigated the effects of ammonia injection on the resulting concrete mixes. An experimental apparatus was designed to measure ammonia loss from the cement mortar over time, using a trap solution which could be periodically measured during curing of the cement mortar. The effects of various water to cementitious ratios on the ammonia loss rate were examined. The results indicate that, unlike aqueous solutions, the rate of ammonia loss occurs in two phases: a rapid rate followed by a much slower linear rate that began after about 24 hours of curing and persisted throughout the

three-week test period. Surprisingly a significant portion (greater than 80%) of the ammonia was calculated to have remained in the mortar. This has implications for certain applications where post-construction wetting such as during rainfall, could release ammonia to the detriment of the end-user (Bittner and Gasiorowski, 2007). Porbatzki and Brandenstein (2010) have similarly outlined the problems with ammonia in fly ash and stressed the importance of operating post combustion processes to minimise ammonia slip. Ammonia in fly ash can be reduced by heat treatment at 150–200°C and a commercial process, the ASH PRO Liberation Process, (Fisher and Blackstock, 1997) now marketed as ProAsh, has been developed for this purpose.

4.3 Summary

The change in combustion environment associated with NOx reduction technology has a direct impact on the properties of the coal ash produced. An increase in unburnt carbon is common, particularly for older units that have been retrofitted with low NOx burners or furnace staging technology. Newer boilers are less prone to give high carbon in ash, but the longer residence times and cooler furnace affect the ash mineralogy which in turn affect its performance negatively in, for example, construction products. Post-combustion NOx removal with ammonia, or ammonia generating species can lead to contamination of the ash with excess ammonia, unless ammonia 'slip' is very carefully managed. Contaminated ash can release free ammonia even when incorporated in a cement formulation and pose a nuisance to end users.

5 Circulating fluidised bed combustion plant

Although pulverised coal firing remains the dominant technology for power generation, newer cleaner coal technologies have been steadily gaining ground, particular circulating fluidised bed technology (CFBC). In CFBC, combustion takes place at temperatures of 800–900°C resulting in reduced NO_x formation compared with pulverised coal combustion. N₂O formation may, however, be increased. Sulphur dioxide emissions can be reduced by the injection of sorbent into the bed, followed by the subsequent removal of ash together with reacted sorbent.

Circulating beds use a relatively high fluidising velocity, so the particles are constantly held in the flue gases, and pass through the main combustion chamber and into a cyclone, from which the larger particles are extracted and returned to the combustion chamber (Figure 12). Individual particles may recycle ten to fifty times, depending on their size, and how quickly the char burns away. Combustion conditions are relatively uniform through the combustor, although the bed is denser near the bottom of the combustion chamber. There is a great deal of mixing, and the residence time during one pass is very short. Fluidised bed combustors generate two major ash streams:

- the fly ashes, which have been elutriated from the fluidised bed and are collected from the flue gas stream in either a bag filter or electro-static precipitator;

- the bottom ash, from the bed off-take.

In both cases, the ashes contain a mixture of fuel ash, unburnt carbon residues, calcium sulphate and sulphite and unreacted lime or limestone, if the latter has been added for sulphur capture. The ash properties are substantially different from the ashes from pulverised coal firing since the coal is not necessarily pulverised prior to combustion and, as a consequence, the fly ash particles are very much larger than fly ashes from pulverised coal combustion (Sellakumar and Conn, 1999). Because of the relatively low combustion temperatures in fluidised beds, the ash residues are largely unfused and exhibit significant crystalline character. The chemical compositions of the fly ash residues from a number of large CFBCs are presented in Table 19 (Hall and Livingston, 2001).

These analyses indicate that the residues comprise a mixture of coal ash species, heavily modified by calcium species (unreacted lime and limestone and the products of the SO₂ and Cl retention process, that is calcium sulphate, sulphite and chloride). The utilisation of the ash from fluidised bed combustors in the manufacture of construction materials is not common practice, and the majority of these materials are used for low value infill and land reclamation purposes, or are sent for landfill. The specifications for the ashes to be used in

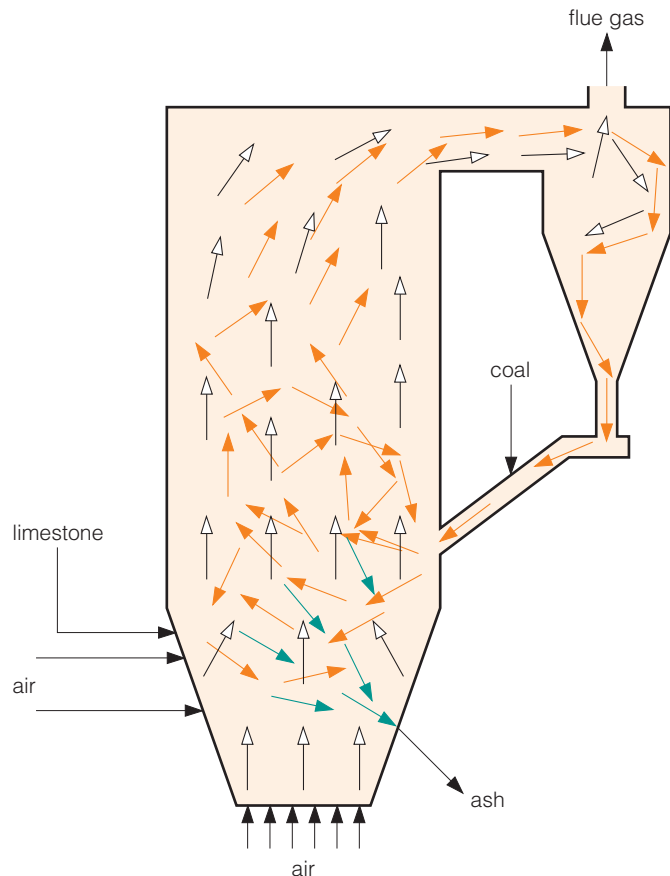


Figure 12 Generalised schematic of a circulating fluidised bed combustor (CFBC) (Barnes and Sear, 2004)

Table 19 Analytical data for fly ash residues from CFBC (Hall and Livingston, 2001)			
Ash component, wt%	Ash One	Ash Two	Ash Three
CaSO ₄ ·2H ₂ O	1.0	1.4	1.9
CaSO ₃ ·0.5 H ₂ O	0.9	<0.1	<0.1
CaCO ₃	0.9	2.6	1.6
CaCl ₂	0.6	0.1	0.1
SiO ₂	45.9	26.1	18.1
Al ₂ O ₃	1.4	11.3	11.1
Fe ₂ O ₃	7.7	3.1	5.6
CaO	25.7	39.9	19.6
MgO	4.2	1.1	1.2
TiO ₂	0.2	0.5	0.4
Na ₂ O	1.0	0.3	0.3
K ₂ O	0.3	1.0	1.1
P ₂ O ₅	0.0	0.2	0.4
SO ₃	11.2	9.2	9.6
Loss on ignition	0.7	3.8	28.6
%<75 μm	32	91	75

the manufacture of cements and other products consider only the fly ashes from pulverised coal combustion, and this can lead to ashes from alternative sources being automatically excluded. The use of the fluidised bed ashes as structural infill materials is a relatively attractive option, and this is likely to be the most widely practised option in the short- to medium-term future. One particular advantage in this regard is the relatively high alkalinity of these ashes, which makes them attractive for use in the neutralisation of acidic mine soils in the reclamation of strip mined land, and for the control of subsidence in abandoned mine workings (Schueck and others, 2001).

Because of their significant lime content, these residues are frequently classified as hazardous wastes with consequentially high disposal costs. These high costs make it important to identify utilisation options for the ashes for the economic operation of plant.

5.1 Cofiring in CFBC plant

CFBC technology can use a wide range of fuels as well as coal and emit low levels of pollutants and consequently the cofiring of coal with other solids has been considered as an approach to waste remediation and energy production (Tsaia and others, 2002). The co-utilisation of biomass or wastes has consequences for combustion behaviour, emissions, operational conditions and ash. Some kinds of biomass require additional pre-combustion measures such as gasification or pyrolysis (Spliethoff and others, 2001). The following sections consider specific examples of co-combustion.

5.1.1 Coal and wood waste

Brunello (1999) studied the co-combustion of coal with wood wastes in a 1 MWth CFBC with operating conditions corresponding to those in full-scale 125 MWe and 250 MWe plant. Three types of coal (A, B, C), three types of sawdust (D, E, F) and two types of woodchip (G, H) were co-combusted with the following biomass-coal thermal ratios (%) in order to produce ashes for subsequent characterisation studies: -/A=0/100, D/A=42/58, G/A=49/51, -/B=0/100, E/B=13/87, F/B=10/90, H/B=8/92, -/C=0/100 and H/C=7/93. An addition of up to 50% sawdust and woodchip did not modify significantly the chemical characteristics of ash as compared to coal-only combustion. Concentrations of trace elements in these ashes were much lower than the statutory limit values current at the time of the work. Characterisation studies showed that ashes B, E/B, F/B, H/B, C and H/C reached satisfactory chemical requirements, other than a high LOI. The physical requirements of the ash were considered to be a good match for use in concrete formulations.

5.1.2 Coal and paper mill sludge

Coal and paper mill sludge have been cofired in a 103 MWth atmospheric circulating fluidised bed boiler (ACFB) in Taiwan, to investigate the effect of the sludge feeding rate on

emissions of SO_x, NO_x and CO (Tsaia and others, 2002). The coal feeding rate was based on 450 t/day without sludge addition. Each tonne of sludge added was used as substitute for 25 kg of coal. The fly ash and bottom ash produced were analysed using the US Environmental Protection Agency (US EPA) Toxic Characteristic Leaching Procedure. All of the dissolved heavy metals met the Taiwanese environmental requirements and are therefore considered safe for disposal. Alternatively, the combustion ashes could be recycled and used in cement manufacture. The SiO₂ content of the fly ash was low at 38.50%, but it was considered suitable for use as a clay substitute. The bottom ash was richer in silica, 87.06% SiO₂, and so could be used as a substitute for sand in the cement process.

5.1.3 Coal and straw

CFBC boilers have been used for the co-combustion of coal and straw. In Grenå, Denmark, an Alstom Pyroflow cogeneration plant designed for 0–60% straw and 40–100% coal on an energy basis was commissioned in 1992. The plant has a thermal output of 60 MJ/s (district heating and process steam) and an electric capacity of 17 MW. Many different types of coal have been tested but only a few are suitable for combustion with straw. Colombian coal has been used successfully. South African coal has to be blended with others such as Polish or Colombian to reduce the dust emissions.

The Colombian coal used had the following properties:

Moisture, %	10.5
Ash, %	11.5
Volatiles, %	31
Q _{eff} , MJ/kg	24.91
S, %	0.92
Cl, %	0.027
N, %	1.37
K, %	0.017

Wieck-Hansen and Sander (2003) compared the fly ash composition for 100% coal combustion with fly ash from cofiring 50% straw. The composition was calculated from analyses of the main part of the ash and the water-soluble part which is related to the KCl and K₂SO₄ content. They found that the amount of KCl and K₂SO₄ present increased dramatically with an increased ratio of straw. The high amount of water soluble material makes the residue difficult to utilise. High concentrations of salts such as KCl can increase the risk of agglomeration and deposit formation on the superheater. When the salt concentration is likely to be too high, it may be necessary to reduce the proportion of straw and to use other forms of biomass with a limited KCl content such as sunflower shells and wood chips.

Zhenga and others (2007) investigated the interaction between coal and straw ash and the effect of coal quality on fly ash and deposit properties by cofiring straw with three kinds of coal in an entrained flow reactor. The compositions of the ashes produced were compared to the available literature data to find suitable scaling parameters that can be used to predict the composition of ash from straw and coal cofiring at larger scale. Reasonable agreement in fly ash compositions

regarding total K and fraction of water soluble K was obtained between cofiring in an entrained flow reactor and full-scale plants. The capture of potassium and subsequent release of HCl can be achieved by sulphating with SO₂ and more importantly, by reaction with Al and Si in the fly ash. About 70–80% of the potassium reports in the fly ash as alumina silicates while the remaining potassium is mainly present as sulphate. Lignite/straw cofiring produces fly ash with a relatively high chlorine content. This is probably because of the high content of calcium and magnesium in lignite reacts with silica, so it is not available for reaction with potassium chloride. A reduction of chlorine and increase of sulphur in the deposits compared to the fly ashes could be attributed to the sulphation of the deposits.

limestone injection the free lime present in the ash renders them self-cementing, limiting their use to specific applications. Free lime after setting may still be a problem, however.

5.1.4 Coal and sewage sludge

The performance of CFBC furnaces does not deteriorate with sewage sludge co-combustion. Sewage sludge has an ash content of about 15%, so the overall ash load increases. The pollutants in the sludge are captured inertly in the ash, except for mercury which is transported in the flue gas. The ash may be utilised for recultivation in open-cast brown coal mining and it has been found to comply with the values for grade landfill in the German technical instructions for municipal solid waste (Spliethoff and others, 2001).

5.1.5 Coal and petcoke

Sheng and others (2007) studied fly ash from a circulating fluidised bed combustion (CFBC) boiler cofiring coal and petroleum coke. They recognised that the ash is very different from coal ash arising from traditional pulverised fuel firing due to many differences in their combustion processes, and thus would have different effects on the properties of Portland cement. The effects of the CFBC fly ash on the strength, setting time, volume stability, water requirement for normal consistency, and hydration products of Portland cement were investigated. The results showed that CFBC fly ash had little effect on the strength of the Portland cement when included at levels up to 20%, but that the cement strength decreased significantly if the ash content was increased over 20%. The water requirement for the normal consistency of cement increased from 1.8% to 3.2% (absolute increment value) with an addition of 10% CFBC fly ash and it is thought that the free lime content of CFBC fly ash was responsible for this observation. The setting time decreased with an increase of CFBC fly ash content. The main hydration products of cement with CFBC fly ash were hydrated calcium silicate, ettringite, and portlandite.

5.2 Summary

CFBC presents specific issues for ash utilisation and it is difficult to generalise on this topic. The wide flexibility of a CFBC unit means that a range of coal types and co-fuels can be accommodated which in turn gives rise to a range of ash compositions. These are best considered on a case by case basis. Additionally, if in-bed sulphur capture is employed, via

6 Advanced pulverised coal fired plant

A number of utility companies worldwide are considering the introduction of new coal-fired power plants. These new installations are likely to be of the ultra-supercritical type with steam temperatures above 610 °C and steam pressures above 25 MPa. These new installations will have to meet very stringent emission targets, including (near-) zero CO₂ emissions (through carbon capture) whilst simultaneously being able to utilise a wide range of coals and secondary fuels such as biomass and possibly waste. Along with these enhanced steam conditions and attendant higher efficiency, further gains can be achieved through oxy-firing, discussed in more detail in later sections. In oxy-firing a modified conventional boiler is fed with pure oxygen rather than air, and a proportion of the flue gases is recycled through the combustion chamber. This has the effect of significantly raising the concentration of CO₂ in the flue gases. The low concentration of CO₂ in the flue gases of conventional power stations is the major barrier to CO₂ capture because it makes it very expensive to separate and process.

Current boiler designs optimised for NO_x control tend to be larger than existing units, and have fewer mills and burners. Flames have 'more room', and past problems of flame impingement with attendant slagging and corrosion have mostly been designed out. Larger furnaces tend to produce lower furnace exit temperatures and longer residence times (1.5–2s) allowing more complete carbon burnout (Hough, 2008).

6.1 Oxyfuel combustion

Oxyfuel combustion is being developed for pulverised coal plants and turbine power cycles in connection with plans for carbon capture. The main products of oxyfuel combustion are carbon dioxide, and water, and since the water is easily separated, a stream of CO₂ ready for sequestration is obtained.

Temperatures in an oxyfuel system are controlled by recycled water (or CO₂) in a complete power system. Multiple oxy-combustion facilities at various scales are being constructed or are in operation around the world.

The radically different combustion environment in an oxyfuelled boiler mean that ash interactions in the solid and vapour phase will lead to changed properties in the resulting fly ash. Suriyawong and others (2005) point out that, since fly ash particles are formed by means of nucleation of vaporised ash components and growth by coagulation and heterogeneous condensation, under oxyfuel combustion conditions, the formation mechanisms of fly ash and their aerosol characteristics could be altered, and may eventually affect their removal efficiency in particle control devices. They studied submicron (<0.5 µm) particle formation under oxyfuel combustion of subbituminous Powder River Basin coals with a mean particle size of 50 µm. It was found that the geometric mean size of fly ash formed under higher CO₂/O₂

ratios is smaller than the geometric mean size of fly ash formed by conventional combustion at all three temperatures studied (800°C, 1000°C, and 1200°C). A later report confirmed the reduction in mean size together with a decrease in the total number concentration of particles when nitrogen is replaced with carbon dioxide in the combustor in both drop tube and flame reactors (Suriyawong and others, 2006).

Oxyfuel combustion is currently being studied at laboratory and pilot scale and most of the projects are at a relatively early stage and are concentrating on the optimisation of combustion conditions, before proceeding to study secondary effects such as ash composition. For example, studies on ash effects on the Vattenfall Schwarze Pumpe pilot plant (Hultqvist and others, 2009) are currently scheduled for 2011 (Jidinger, 2010).

Sheng and Li (2008) studied mineral matter transformations and ash formation during the simulated oxyfuel combustion of pulverised coal. Five typical Chinese thermal coals were burnt in a drop tube furnace to generate ashes under various combustion conditions. The ash samples were characterised with XRD analysis and Mössbauer spectroscopy to study the transformations of the main minerals in the coals. Fine ash particles were collected by a low pressure impactor and their size distribution and elemental composition were analysed to study the fine ash formation. The impacts of O₂+CO₂ combustion on the mineral transformation and fine ash formation were explored through extensive comparisons between O₂+CO₂ combustion and O₂+N₂ combustion. They found that, O₂+CO₂ combustion does not significantly change the mineral phases formed in the residue ash, but does affect the relative amounts of the mineral phases. Moreover, it was found that O₂+CO₂ combustion significantly affects fine ash formation behaviours, including lowering the mass fraction of sub-micron particles in ash and significantly changing the elemental composition of sub-micron particles as compared to O₂+N₂ combustion.

In a more detailed investigation Zulfiqar and others (2006) undertook the evaluation of oxyfuel combustion performance on a pilot-scale furnace (fired at a nominal 0.8 MWth) at the IHI-test facility in Japan. Three Australian coals were selected for experiments under two different combustion conditions, air-firing and oxy/recirculated flue gas (RFG) firing, with measurements made on ash character and particle size distribution. They found that the chemical compositions or size distribution of fly ash did not differ significantly when produced in oxyfuel combustion and air combustion.

In another pilot-scale based study of the effects of oxy-firing on ash deposition, a comprehensive suite of ash deposits was collected during oxyfuel combustion trials on the 1 MW combustion test facility (CTF) at E.ON UK. Combustion parameters that were investigated included firing mode (air or oxyfuel), excess oxygen level, proportion of air staging and degree of oxygen enrichment. The deposit samples were characterised by scanning electron microscopy and X-ray

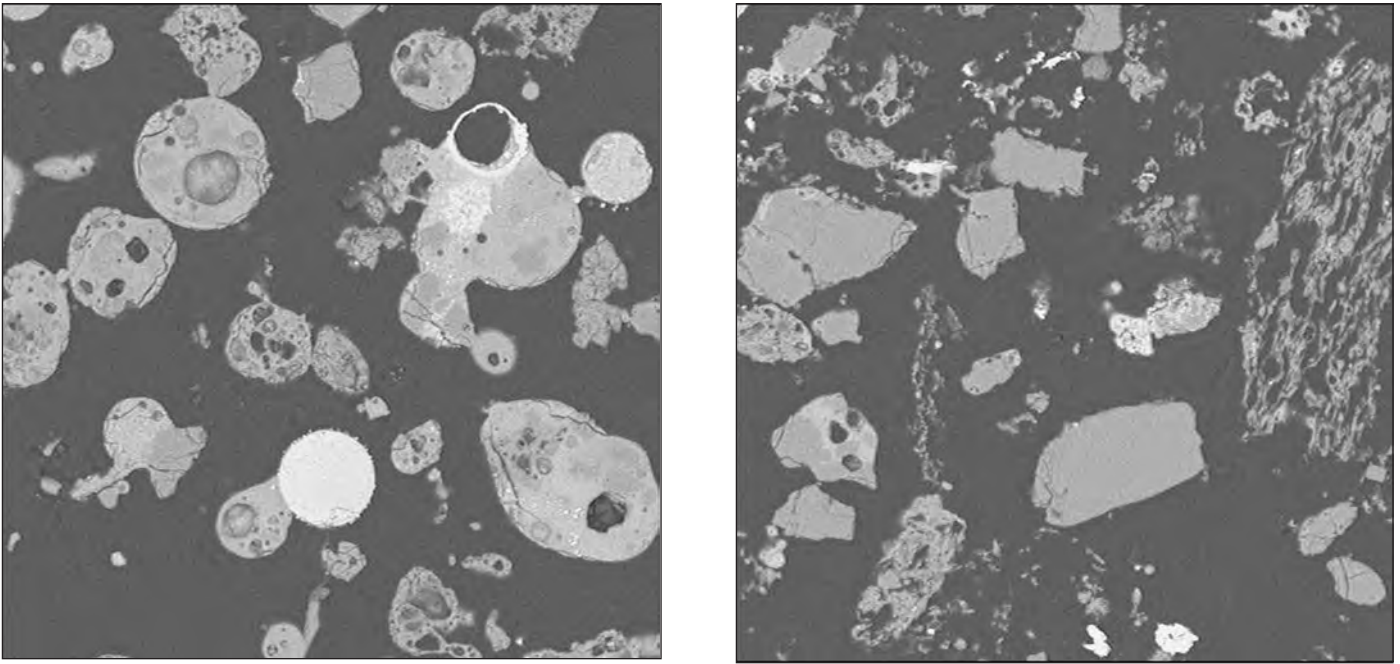


Figure 13 Typical particles within CTF deposits (left – air-fired; right – oxy-fired,) (Wigley and Goh, 2008)

diffraction (Wigley and Goh, 2008). The workers concluded that for oxy-firing, compared to air-firing, coal minerals showed the same transformations, but to a lesser extent because of lower flame temperatures (Figure 13). There is some evidence that carbonates may have persisted through the flame.

In a large collaborative international study led by Doosan Babcock, (OxyCoal-UK Phase 2) it is planned to study the effects of oxyfuel combustion on ash properties, making use of large pilot scale work carried out during the first phase of the project (Seneviratne, 2009).

6.2 Summary

New pulverised coal fired units are generally larger and cooler than their precursors and this will affect ash properties. It is likely that ash will be less glassy and contain more mineral residues than current materials. Carbon capture related technologies such as oxyfuel combustion present a radically changed combustion environment. The early experimental nature of the work means that very few characterisations of ash from plant larger than laboratory scale have been undertaken. The impact of the oxyfuel environment on the ash is unclear at this time, but this is a very important area for future ash developments.

7 Ash utilisation in the construction sector

7.1 Key properties of ash and cement formulations

Previous chapters have described the impact of different situations on ash quality with respect to utilisation. The following sections deal with specific issues for the construction sector, the largest user of ash.

Fly ash can be divided into two specific types in relation to its use as a cement component in concrete:

- Low-lime fly ash which is produced from bituminous coal and anthracites. The resulting ash is pozzolanic and can be used with Portland cement or another ‘activator’ to give cementitious products. This is, by far, the most common ash type.
- High-lime fly ash produced from brown coal (or lignite) combustion. This fly ash exhibits cementitious properties, as it contains free lime as well as pozzolanic phases. This ash is common to regions of the world where lignite is the dominant coal source such as Canada, the USA, Germany, Greece, Poland and Russia.

There are several properties of fly ash that are important with respect to ash use in concrete formulations, specifically:

7.1.1 Loss on ignition (LOI)

The LOI is used as an indicator of the unburnt coal residue in fly ash, or carbon in the case of co-combustion material, and reflects the combustion conditions under which the material was produced. The LOI can influence the colour, water demand, fineness, with performance in concrete generally becoming poorer as LOI increases. Limits are, therefore, normally set for LOI in national standards. The European Standard EN450-1:2005 specifies LOI in three categories:

- Category A, not greater than 5.0%;
- Category B, between 2.0 and 7.0%;
- Category C, between 4.0 and 9.0%. Unburnt residual carbon can also significantly influence air-entrainment in concrete, and has restricted its use in highway structures in temperate climates.

7.1.2 Sulphate content

The presence of sulphate in fly ash is reported to cause expansion when used in concrete due to ettringite formation and, as a result, its content is also limited in standards. EN450-1:2005 sets the limit for sulphate content, expressed as sulphuric anhydride (SO_3), at 3.0% by mass.

7.1.3 Alkali content

The alkalis arising from Portland cement and fly ash can

sometimes react with certain silicate aggregates, leading to the formation of an expansive gel, which in time can cause cracking and degradation of concrete. A limit on total alkali content as Na_2O (equivalent) of 5.0% by mass is specified in EN450-1:2005.

7.1.4 Water requirement

Water requirement is generally considered to be a good indicator of fly ash ‘quality’; that is, ashes that reduce water requirement compared to Portland cement may be expected to perform well in concrete, as a cement component. The water requirement (applicable to fineness Category S to EN450-1:2005) is measured using a standard flow test and mortar, with 30% fly ash in cement. Category S fly ash (with fineness less than 12.0% retained on a 45 μm sieve) should have a water requirement of not greater than 95% of its Portland cement mortar reference. It has been argued that the test is not sensitive to changes in fly ash quality, particularly when its inherent variability is considered.

7.1.5 Activity index

EN450-1:2005 uses an activity index test to provide a measure of fly ash reactivity. This adopts a fixed water/cement ratio and 25% fly ash by mass as a cement component in the mortar, with mixes therefore having potentially variable flow. In this test, fly ash mortar strength is expected to be at least 75% of the Portland cement reference mix at 28 days, and 85% by 90 days.

7.1.6 Fineness

Fineness is probably the single most important characteristic of fly ash in relation to its use in concrete, with the basic rule being ‘the finer the better’. Fineness is widely specified as a limit on the mass of material retained on a 45 μm sieve. Although a full particle size distribution is probably more indicative of quality, the simplicity of the 45 μm sieve test means that a full particle size distribution is rarely specified. EN450-1:2005 defines two categories of fineness:

- Category N – the fineness should not exceed 40.0 wt% retained on a 45 μm sieve and should not vary by more than 10 percentage points from the declared value;
- Category S – the fineness should not exceed 12.0 wt%. The fineness variation (10.0 percentage points) does not apply in this case.

7.1.7 Concrete durability

Permeation properties

The permeation properties – that is, absorption, permeability and diffusion – are the principal mechanisms by which aggressive liquids, ions and gases pass into concrete. These

are indicative of the concrete microstructure and durability performance. The use of fly ash generally improves these properties, making concrete more resistant to environmental deterioration. The pozzolanic reactions convert free lime in concrete to cementitious gel, blocking pores, enhancing permeation and reducing the level of portlandite that can be leached. The only negative issue arising from this is that it results in a lower pore fluid alkalinity. While this reduces the risk of alkali-aggregate reaction, it may increase the rate of carbonation.

Carbonation

As noted above, the pozzolanic reactions result in reduced pore fluid alkalinity and this effect is not wholly offset by the improvement in concrete permeation properties. Overall, the rate of carbonation may be slightly higher than Portland cement concrete of equal strength, depending on the mix proportions. There are no reported instances of these effects causing any problems in correctly specified and compacted concrete in real structures.

In turn, concrete specifications for durability do not distinguish between Portland cement and fly ash concrete, although care has to be exercised at higher fly ash contents; say, >40% by mass. Rates of reinforcement corrosion in carbonated concrete are generally similar between fly ash and Portland cement concretes, where the main controlling factor is the environmental conditions, in particular relative humidity.

Chloride ingress

Chloride from the environment, either de-icing salts or in a

coastal exposure site, can penetrate concrete and when present in sufficient quantities at the site of reinforcement lead to corrosion, which can threaten the serviceability of structures. Work investigating the use of fly ash concrete indicates that the material is effective in reducing rates of chloride transmission (by absorption and diffusion). The main benefits of fly ash in this respect are due to;

- (i) its high alumina content and ability to bind chloride;
- (ii) the large number of fine particles to adsorb chloride;
- (iii) the decreased interconnected porosity and pathways into concrete.

Furthermore, it appears that it is the quantity of fly ash rather than its quality that is the critical factor influencing resistance to chloride ingress. Other work suggests that at a given level of chloride in concrete, at the depth of reinforcement, less corrosion may occur in concrete containing fly ash.

Sulphate attack

The use of fly ash improves the sulphate resistance of concrete and can be used in all but the most extreme exposure conditions.

7.2 Impact of cofiring on construction product properties and performance

Saraber and van den Berg (2006), reported an extensive study into the effects of a range of co-combustion ashes produced at full- and pilot-scale on cement formulations. The ashes and their source fuels are listed in Table 20.

Table 20 Co-combustion ashes – sources and composition (Saraber and van den Berg, 2006)

	Coal	Cofired fuel	Co-combustion, wt%	
			fuel	ash
PD*	Paso Diablo	poultry dung	36	56
SRF*		solid recovered fuel	34	39
MBM+17	blend	meat and bone meal	10.2	11
		biomass pellets	4.2	5.4
		poultry dung	1	0.9
		soot paste	0.3	0.0
		sewage sludge	0.1	0.1
		total	15.8	17.4
PS+24	blend	paper sludge 1	4.4	18
		paper sludge 2	1.5	5.1
		wood	2.9	1.0
		total	8.8	24.1
WHP9		wheat husk pellets	19.0	9.0
PK		palm kernels	19.6	9.7
* co-combustion experiments at pilot scale				

The fly ashes generated during the co-combustion experiments were tested according to EN450 (2005) and are supplemented by the following additional analyses:

- The elemental composition with respect to Al, Ca, Fe, K, Mg, Na, P, S, Si and Ti was analysed by X-ray fluorescence or inductively coupled plasma (ICP) after total digestion.
- The amount of reactive SiO₂ was determined in accordance with EN196-2 (Methods for testing cement; Chemical analysis of cement; 1994). Analysis was carried out by determining the amount of SiO₂ that is dissolved when fly ash is boiled for four hours in a solution of potassium hydroxide.
- The amount of soluble phosphate was analysed according to the method that is described in EN450 (2005).
- The setting time of the cement formulation was tested in accordance with EN450 (2005).

An experimental cascade approach was used to assess the mineralogical composition. This approach consisted of the following steps (Figure 14):

- X-ray diffraction (XRD) of the original sample;
- dissolving and removing the fraction that is soluble in acid (HCl). The concentration of macro-components in the eluate is analysed;

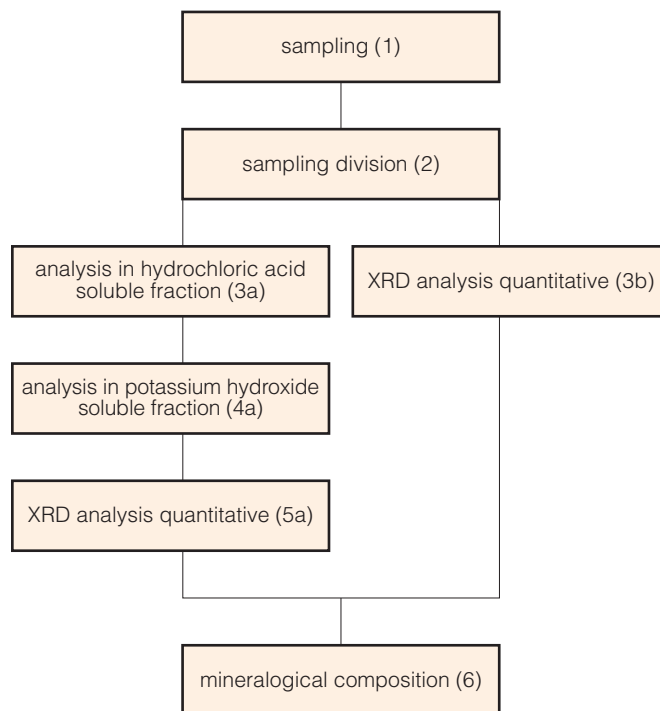


Figure 14 Cascade approach for mineralogical analyses of fly ashes (Rietveld, 1969)

Table 21 Chemical composition of fly ashes (Saraber and van den Berg, 2006)

	SRF 39	PD 56	REF (SRF39 PD56)	MBM+17	PS+24	REF (PS+24)	WHP9	PK10
Al ₂ O ₃	17.0	10.4	19.4	25.1	21.7	23.7	20.2	27.9
CaO	8.1	22.5	3.6	9.1	7.5	2.2	4.8	4.7
Fe ₂ O ₃	7.6	4.0	6.7	4.5	7.5	9.0	5.4	5.2
K ₂ O	2.1	7.0	1.8	1.6	2.2	2.0	3.7	1.8
MgO	2.5	3.2	2.7	1.3	1.6	1.4	4.5	1.7
Na ₂ O	1.2	1.1	0.7	0.8	0.3	0.3	0.7	0.4
P ₂ O ₅	0.5	5.8	0.2	4.0	0.8	0.6	5.2	2.8
SiO ₂	53.5	34.0	58.2	47.1	52.0	54.4	48.7	48.3
SO ₃	2.4	7.1	1.8	0.3	0.4	0.3	0.7	0.6
TiO ₂	1.3	0.4	0.9	1.3	0.9	1.1	1.0	1.7
LOI	25.1	11.9	35.6	4.6	4.0	5.3	4.0	2.7
Na ₂ O-eq	2.6	5.7	1.9	1.9	1.7	1.7	3.1	1.6
Cl	0.11	0.99	<0.01	<0.01	<0.08	<0.08	<0.01	0.01
free CaO	0.50	10.57	0.20	1.02	0.05		0.43	0.68
Free/total CaO	0.06	0.47	0.06	0.10	0.01		0.08	0.13
Soluble P ₂ O ₅	–	–	–	19–26	32–49	34–37	21–22	<0.002
Reactive SiO ₂	27.1	14.7	33.6	33.5	26.4	23.0	31.7	(43)
Al ₂ O ₃ /SiO ₂	0.32	0.31	0.33	0.53	0.42	0.44	0.42	0.58
Al ₂ O ₃ + Fe ₂ O ₃ + SiO ₂	78.1	48.4	84.3	76.6	81.2	87.1	74.4	81.3

All concentrations, with exception of LOI, are normalised to LOI=5% to allow comparison

- dissolving and removing the fraction in the residue that is soluble in potassium hydroxide (both steps are the same as for the determination of the amount of reactive SiO₂). The eluate is analysed for the macro-components. This gives the bulk composition of the glass phase of fly ash;
- XRD analysis of the residue from both steps. In different cases Rietveld's method (1969) was used to quantify the patterns.

The composition of the fly ashes, the mineral phases identified in them, and the chemical composition of the glassy phases identified are given in Tables 21 to 23, respectively.

Fly ash from co-combustion of SRF has a decreasing activity index after 28 and 91 days (Figure 15). This was explained by the authors as the reduction of the amount of reactive SiO₂/glass content (Figure 16). The incorporation of SRF

co-combustion ash was also found to retard the setting time. As can be seen in Figure 17, the initial and final setting time increases in contrast to that of fly ash from the co-combustion of demolition wood and poultry dung. The authors suggested that this may be caused by the high concentrations of lead and zinc, totalling 1837 mg/kg. However, the sample containing fly ash from the co-combustion of demolition wood has an even higher concentrations of both elements (totalling 7478 mg/kg), but exhibits no retardation. They suggested that speciation of lead and zinc may play a key role and that further research was required.

For the samples generated from fly ash from the co-combustion of 56 wt% poultry dung, the activity index showed a positive relation with increasing co-combustion percentage. However, the glass content/amount of reactive SiO₂ decreased significantly. At the same time, the amounts of sulphates and free lime increased. These reactive components

Table 22 Mineralogical composition of fly ashes (Saraber and van den Berg, 2006)

	SRF 39	PD 56	REF (SRF 39 PD56)	PS+24	REF (PS+24)	MBM+17	WHP9	PK10
Amorphous phases	yes	yes	yes	yes	yes	yes	yes	yes
Unburnt matter	yes	yes	yes	yes	yes	yes	yes	yes
Anhydrite	yes	yes	yes					
Free CaO	yes	yes	yes					yes
Quartz	yes	yes	yes	yes	yes	yes	yes	yes
Hematite	yes	yes	yes	yes	yes	yes	yes	possible
Mullite	yes	yes	yes	yes	yes	yes	yes	yes
Calcite								
Magnetite				yes	yes		yes	possible
K ₂ SO ₄		yes						
Langbeinite		yes						

Table 23 Chemical composition of the glass phase (Saraber and van den Berg, 2006)

	SRF 39	PD 56	REF (SRF 39 PS56)	PS+24	REF (PS+24)	MBM+17
Al ₂ O ₃	20.3	16.5	20.9	22.2	29.1	21.7
CaO	2.5	1.2	0.9	5.0	0.0	4.6
Fe ₂ O ₃	4.0	3.9	3.3	4.2	0.7	3.2
K ₂ O	1.8	3.5	1.4	3.1	2.5	2.5
MgO	2.0	1.8	1.9	2.0	0.0	1.4
Na ₂ O	0.9	0.7	0.5	0.4	0.4	1.1
P ₂ O ₅	0.2	0.2	0.2	0.4	0.4	1.3
SiO ₂	68.2	72.2	71.0	62.0	66.8	63.5
TiO ₂	–	–	–	0.8	0.1	0.7

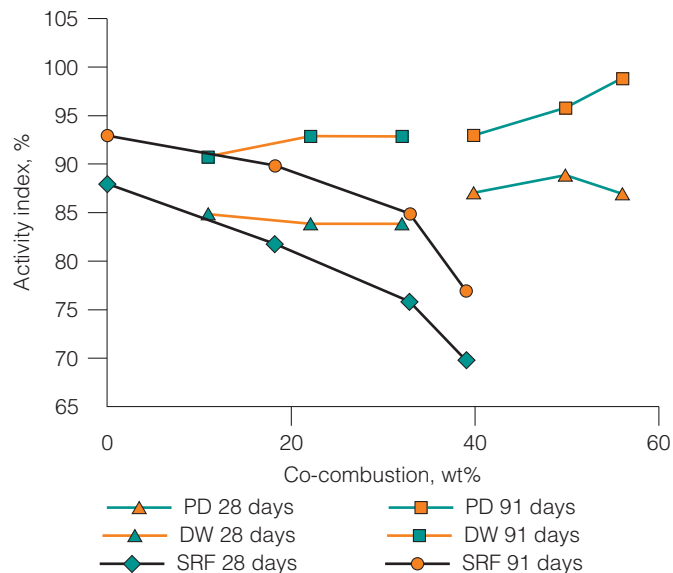


Figure 15 Activity index after 28 and 91 days in relation to cofired fuel and co-combustion percentage (Saraber and van den Berg, 2006)

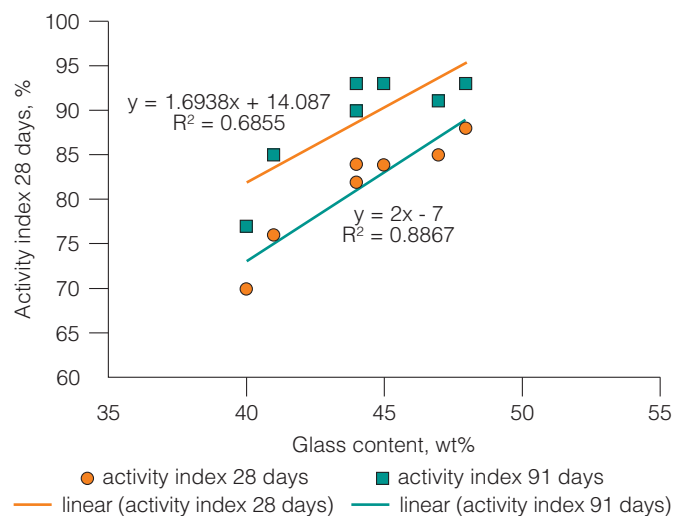


Figure 16 Activity index as function of glass content for fly ashes from co-combustion of SRF and demolition wood (Saraber and van den Berg, 2006)

are believed to over-compensate the reaction of the glass content by participating in ettringite formation, as indicated by XRD analysis. The setting time was unchanged.

In fly ash from co-combustion of 23% m/m paper sludge/wood, it was expected that the free lime content would be high due to the high calcite content in the paper sludge. However, the lime content in the generated fly ash was very low. From the analyses of the bulk glass composition it is clear that the CaO content increases in relation to the reference fly ash. A CCSEM picture of this fly ash is presented in Figure 18. CCSEM analyses showed the

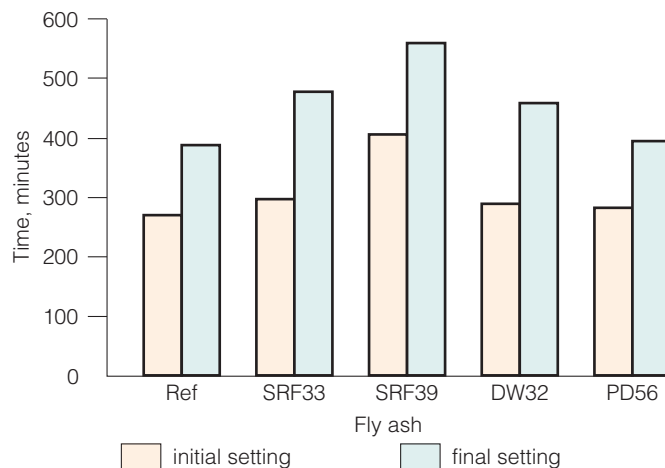


Figure 17 Setting time in relation to cofired fuel and co-combustion percentage (Saraber and van den Berg, 2006)

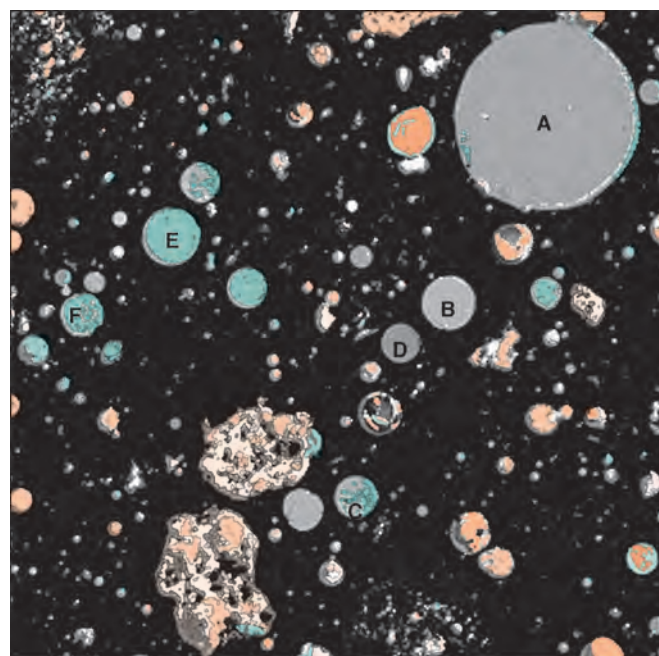


Figure 18 CCSEM picture of PS+24 showing the distribution of Ca (Saraber and van den Berg, 2006)

presence of spherical (glassy) particles. The particles marked with A, B, C, and F are aluminosilicates with about 41–53% CaO, which is, on average, comparable to that of the paper sludge. This indicates that a second glass phase is introduced, originating in the melting and fusion reaction of kaolinite and calcite in the paper sludge. It is suggested that the distribution of these minerals in the secondary fuel made this synthesis possible. The performance of mortar and concrete made with

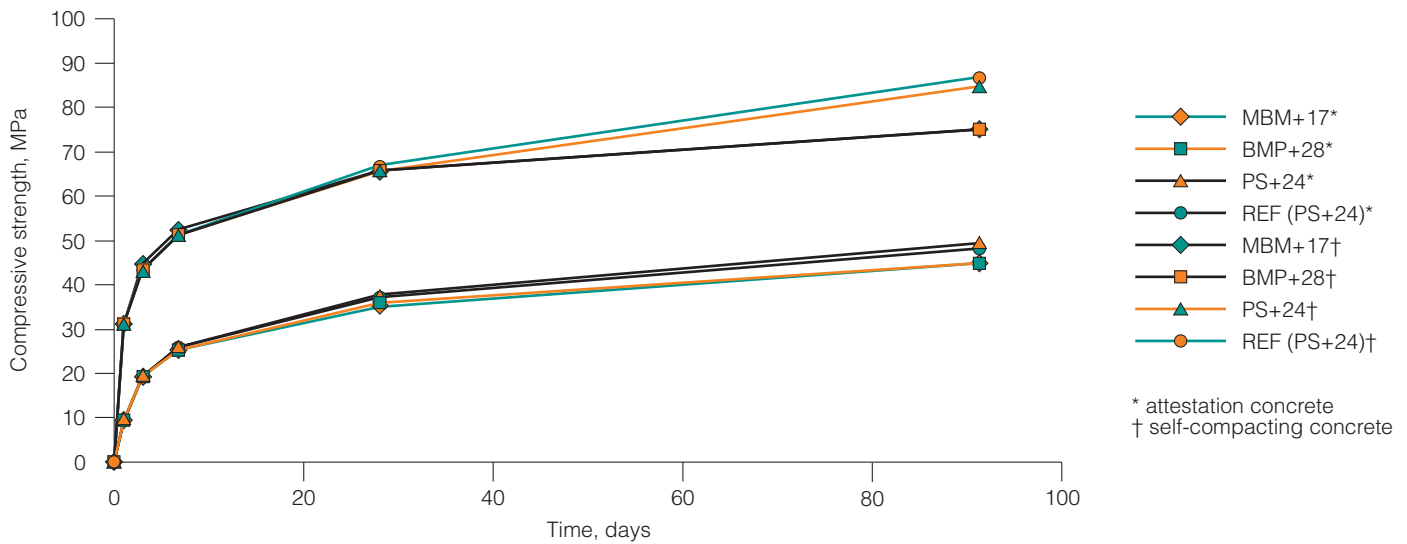


Figure 19 Development of compressive strength (Saraber and van den Berg, 2006)

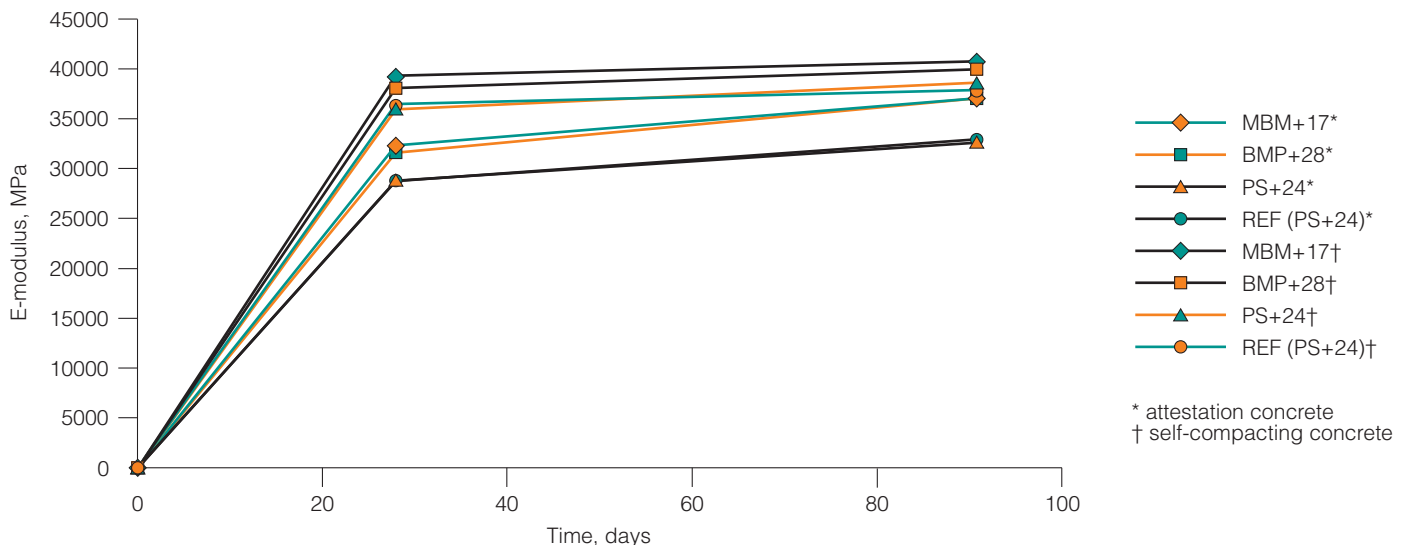


Figure 20 Development of E-modulus (Saraber and van den Berg, 2006)

Table 24 Concrete mixtures (in kg/m ³ unless otherwise indicated) (Saraber and van den Berg, 2006)		
Component	Attestation concrete	Self-compacting concrete
Cement CEM I 42.5 R	210	350
PFA	100	150
Water, L/m ³	165	170
Sand	713	639
Gravel	1163	1045
D _{max} , mm	31.5	
Water/cement ratio	0.53	0.34
Type admixture (wt% on cement)	–	Glennium, 0.34 wt%
Volume of fines, L/m ³	146	208

this fly ash was comparable to that of the reference samples. Figures 19 and 20 show the development of compressive strength and E-modulus; the mix composition of the concrete is presented in Table 24.

The fly ash from the co-combustion of 13 wt% meat and bone meal (in combination with biomass pellets and some other fuels) showed high contents of calcium and phosphorus. CCSEM observations indicate the presence of phosphate in combination with Ca as well as Fe in combination with Ca and Mg. The presence of P in low soluble minerals such as calcium phosphate (a conversion product of apatite) may explain why this fly ash has a normal setting behaviour.

The P₂O₅ content present in the glass phase is only a minor part of the total 4.3% P₂O₅ in the fly ash which suggests that the fusion reactions (due to collision) between mineral matter from coal and meat and bone meal are limited, otherwise the glass phase would show enrichment of P₂O₅.

The compressive strength of concrete sample MBM+17 was

somewhat lower than concrete with fly ash REF (PS+24). However the E-modulus of the former is higher than the latter. The activity index of MBM+17 met the requirements of EN 450.

The fly ash from co-combustion of 9 wt% wheat husk pellets or 10 wt% palm kernels showed an increase of the concentration of potassium and phosphorus. The performance of mortar made with these fly ashes met the limits of EN450 and the ETA. Cement formulations prepared with these fly ashes showed no sign of retardation.

Jones and others (2006) undertook an intensive investigation into the characteristics of co-combustion ashes in cement formulations. A total of eight co-combustion fly ash samples and where available, their coal-fired references, were obtained from the UK, Europe and USA; all were from full-scale electricity generation operations (Table 25). The reference ashes were produced under similar combustion conditions to the co-combustion fly ash materials.

Table 25 Co-combustion fuels (Jones and others, 2006)

Ash code	Co-fuel material	Co-fuel/Coal ratio, wt%
CS*	Cacao 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	Sawdust	10.0
SS*	Sewage sludge	5.0
W	Wood chips	5.0

* Materials with reference coal-fired fly ash test samples, denoted by R: for example CSR is reference for CS

The main compositional characteristics of the co-combustion and reference ashes are given in Table 26. The effect of co-combustion on ash composition, at the levels used, was generally negligible, although the wood chip co-combustion ash had 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. Co-combustion ashes tended to have a slightly higher CaO content compared to the reference materials. In addition, sawdust and paper sludge ashes gave the highest CaO contents measured. In terms of alkali contents and sulphates, most co-combustion ashes gave similar values compared to their references, except for cacao shells, where the co-combustion material gave minor increases in some components.

Table 27 Effects of co-fuelling on fineness and loss on ignition (Jones and others, 2006)

Fly ash	Fineness, % ret 45 µm	Loss-on-Ignition, wt%
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
<i>MBR</i>	<i>25.8</i>	<i>6.4</i>
CW	12.2	6.7
PL	29.2	5.9
<i>PLR</i>	<i>25.3</i>	<i>4.9</i>

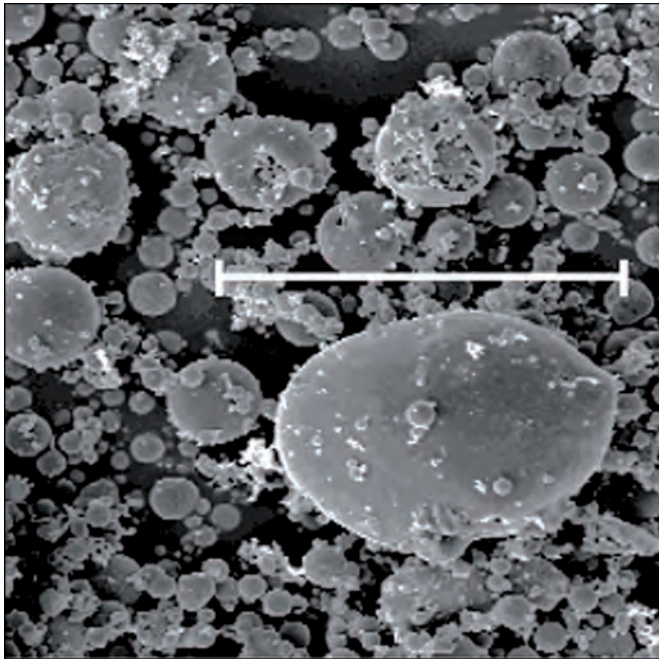
Characteristics in italics are for the reference ashes

Table 26 Key characteristics of the co-combustion and reference ashes (Jones and others, 2006)

Oxide, wt%	Fly ash type									
	CS	CSR	MB	<i>MBR</i>	PL	<i>PLR</i>	PS	SS	SSR	W
SiO ₂	44.05	<i>44.75</i>	46.08	<i>46.64</i>	46.50	<i>47.85</i>	43.30	47.98	<i>47.69</i>	67.33
Al ₂ O ₃	22.56	<i>23.23</i>	25.38	<i>25.84</i>	23.22	<i>24.00</i>	23.02	29.29	<i>29.92</i>	12.30
Fe ₂ O ₃	6.16	<i>6.12</i>	4.85	<i>4.61</i>	6.89	<i>6.89</i>	6.16	5.24	<i>5.07</i>	4.51
CaO	3.93	<i>3.49</i>	3.46	<i>3.16</i>	3.33	<i>2.88</i>	4.92	3.91	<i>3.09</i>	2.04
Na ₂ O	2.27	<i>1.83</i>	0.51	<i>0.50</i>	0.63	<i>0.72</i>	0.96	0.40	<i>0.31</i>	0.43
K ₂ O	1.96	<i>1.75</i>	0.60	<i>0.58</i>	0.86	<i>0.85</i>	1.63	1.11	<i>1.28</i>	0.55
SO ₃	1.21	<i>0.84</i>	0.36	<i>0.27</i>	0.66	<i>0.44</i>	0.38	0.93	<i>1.61</i>	0.72

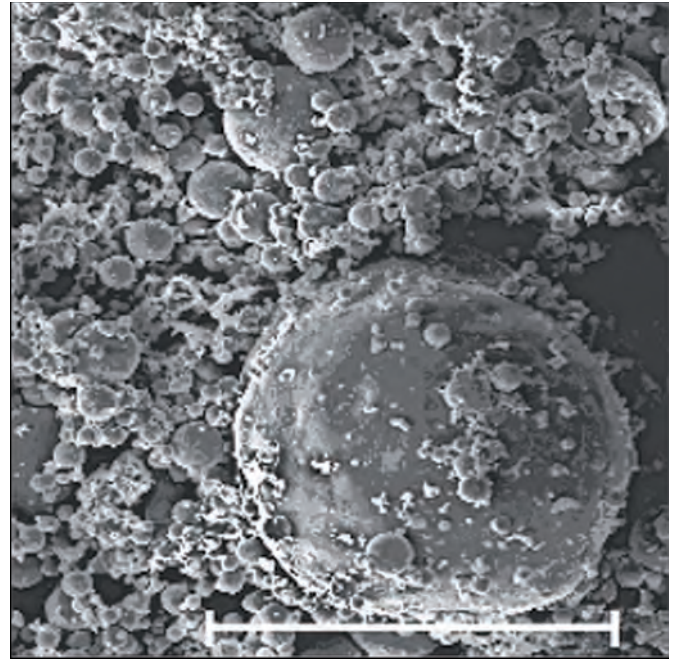
Characteristics in italics are for the reference ashes

a) reference ash

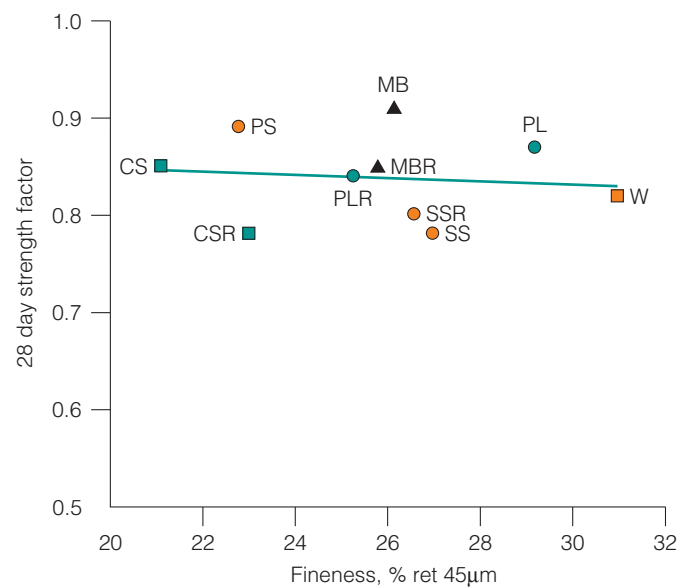
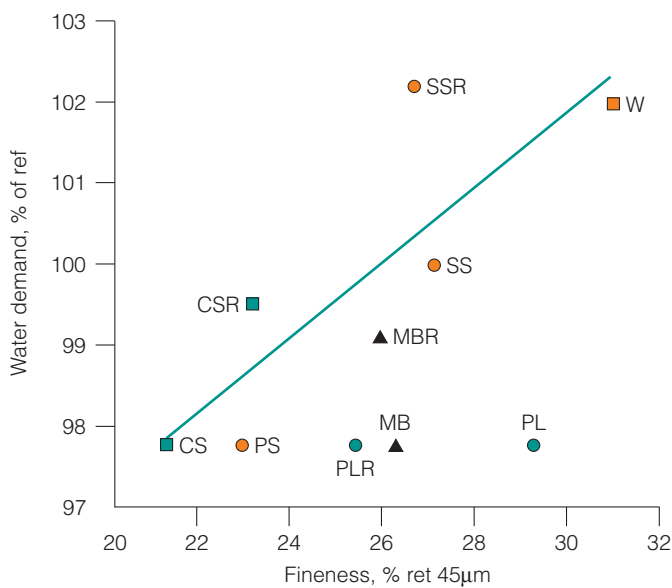


scale bar = 100 μm

b) co-combustion with cocoa shell



scale bar = 100 μm

Figure 21 Morphologies of reference and co-combustion fly ash (Jones and others, 2006)**Figure 22 Water demand and strength factors for the reference and co-combustion ashes (Jones and others, 2006)**

The effects of co-combustion on ash fineness and LOI are given in Table 27. All of the ashes were in the range 20–35% retained on a 45 μm sieve, conforming to BS EN450, 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.

Analysis of the particle size distribution showed that there was, typically, an increase in the number of coarse (larger) particles above 10 μm. It is suggested 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 21.

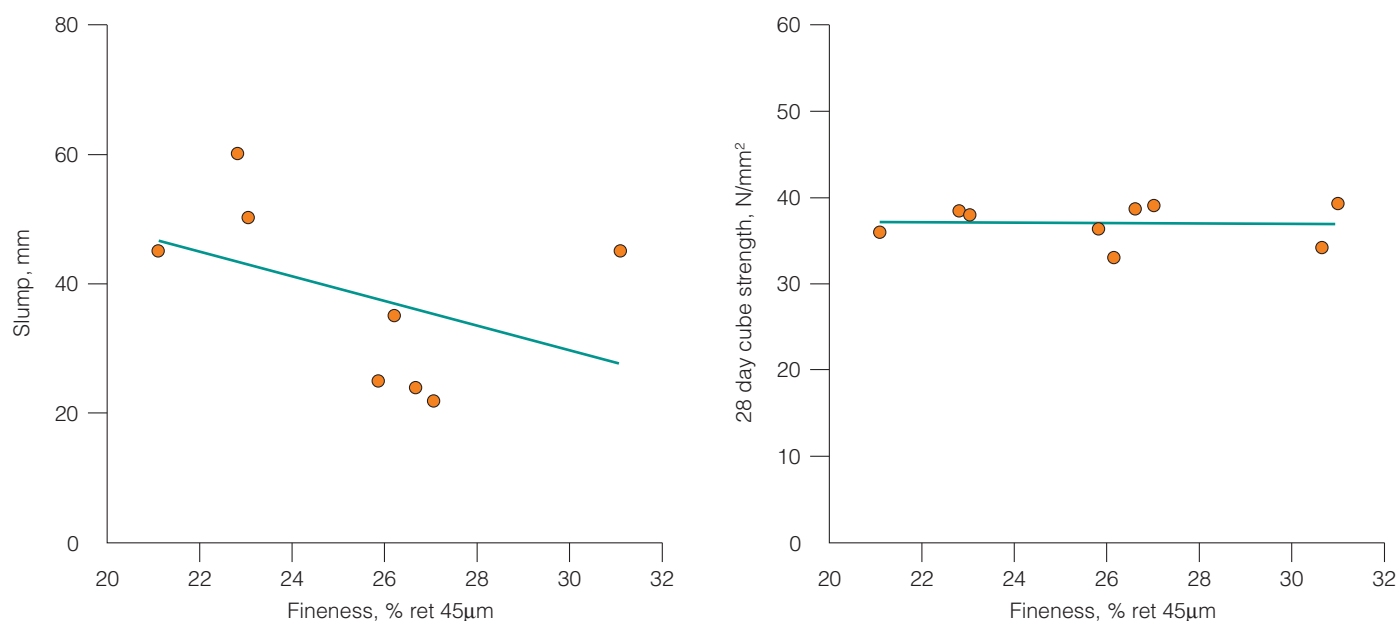
Compression strength factor tests were carried out using the material from water demand tests cast in prism moulds (that is the material with water contents giving equivalent flow to the reference Portland cement). The results from both tests are given in Figure 22.

The dependence of water demand on fineness was no different

Table 28 Test concrete mix constituent proportions for the co-combustion and reference ashes (Jones and others, 2006)

Test mix	W/C ratio	Free water	Concrete mix proportions, kg/m ³				
			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 superplasticising admixture to achieve target 75 mm nominal slump

**Figure 23 Effect of co-combustion ash on consistence and standard cube strength for the fixed water/cement ratio concrete test series (Jones and others, 2006)**

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 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.

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 water/cement 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, that is 35 and 50 N/mm² and were tested for aspects of durability. Details of the test mix proportions are given in Table 28.

The consistence (slump to BS EN12350, Part 2) and standard cube strength (to BS EN12390, Part 3) data for the fixed water/cement ratio test series are given in Figure 23.

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 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/mm² (see Table 28). Accelerated tests were used for both carbonation, that is 4% CO₂, 60% RH and 20°C (Dhir and others, 1985), and chloride ingress, that is 2-cell, 5M NaCl at 12v DC according to Dhir's method (1990), typical results for which are given in Table 29.

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.

Wardle and others (2009) investigated the hydration behaviour of fly ash-Portland cement (PC) blended cements, comparing conventional coal fly ash with that obtained from cofiring of coal with biomass (palm kernel expeller). Calorimetry, thermal analysis and electron microscopy were used to investigate the compositions and microstructures of

the hydrated pastes and to link structural composition to the materials' engineering properties (strength development and workability). The results showed that, in the short term, the behaviour of the cofired material was comparable with that of conventional coal fly ash, there being no discernable differences between the two systems.

The elemental compositions of the starting materials were determined by x-ray fluorescence (Table 30). Mixes were prepared in the ratios Portland cement:sand:water 1:3:0.5, with replacement of the Portland cement by 40% of either the conventional or cofired fly ash where necessary. Forty per cent replacement was chosen to exacerbate any differences between the two fly ash samples. The mortar samples were then investigated by the following methods – workability via the flow table method, compressive strength, scanning electron microscopy, thermal gravimetric analysis and isothermal calorimetry.

Table 29 Results of the accelerated carbonation and chloride-ingress tests (Jones and others, 2006)

Fly ash	Accelerated* carbonation depth, mm		Accelerated† chloride diffusion coefficient, cm ² /s x 10 ⁻⁹	
	35 N/mm ²	50 N/mm ²	35 N/mm ²	50 N/mm ²
CS	31.0	11.0	12.0	3.6
CSR	30.5	11.0	8.5	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

* after 30 weeks exposure

† exposure period sufficient to achieve steady state

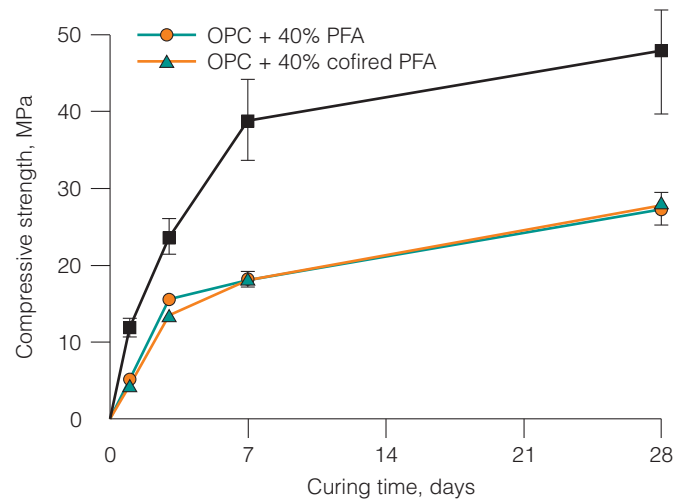


Figure 24 Compressive strength development of the various mixes (Wardle and others, 2009)

Table 30 Elemental composition of the materials used to investigate cofiring effects on ash quality (Wardle and others, 2009)

Oxide	PC, %	PFA, %	Cofired PFA, %
SiO ₂	21.0	49.8	51.46
Al ₂ O ₃	4.63	26.4	19.32
Fe ₂ O ₃	2.26	9.3	5.49
CaO	65.6	1.4	4.29
MgO	1.18	1.4	1.71
SO ₃	2.69	0.8	9.36
Na ₂ O	0.16	1.5	1.02
K ₂ O	0.78	3.5	2.34
Cl	0.01	0.01	0.04
LOI	0.99	4.9	12.36

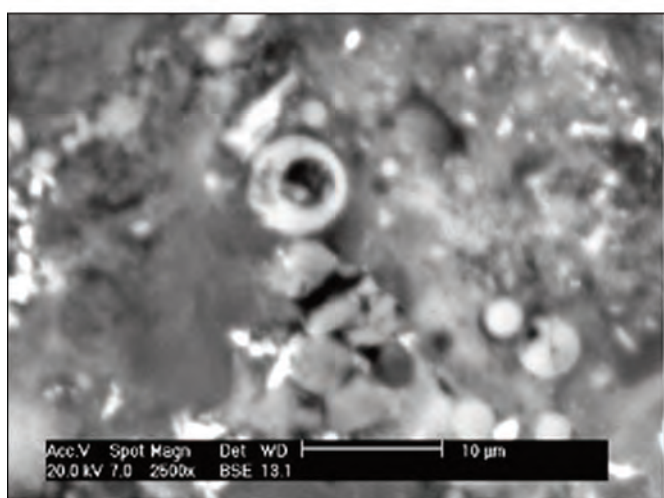
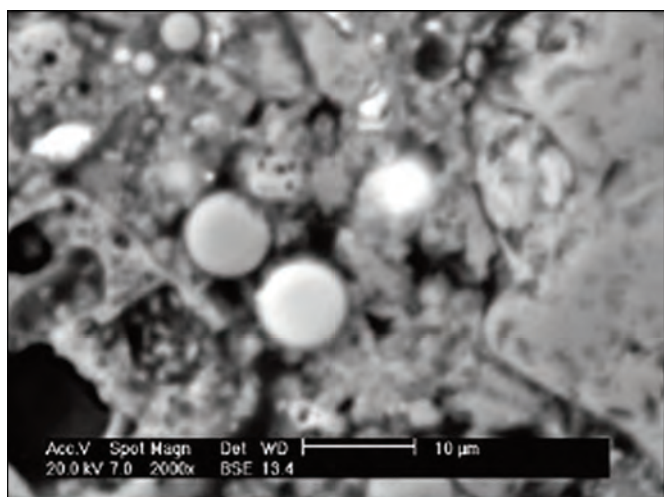


Figure 25 SEM micrographs of the blended cement mortars, (cofired fly ash left conventional fly ash right) (Wardle and others, 2009)

Figure 24 shows the strength development of the three mixes. Whilst the Portland cement mortar was considerably stronger, there were no discernible differences between the two fly ash-containing mixes. Figure 25 shows SEM images obtained from the two blended cements, comparing cofired fly ash with conventional fly ash. There is little difference between the samples, with similar sized spherical fly ash particles distributed throughout the matrix. However, in the image from the sample containing cofired fly ash there are a number of dark features, possibly due to the slightly elevated levels of carbonaceous material in the fly ash.

Johnson and others (2010) studied conventional coal fly ash and two coal-biomass fly ashes obtained at a thermoelectric power station (Atikokan, Ontario) from combustion of undiluted lignite coal and co-combustion of lignite coal with up to 66% wood pellets (on a thermal basis). Fly ashes were characterised and analysed for use as cement admixtures. Co-combustion did not markedly change the fly ash composition, owing to an extremely low ash content of wood pellets compared to lignite coal; toxic metals and minor elements were within ranges reported for other coal fly ashes.

All fly ashes had losses on ignition (LOI) <1 wt% and therefore complied with ASTM LOI regulations for use in concrete. All fly ashes contained major amorphous phases, along with quartz and periclase. Partial substitution of cement with fly ash (up to 40 wt%) had a moderate effect on the entrained air content of mortars (up to 2.5%), but this difference vanished upon addition of air entraining agent (0.6 mL/kg of cementitious material). Substituted mortars exceeded 75% of the strength of ash-free mortar after 28 days of curing (therefore meeting ASTM requirements for strength development), and by 90 days, met or surpassed 100% of the strength of ash-free mortar. Amending mortar with 20 wt% coal fly ash or co-combustion fly ash had no effect on its durability following repeated freeze–thaw cycles when air content was kept constant. Also, no micro-mineralogical differences were observed between hydrated coal fly ash and co-combustion fly ash-amended mortars, with fly ash particles reacting with Ca ions originating from dissolution of cement clinker or calcium hydroxide.

7.3 Summary

Generally, the use of non-fossil based co-fuels result in fly ashes that are of essentially equal performance to coal fly ash, over a wide range of coal/co-fuel ratios. Morphological observations revealed that co-combustion gave minor changes in composition. Whatever differences in composition were noted were, with one or two exceptions, within the range of normal variability for power generation coal deliveries. In terms of loss on ignition, again, there were only minor differences between materials. The main properties of construction application materials did not show any difference between performance for 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.

8 Ash standards

Specifications for developed uses for coal ashes have been established in many countries. The aim of these specifications is to set minimum requirements for the performance of ash-derived products tested under laboratory conditions. Although a full review of international standards lies outside the scope of this report, the experience of European workers is useful in illustrating how existing standards may be upgraded to cover cofiring practices.

European utilities and supporting research institutes have historically led the way in co-combustion and this is reflected by the evolution of the European standards relating to ash to cover co-combustion products. The European EN450 standard was introduced in 1994 and revised in 2005 to cover the experience with co-combustion materials. The following

section describes the background to the latest revision, as reported by Saraber and others (2009).

Five years' experience with EN450-1 and EN450-2 had shown that some clauses needed improvement. In the original standards the maximum amount of fly ash from co-combustion was limited to certain amounts. Subsequent experience with fly ashes, where higher amounts of the co-fuel were used, showed that the requirements in the corresponding Common Understanding of Assessment Procedures (CUAP), were sufficient to guarantee fly ash performance in concretes, mortars, grouts and cements.

Furthermore, the opportunity was taken to propose improvements to requirements in the original specification

Table 31 Properties and requirements of fresh and hardened mortar and concrete (Saraber and others, 2009)

Phase	Property	Existing	Revised
Workability	Loss on ignition, wt%		
	Class A	≤5.0	≤5.0
	class B	2.0–7.0	≤7.0
	class C	4.0–9.0	≤9.0
	Water requirement*, %	≤95	not modified
	Fineness fraction >45 μm, wt%	≤40 (cat N)§ ≤12 (cat S)	not modified
Initial strength development	Soluble phosphate (P ₂ O ₅), mg/kg	≤100	not modified
	Total phosphate (P ₂ O ₅), wt%	–	<5.0
	Initial setting, min	2C†	not modified
Strength development	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , wt%	≥70	not modified
	Reactive SiO ₂ , wt%	≥25	not modified
	Activity index 28 days Activity index 91 days, %	≥75 ≥85	not modified not modified
Alkali silica reaction(ASR)	Total content of alkalis (Na ₂ O equivalent), wt%	≤5.0	not modified
	Reactive calcium oxide (CaO), wt%	≤10.0	not modified
Soundness/durability	Sulphuric anhydride (SO ₃), wt%	≤3.0	not modified
	Free calcium oxide (CaO), wt%	≤2.5‡	¶
	Soundness, mm	≤10	not modified
	Magnesium oxide (MgO), wt%	≤4.0	not modified
	Chloride (Cl), wt%	≤0.10	not modified

* only applicable for category S fly ash

† initial setting time of fly ash cement mix shall not be more than twice as long as the initial setting time of the test cement alone

‡ if the content of free lime is greater than 1.0 wt%, the fly ash must be tested for conformity to the requirement for soundness

§ the fineness shall not vary by more than 10% from the declared value

¶ if the content of free lime is greater than 1.5 wt%, the fly ash must be tested for conformity to the requirement for soundness

Table 32 Requirements for fly ash for fresh and hardened concrete for products containing co-combustion ash (Saraber and others, 2009)					
Phase	Requirement EN450-1	Main influence co-combustion			
		Ca	K	Mg	P
Workability	Loss on ignition				
	Water requirement				
	Fineness fraction >45 µm		x		
Initial strength development	Soluble P ₂ O ₅				xx
	Total P ₂ O ₅				xx
	Initial setting				xx
Strength development	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	x	x	x	x
	Activity index				x
Alkali silica reaction	Na ₂ O equivalent		xx		
	Reactive CaO	xx			
Soundness/durability	SO ₃				
	Free CaO	xx			
	Soundness	x			
	Total MgO			xx	
	Cl				

that had been found to be unrealistic, specifically the definition of fly ash, the loss on ignition, free calcium oxide, reactive silicon dioxide and the limits for phosphate.

The revised version of the standards incorporates the European Technical Approvals (ETA) and EU members' experience gained with fly ash in concrete. The requirements of the revised standards will result in fly ashes which will perform similarly to those conforming to EN450:2005 (Table 31). In the revised standard the minimum proportion of coal has been decreased from 80 wt% to 60 wt%. Further, the maximum proportion of ash derived from secondary fuels has been increased from 10 wt% to 30 wt%. Co-combustion may increase the content of Ca, K, P and Mg in some cases while the other macro elements (Fe, Al, Si, Na, Ti) may become diluted by the incorporation of a higher concentration of species from the co-fuel. In most secondary fuels from vegetable and animal origin the macro-elements are present in low concentrations (ash based), relative to coal. Fuels of industrial origin may be different, such as Al, Si and P in sewage sludge and Al, Si and Ca in paper sludge. The revised EN450 contains an adequate set of requirements that covers these influences (Table 32).

Based on a more detailed understanding of the impact of co-combustion on the properties and quality of fly ash it has been

Table 33 Overview of requirements in ETA, related to the life-cycle phase of concrete (Saraber and others, 2009)		
Life-cycle phase of concrete	Requirement	Value
Workability	Loss on ignition, wt%	≤5.0
	Fraction >45 µm, wt%	≤40
Initial hydration	Soluble phosphate (as P ₂ O ₅), wt%	≤0.01
	Retardation setting time, h	<2
Hydration period	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , wt%	≥70
	Reactive SiO ₂ , wt%	≥25
	Activity index, % MPa/MPa 28 days	≥75
	91 days	≥85
Durability (positive context)	Na ₂ O equivalent, wt%	≤5.0
	Reactive/free CaO, wt%	≤10.0/≥1.0
	SO ₃ , wt%	≤3.0
	Mineralogy	
	Total P ₂ O ₅ , wt%	≤5
Durability (negative context)	Free CaO, wt%	≤1.0*
	Total MgO, wt%	≤4.0
	Cl, wt%	≤0.10

possible to shift from technical regulations based on equivalent performance (initially) to a concept based on the relationship between mineralogy and performance. Table 33 presents an overview of the requirements that are adapted in European Technical Approval 05/0095 for the different phases of the development of concrete. For this approach concrete durability is considered from two viewpoints:

- Positive durability is when fly ash is used to improve the durability of concrete by reducing the risk of alkali silica reactions and sulphate attack. In these cases it is always important to keep the content of alkalis, reactive/free CaO and/or sulphate low and to meet the requirements on mineralogy and total phosphate.
- Durability in a negative context. In these cases the compounds are limited to avoid a negative influence of fly ash on durability of concrete, namely unsoundness resulting from high levels of free CaO and free MgO, or chloride induced corrosion.

The performance requirements are:

- the initial setting time shall not be more than 120 minutes longer than the initial setting time of the test cement;
- the activity index shall not be less than 75% and 85% after 28 and 91 days respectively.

The physical requirement of the ash is limited to the fineness,

Table 34 List of minerals that may be present in fly ashes (class F) (Saraber and others, 2009)		
Group	Classification	Phases
0	Non-crystalline and organic phases, always present	Amorphous phases Unburnt matter
1	Crystalline phases, nearly always present	Anhydrite (CaSO_4) Free lime (CaO) Quartz ($\alpha\text{-SiO}_2$) Hematite ($\alpha\text{-Fe}_2\text{O}_3$) Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$)
2	Crystalline phases, sometimes present	Calcite (CaCO_3) Magnetite (Fe_3O_4)
3	Crystalline phases, incidentally present	Periclase (MgO) Rutile (TiO_2) Corund (Al_2O_3) Sillimanite (Al_2SiO_3) Feldspars

namely that the fraction $>45 \mu\text{m}$ should not be greater than 40 wt%, but it is recognised that this is a relatively empirical value.

Mineralogically, only minerals that are normally found in fly ash from 100% coal are permitted (to be analysed with XRD); these are listed in Table 34. Further mineralogical requirements are:

- the amount of reactive silicon shall not be less than 25 wt%;
- the free lime content shall not be higher than 1.0 wt%, but if the LeChatelier test is passed this may be a maximum of 2.5 wt%.

Chemical requirements are:

- the P_2O_5 content shall not be greater than 5 wt%;
- the amount of soluble phosphate shall not be greater than 100 mg/kg;
- the total content of alkalis shall not be greater than 5.0 wt% (Na_2O equivalents);
- the total MgO content shall not be greater than 4 wt%. This requirement is a simplification of an old requirement to restrict the periclase content to 4 wt%;
- the sum of Al_2O_3 , SiO_2 and Fe_2O_3 shall be not be less than 70 wt%. This requirement is to ensure that enough potential glass-forming matter is present in the fly ash.

At the time of writing, the US standard for ash utilisation, ASTM C618 still required the ash to be sourced from a 100% coal feedstock. This meant that unless a local dispensation was granted, the ash from cofiring could not be used in cement formulations. This has the effect of turning a useful by-product stream into a disposal cost, with subsequent implications for the plant economics. A new task force has recently been formed to look at the issues relating to the upgrading of C618 to include cofiring ashes (Goss, 2010).

9 Environmental impacts

te Winkel and others (2007) undertook a comprehensive assessment of the technical, environmental and health aspects of the co-combustion ashes. The health and safety properties of coal fly ash from co-combustion were assessed using the KEMA-DAM (Dust Assessment Methodology) and the judgement on whether the ashes constitute a hazard was carried out according to the procedures in the European Waste Catalogue, using the proprietary KEMA TRACE MODEL. The essential methodology of KEMA-DAM is summarised in Table 35 .

The KEMA DAM procedure was applied to calculated fly ash

compositions at co-combustion in proportions of 10 wt%, dry, 30 wt%, dry and 50 wt%, dry of five selected secondary fuels. At up to 50% co-combustion of paper sludge, sewage sludge, residual wood, chicken manure and RDF of average composition, occupational exposure limits were not exceeded at an inhalable coal fly ash dust exposure of 10 mg/m³. The sum of the average concentrations of the potential carcinogenic trace elements As, Be, Cd, Co, Cr(VI) and Ni in total coal fly ash amounts in all cases to less than 40% of the limit value for carcinogenic components and mixtures of 1000 mg/kg. For the cases studied, it was concluded the co-combustion ashes could be assigned as 'nuisance dust'.

Table 35 Concise description of KEMA-DAM (te Winkel and others, 2007)

1 Acceptance maximum allowable exposure = 10 mg/m ³
2 Choice of elements to be considered
3 Determination concentrations of elements
4 Calculation concentrations of elements in the inhalable fraction
5 Determination of element's speciation
6 Determination of the choice of TLVs and conversion into elements
7 Calculation exposure per individual element
8 Calculation quotient exposure and TLV
9 Choice components with similar toxic action on the same organ system
10 Summation of results of step 8 on the basis of step 9 (addition rule)
11 Determination of which components are carcinogenic
12 Determination of concentration of elements from 11 in the total amount of dust
13 Testing result #8, criterion is <0.5 (statistic inaccuracies)
14 Testing result #10, criterion is <1 (addition rule)
15 Testing result #12, criterion is 0.1% ρ determination carcinogenicity
16 Determination whether the substances in question can be considered as a nuisance dust

10 Future directions

Future coal-fired power plant seems likely to evolve into a high-efficiency low emissions system, using technology to allow carbon capture and storage. It is probable that the plant will be designed to operate with higher levels of co-combustion feedstocks. Additionally, new clean coal technologies such as integrated combined cycle gasification plant may be built in significant numbers.

These drivers have implications for the quality and quantity of ash produced, and for the organisations that trade and use coal-derived ash. The wide-scale use of low NO_x technologies has had an adverse impact on levels of carbon in ash (LOI), although as new boilers replace old stock, this situation is likely to improve. In the meantime, a number of technologies have been developed to beneficiate fly ash by removing carbon, with very good results. However, these technologies should not be regarded as a panacea for applications in cement and concrete as the process can sometimes worsen the performance of an ash in an established application (Jones, 2010). Ash processing companies have continued to develop their technologies and an increasingly refined product stream from 'raw ash' is now becoming more commonplace and may be an important direction for the future.

Changed combustion conditions in new plant, whether for NO_x control or as a consequence of technologies such as oxyfuel combustion, represent a 'great unknown'. Potentially, these changes could modify the nature of ash fundamentally with, as yet, largely unknown implications for long established uses. This is considered to be an area warranting detailed study.

Newer coal utilisation technologies such as CFBC and IGCC are becoming more established, particularly CFBC and with an increased installed capacity, will generate an increasingly large ash stream. While applications for these materials have been researched and demonstrated, they are fundamentally different in character to pulverised coal ash and should not be regarded as direct replacements.

An area that is considered likely to see further expansion, based on its track record to date is the cofiring of coal with a range of opportunity fuels. Cofiring at levels of 20% coal replacement and higher have been shown to be extremely successful, and workers in this sector are now looking to increase the level of cofiring to levels as high as 80% coal replacement (Kiel and others, 2009). At these scales, the composition of the resulting ash becomes increasingly influenced by the composition of the co-fuel, until at the higher levels, and for the higher ash co-fuels, it is dominated by the non-coal component. As with the new technologies, the composition of these high-level cofiring ashes may be very different from 'pure' coal ash and may, or may not, be suitable for established uses. Work in this area is required to ensure that suitable technological solutions are available for the industry built up around coal ash. The body of work that

exists based on the utilisation of ash from 'pure' biomass combustion may be a good starting point.

II Conclusions

The markets for ash are important to the economics of power generation and to a number of industries that have been developed to promote ash use, particularly in the construction sector where large quantities of ash are used. Ash utilisation is a mature market and is covered by relevant product legislation, international standards and codes of practice.

During the last two decades a number of changes have occurred in the coal-fired power generation sector that have affected ash production, and trends for the future use of coal are likely to have a continuing impact on ash in respect to quality and quantity.

The cofiring of coal with a wide range of different co-fuels has been demonstrated successfully. Through interactions in the solid and gaseous phase, species derived from the mineralogy of the coal and co-fuel respectively coalesce to give rise to a hybrid fly ash. The composition of the cofiring fly ash tends to be dominated by the composition of the coal, as most co-fuels have a relatively low ash content. However, in some cases, a co-fuel may be rich in a specific component, for example vanadium and nickel in petcoke, and care must be taken to ensure that these do not impact adversely on the use of the ash, or on its environmental impact. In most cases reported in the literature, adverse effects are rare and the cofiring ash may be used without penalty, at co-fuel levels up to 20 wt%.

The change in combustion environment associated with NO_x reduction technology has a direct impact on the properties of the coal ash produced. An increase in unburnt carbon is common, particularly for older units that have been retrofitted with low NO_x burners or furnace staging technology. Newer boilers are less prone to give high carbon in ash, but the longer residence times and cooler furnace affect the ash mineralogy which will in turn affect its performance in construction products, for example. Post-combustion NO_x removal with ammonia, or ammonia-generating species can lead to contamination of the ash with excess ammonia unless ammonia 'slip' is very carefully managed. Contaminated ash can release free ammonia even when incorporated in a cement formulation and poses a nuisance to end users.

Newer technologies like CFBC present specific issues for ash utilisation and it is difficult to generalise on this topic. The wide flexibility of a CFBC unit means that a range of coal types and co-fuels can be accommodated which in turn gives rise to a range of ash compositions. These are best considered on a case-by-case basis. Additionally, if in-bed sulphur capture is employed, via limestone injection, the free lime present in the ash renders it self-cementing, limiting its use to specific applications. Free lime after setting may still be a problem, however.

Generally, the use of non-fossil based co-fuels result in fly ashes that are of essentially equal performance to coal fly ash, over a wide range of coal/co-fuel ratios. Morphological observations revealed that co-combustion gave minor changes

in composition. Any differences in composition noted were, with one or two exceptions, within the range of normal variability for power generation coal deliveries. In terms of loss on ignition, again, there were only minor differences between materials. The main properties of construction application materials did not show any difference between performance for 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.

Future coal-fired power plant seems likely to evolve into a high-efficiency low emissions system, using technology to allow carbon capture and storage. It is probable that the plant will be designed to operate with higher levels of co-combustion feedstocks. Additionally, new clean coal technologies such as integrated combined cycle gasification plant may be built in significant numbers.

The wide-scale use of low NO_x technologies has had an adverse impact on levels of carbon in ash (LOI), although as new boilers replace old stock, this situation is likely to improve. Ash processing companies have continued to develop their beneficiation technologies and an increasingly refined product stream from 'raw ash' is now becoming more commonplace and may be an important direction for the future.

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